Journal of Alloys and Compounds 657 (2016) 296–301

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Fabrication and characterization of optical and electrical properties of Al–Ti Co-doped ZnO nano-structured thin film

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ARTICLE INFO

Article history:
Received 3 August 2015
Received in revised form
5 October 2015
Accepted 13 October 2015
Available online 23 October 2015

Keywords:
Nanostructured materials
Thin films
Sol–gel processes
Optical properties

ABSTRACT

Al and Ti Co-doped zinc oxide (ATZO) nano-structured thin films with 1 at % Al and 0.1 at % Ti were deposited on glass substrate via sol–gel technique. X-ray diffraction (XRD) analysis, field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) methods were used to investigate the structure, morphology and surface roughness of the thin films. The optical properties were investigated by spectroscopic ellipsometry (SE) and UV-VIS spectrophotometer. The resistivity measurement was performed using a LCR-meter. XRD analysis confirmed the zinc oxide hexagonal wurtzite structure for the thin films. It was found that Ti doping reduces the roughness and grain size values to 8.2 nm and 50 nm, respectively. The optical band gap energy was concluded to be 3.23 eV for ZnO film and it increases to 3.26 eV for ATZO films. Refractive index decreased upon Ti doping as a consequence of increase in charge carrier concentration. All the thin films exhibit high transmittance over 85% in the visible wavelength region. Ti replacement causes to decrease in resistivity and minimum resistivity value of 13×10^6 Ωcm was measured for ATZO thin film.

1. Introduction

Vast field of applications due to tunable properties are responsible for growing attraction of ZnO-based compounds. As a promising transparent conductor or semiconductor category of materials, it can be employed in thin film transistors (TFT), solar cells, light emitting diodes (LED) and flat panel displays [1]. Hexagonal wurtzite ZnO is a natural n-type semiconductor with direct wide band gap of 3.37 eV and large exciton binding energy of 60 meV. It has profitable properties of high transmittance, high chemical stability, non-toxicity and low cost, but, it is highly resistive unfortunately [2]. The substitution of several cations such as Cu^{2+} [3], Co^{2+} [4], Ni^{2+} [5], Mn^{2+} [6], Al^{3+} [7], Ga^{3+} [8], In^{3+} [9], Sn^{4+} [10] and V^{5+} [11] have been widely investigated in order to improve the electrical and optical properties of ZnO. Progressing investigations move to use of Al^{3+} as one of the most promising substitutes [12] along with other cations, for example Al^{3+}–Cu^{2+} [13], Al^{3+}–Ni^{2+} [14], Al^{3+}–In^{3+} [15], Al^{3+}–Ga^{3+} [16], and Al^{3+}–Sn^{4+} [17]. It have been previously claimed that replacement of Zn^{2+} with Ti^{4+} enhances the properties of ZnO thin films and Ti^{4+} can act as an effective n-type donor to generate free charge carriers [18]. Thin films of Al–Ti Co-doped ZnO have been manufactured by radio frequency magnetron sputtering with the composition of 97% ZnO +1.5% Al_2O_3 + 1.5 TiO_2 (wt %) [19]. Based on our knowledge there is not a comprehensive scientific reports of sol–gel derived Al–Ti Co-doped ZnO thin film at concentration of 1 at % Al and 0.1 at % Ti. In the present study, the Al–Ti Co-doped ZnO thin film has been grown on glass substrate by a sol–gel method. The influence of Al–Ti Co-doping on the optical, electrical and structural properties of the samples were investigated.

2. Experimental details

Utilizing sol–gel method, Al–Ti Co-doped ZnO thin films were deposited on glass substrate by a dip-coating technique. Before deposition, the substrates were carefully pre-cleaned by detergent solution and then were successively cleaned with acetone, ethanol and de-ionized water. High purity materials all from Merck company included zinc acetate dehydrate (Zn $(CH_3COO)_2.2H_2O$, purity ≥ 99.5%), aluminum nitrate nonahydrate (Al $(NO_3)_3\cdot 9H_2O$, purity ≥ 98.5%) and titanium tetra-n-butoxide ($C_{16}H_{36}O_4Ti$, purity ≥ 98%) were used as the starting materials in synthesis of the samples. 2-methoxyethanol ($C_3H_8O_2$, purity ≥ 99.5%) and

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http://dx.doi.org/10.1016/j.jallcom.2015.10.107
0925-8388/

diethanolamine ($C_4H_{11}NO_2$, purity ≥ 99%) were used as a solvent and a stabilizer, respectively. Zinc acetate dehydrate was first dissolved in a mixture of 2-methoxyethanol and diethanolamine solution to obtain a uniform precursor solution of ZnO. The molar ratio of diethanolamine to zinc acetate dehydrate was maintained at 1.0 and the concentration of zinc acetate was 0.5 M. Aluminum nitrate nonahydrate was then added in order to obtain a precursor solution of Al doped-ZnO (AZO). The concentration of aluminum nitrate nonahydrate in the solution was adjusted to achieve doped ZnO with 1 at % of Al ([Al/Zn] = 1 at %). Finally for preparation of Al and Ti Co-doped zinc oxide (ATZO) precursor solution, titanium tetra-n-butoxide solution was added to AZO precursor solution at concentration of 0.1 at % Ti ([Ti/Zn] = 0.1 at %). Each solution was stirred using a magnet stirrer at 70 °C for 2 h, after which a transparent and homogenous solution was obtained. The solutions were subsequently aged for 24 h at room temperature before deposition. ZnO, AZO and Al–Ti Co-doped ZnO thin films were deposited by dip-coating method on the glass substrates. After being deposited, the films was dried at 300 °C for 15 min, with a heating rate of 3 °C/min, in an oven to evaporate solvents and remove organic residuals. The procedures from coating to drying were repeated five times for each sample. The samples were then annealed in ambient atmosphere at 550 °C for 2 h. X-ray diffraction (XRD) analysis was performed using a PHILIPS PW3040 diffractometer with Cu K_α radiation (λ = 1.5405 Å) to investigate the crystal structure of the thin films. Counts were collected from 30° to 70° with scan step of 0.05° and scan speed of 5°/min. The morphology and roughness of the thin films were observed by field emission scanning electron microscopy (FE-SEM, HITACHI S-4160, operating at maximum accelerating voltage of 30 kV) and atomic force microscope (AFM, Bruker nanos 1.1, contact mode with precision of 0.1 nm). The optical transmittance measurements were performed by an Avantes spectrophotometer in the wavelength range of 300–900 nm at room temperature in air. Spectroscopic ellipsometry is well known, because of its accuracy and non-destructiveness, by which it is possible to measure the change in the polarization state of the light reflected from the surface and subsequently utilizing a fitting dispersion model to derive the refractive index and extinction coefficient values [20]. It is also possible to measure the thickness of the thin films. Horiba Uvisel Yvon spectroscopic ellipsometer was used with incident angle of 70°. The spectral wavelength range was from 250 to 900 nm with a step of 5 nm. Cauchy model as an appropriate model for Al–Ti Co-doped ZnO thin films was used to extract the optical constants of the samples. The resistivity measurement was performed using a LCR-meter (Hameg, programmable LCR-bridge HM8118).

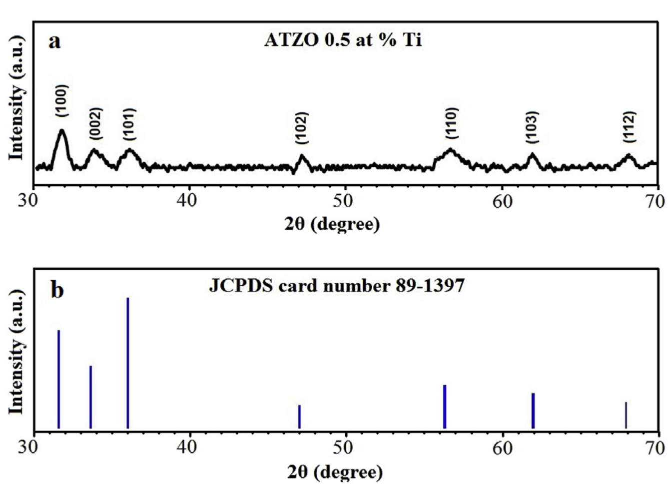

Fig. 1. X-ray diffraction pattern of the ATZO thin film (a) and JCPDS card number 89–1397 (b).

3. Results and discussions

Fig. 1a shows X-ray diffraction pattern of the ATZO thin film deposited at room temperature. As it can be seen, the results are in good agreement with standard data from JCPDS (Joint committee on powder diffraction standards) card number 89–1397 [21], which is provided in Fig. 1b. The observed (100), (002), (101), (102), (110), (103) and (112) peaks in XRD patterns shows that the film has a random orientation. It is obvious that the synthesized film is single phase and there is no evidence of secondary peaks.

The surface morphology of the thin films was characterized by FE-SEM. Fig. 2a–c shows the typical FE-SEM micrographs of the ZnO, AZO and ATZO thin films. An image analyzer was used to estimate the mean grain size of the samples, which are illustrated in Fig. 3. The mean grain size of ZnO, AZO and ATZO thin films were 59, 55 and 50 nm, respectively. It was found that the mean grain size of samples decreased upon doping with Al and Ti. The ATZO thin film exhibits smaller grain sizes with more uniform distribution than those of the ZnO and AZO thin films. This size difference may be attributed to the stress arising from the difference between the ionic radius of zinc and dopant elements; in addition, incorporation of the dopant elements into the ZnO structure may tend to create more nucleation centers [22]. The cross-sectional FE-SEM image of the ATZO thin film is shown in Fig. 2d. As can be seen, the surface is uniform and compact with a typical dense columnar structure, thus implying good crystallinity of the sample. The measured thickness of the ATZO thin film was about 200 nm, which is in accordance with ellipsometry results. Supplementary discussion about the thickness of the thin films is provided in ellipsometry results section.

Energy dispersive X-ray (EDX) analysis was carried out to identify elements present on the thin films. The EDX spectra of thin films are illustrated in Fig. 4. Fig. 4 shows the presence of Zn, Al, Ti along with oxygen in the ATZO thin film.

Fig. 5 presents the typical 3D AFM images of the ZnO, AZO and ATZO thin films. The corresponding root mean square (RMS) roughnesses of the samples are given in Fig. 3. The results clearly indicate that RMS roughness and grain size of the thin films has affected by the addition of Al and Ti substitutes. RMS roughness of the ZnO, AZO and ATZO thin films were found to be 11.7, 9.4 and 8.2 nm, respectively. The decrease in roughness could be described as a consequence of a reduction in grain size with more compact and uniform surface morphology [23], which is in good accordance with FE- SEM results.

The room temperature transmittance spectra as a function of wavelength for ZnO, AZO and ATZO thin films is shown in Fig. 6a. The average transmittance values in the visible range are presented in Table 1. The samples are revealed to be transparent in the visible optical region and the average transmittance of the ZnO, AZO and ATZO thin films were found to be about 85%. The absorption coefficient for a direct band gap semiconductor is calculated using the relation,

$$\alpha = \frac{1}{d}\ln\left(\frac{1}{T}\right) \quad (1)$$

where d is the thickness of the film and T is the optical transmittance [24]. The optical band gap (E_g) of thin films was estimated using Tauc model [21],