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STRUCTURE, MORPHOLOGY AND OPTICAL PROPERTIES OF Al - DOPED ZnO THIN FILMS

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ABSTRACT. Undoped and Al-doped ZnO thin films (AZO) were prepared on Si substrates by using the RF magnetron sputtering technique. In order to improve the film crystallinity of ZnO films, different target-substrate distances were used. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) show that the surface morphology changes function of synthesis parameters and it is influenced by Al doping. From X-ray diffraction (XRD), it is found that all films have c-axis preferred orientation and that the grain size is influenced by both target-substrate distance and doping with Al. The influence of Al doping on electrical properties was studied by electrical resistivity measurement as a function of temperature. Optical reflectance spectra were performed for undoped and Al doped ZnO thin films, both grown under the same conditions.

Keywords*: ZnO, AZO thin films, morphology, structure, electrical resistance, reflectance*

INTRODUCTION

Zinc oxide (ZnO) is a material intensely researched in the last years due to its variety of applications in solar cells, transparent conductors, thin film transistors, laser diodes and ultraviolet diodes. All these electronic and optoelectronic applications can be accredited to its wide band gap of 3.37 eV and its large exciton binding energy of 60meV [1-4]. For ranges between VIS and IR, it displays transparency and it is resistant to reductive ambient, reasons for which it is used in transparent electrode window layer for solar cells [5].

Transparent conducting oxide (TCO) thin films are used in semiconductors industry, due to their high transparency and electrical conductivity and due to their cheap value and no toxicity [6]. There are a couple of techniques used to deposit these thin films. Among these techniques are spray pyrolysis

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[7], metal-organic chemical vapor deposition [4,8], sol-gel synthesis [9,10], magnetron sputtering [11-14], pulse laser deposition [15], etc. The magnetron sputtering technique is considered one of the best techniques in deposition of thin films, because it allows a growth of uniform and transparent ZnO thin films at low temperature and it has a high reproducibility with strong adhesion to substrates [16]. ZnO exhibits an excellent thermal and chemical stability, an exact electrical and optoelectronic properties specific for II-VI semiconductors [17]. It was observed that, when doped with Al, ZnO thin films exhibit comparable high optical transmittance and low electrical resistivity, more stable in hydrogen plasma with respect to other environments [12,18]. These TCO thin films are already used in industry, example Tin –doped or Indium doped oxides (ITO), but the costs are high and they will become higher due to the fact that these materials are non-renewable. Compare with these oxides, Al doped ZnO will have low cost and high availability since only a little amount of Al can give the same properties as ITO [10,14,19]. Also, ZnO thin films have unstable electrical properties at high temperatures, but doped with Al, the thin films generates a better electrical conductivity.

RESULTS AND DISCUSSIONS

The analysis of EDX data (figure 1) shows that the degree of substitution of Zn by Al is around 2% in AZO film and that the chemical formula of thin film is ZnO for the undoped sample.

The crystallinity of ZnO and AZO films was investigated with respect to the distance d between target and substrate. Figure 2 shows the diffraction patterns of ZnO thin films for different distances d and of AZO thin film for d=8 cm. In both cases, the strong (002) reflection is detected at about 51.5°, reflecting the wurtzite structure of the growing films with the c-axis oriented normal to the substrate.

Furthermore, for ZnO thin films, a small shift of the (002) peak toward larger angles is observed with increasing d to 8 cm. This shift is associated with the increment of the lattice constant c with increasing distance. The lattice constant c of the samples calculated by Bragg formula, evidenced a small increase from c=0.549nm for d=2cm to 0.554 nm for d=8 cm. The main effect of increasing distance d, target-substrate in synthesis ZnO thin films is the change of linewidth of (002) diffraction peak, suggesting changes in mean value of the grains size [20]. The crystallite sizes of the films were calculated using the Scherrer equation:

$$D = \frac{0,9\lambda}{B\cos\theta}$$

where λ, θ, and B are the X-ray wavelength $\lambda_{CrK\alpha 1}$, diffraction angle and FWHM (full width at half maximum) of the diffraction (002) peak.

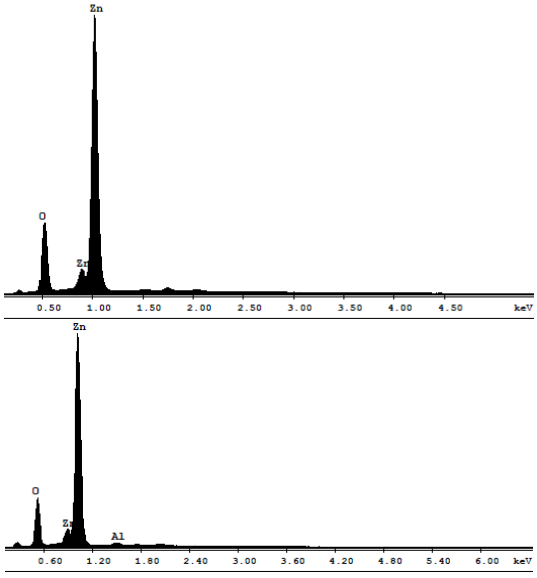

Figure 1. EDAX analysis of ZnO and AZO thin films (d=8cm for both samples)

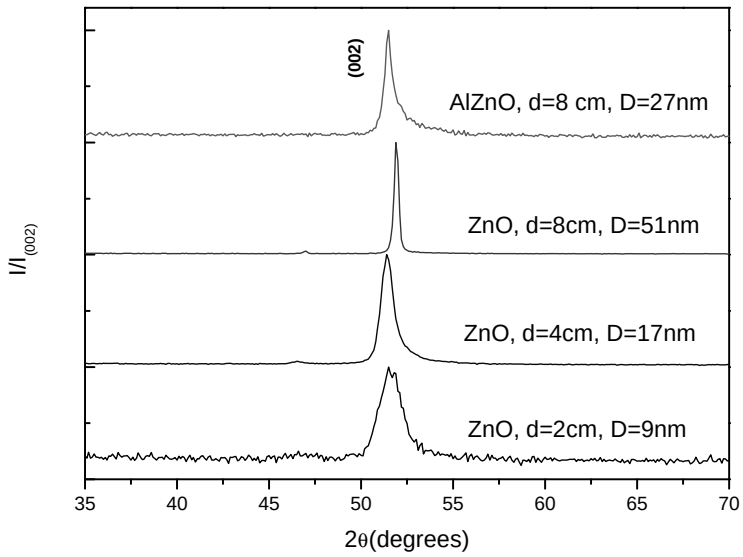

Figure 2. The XRD spectra of ZnO and AZO films grown at the same substrate temperature and varying distance d between target and substrate.

In order to determine more precisely the position and FWHM of the linewidth, the Lorentz fit of (002) peak was performed. The increase of d up to 8 cm leads to the increase of crystallite size from 9 nm (d=2cm) to 51nm (d=8cm). These results are in accordance with other reports on pure ZnO [21,22]. Above d=8 cm a small decrease of crystallite size was observed. The optimal process parameters (including d=8cm) used to obtain the best crystallinity of ZnO thin film were used to obtain AZO films. The partial substitution of Zn with 2%Al leads to the decrease of crystallite size to around 27 nm. The decrease of crystallite size reinforced the decrease of film crystallinity. This behavior may be considered to be due to the moderate quantity of Al atoms that can exist at interstitial sites and to the fact that Al together with Zn atoms share oxygen atoms.

The typical surface morphology of ZnO and AZO thin films grown in optimal conditions and measured by SEM and AFM is shown in figure 3.

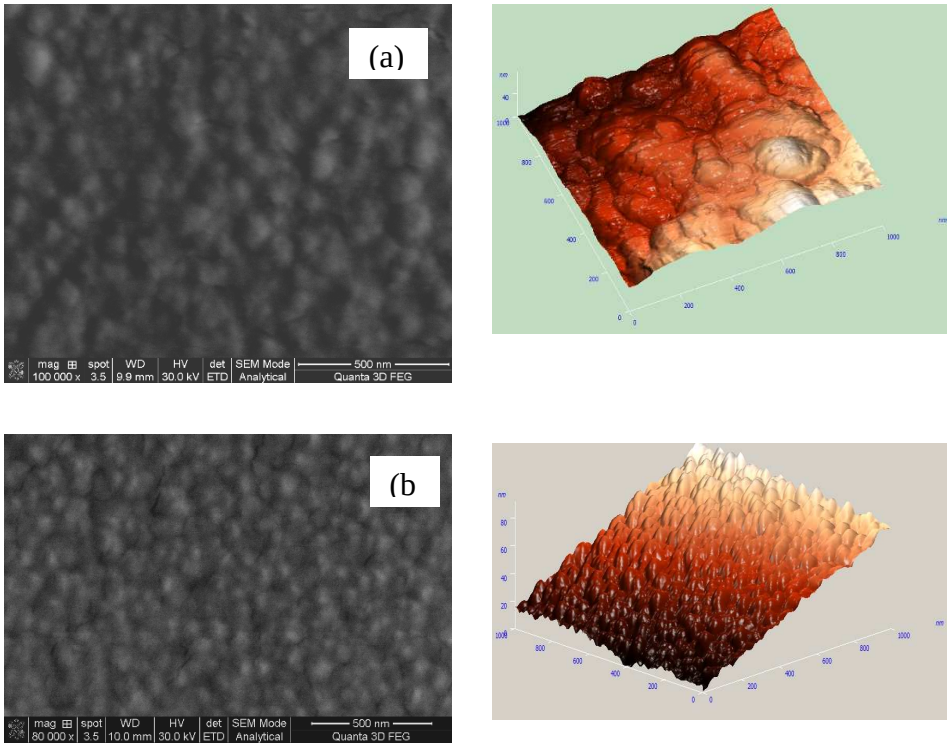

Figure 3. Typical SEM (left) and AFM (right) images of ZnO (figure 2a) and AZO films (figure 2b) surface.

Left side images of figure 3 show the surface morphology from SEM, whereas the right side images of figure 3 show the films microstructure from AFM measurements. SEM and AFM characterization of the film surfaces revealed that grain size decreases after the partial substitution of Zn with Al. The characteristic of these films is the presence of grains of different dimensions with a strong tendency to form agglomerations as it is shown in figure 3. It also shows the presence of columnar morphologies with increased roughness for 2% Al thin films and a small increase in the height of the grains.

A decrease in resistance with increasing temperature following semiconducting behaviour of ZnO and AZO films is observed. The activation energy was determined by using the equation

$$R = R_0 \exp(E_a/kT)$$

where R is the resistance at temperature T, R_0 is a constant, E_a is the activation energy and k is the Boltzmann constant.

The value of activation energy from resistivity measurements is around 0.31 eV for both undoped ZnO and AZO thin films. An activation barrier value of 0.3 eV for ZnO film was reported earlier [23]. A small change in the activation barrier by 2% Al doping is undetectable from resistivity measurements. Electrical resistivity for AZO film at room temperature is 8.6 mΩcm in agreement with results reported in reference [24]. However, for AZO film, the decrease of resistance by approximately 25% in the entire temperature range studied (300K-450K) shows that Aluminum atoms are incorporated into the ZnO lattice and they contribute with conduction electrons which improve the electrical conduction.

Figure 4 shows the reflectance of undoped ZnO film and 2% Al doped film, grown under the same conditions.

The increase in reflectance for wavelength longer than 1000 nm for AZO thin films indicates an increase in free carriers absorption and consequently a higher carrier concentration for the Al-doped film. These results are confirmed by electrical resistivity measurements.

CONCLUSIONS

Epitaxial ZnO and Al doped ZnO thin films deposited on Si substrates were obtained by radio-frequency (RF) reactive magnetron sputtering method. The effect of distance target-substrate and the Al doping on the morphological, structural, electrical and optical properties of the ZnO film was analyzed.

(1) EDX data show that the degree of substitution of Zn by Al is around 2% in AZO films and XRD data evidence the growing films with the c-axis oriented normal to the substrate.

(2) SEM and AFM characterization of the film surfaces revealed that grain size decreases after the partial substitution of Zn with Al

(3) XRD facts that the main effect of increasing the distance target-substrate d in the synthesis of ZnO thin films is the change in the mean value of the grain size. The best crystallinity is obtained for d=8cm

(4) The value of activation energy obtained from electrical resistance function of temperature is 0.31 eV for both undoped ZnO and AZO films. The increase in reflectance for wavelength longer than 1000 nm indicates a higher carrier concentration for the Al-doped film.

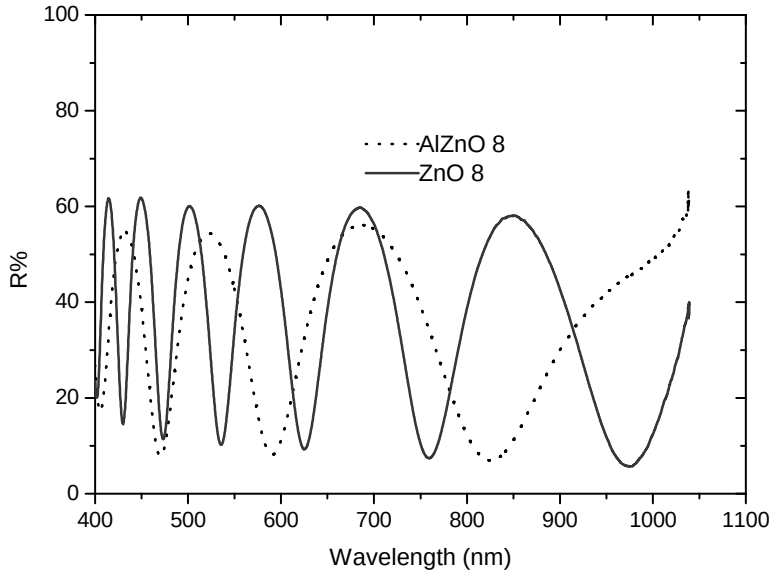

Figure 4. Optical reflectance spectra of undoped and Al doped ZnO thin film, both grown under the same conditions (d=8cm).

EXPERIMENTAL

The ZnO and Al doped ZnO thin films were deposited by RF magnetron sputtering technique. Ceramic targets with chemical formula ZnO and $Al_{0.02}Zn_{0.98}O$ (sample AZO) were obtained by solid state reaction method, using mechanical mixed powders of 99.99% pure ZnO and 99.97% pure A_2O_3. These circular ceramic targets were used to prepare the ZnO and AZO thin films. The films were deposited in an oxygen–argon atmosphere (with the ratio $Ar:O_2$=10:6 sccm) on Si substrates. The substrate temperature was 150^0C. The deposition pressure in the chamber was 2×10^{-2} mbar and the target-to-substrate distance was varied from 2 to

12 cm. The films' thicknesses of ZnO increased from 100 nm to 300 nm by increasing distance from 2 cm to 12 cm. The best cristallinity in ZnO film with thickness 200 nm was obtained for d=8cm. This is the reason for choosing the same process parameters for AZO film.

The surface morphology was characterized by atomic force microscopy (AFM) in tapping mode using NT-MDT Ntegra Solaris atomic force microscope. SEM imagines were recorded using FEI Quanta 3D FEG 200/600 and Scanning Electron Microscope. The samples were covered with metals in order to amplify the secondary electrons signal. This covering was performed with Pt. X-ray diffraction (XRD) using a Bruker D8 diffractometer with Cr K_α X-rays was done in order to determine the crystal structure of the deposited films.

The optical reflectance spectra were measured at normal incidence with a miniature spectrometer (Ocean Optics USB4000 UV-vis). The spectrometer was equipped with a QR200-7-VIS/BX reflection optical fiber probe consisting of a tight bundle of 7 optical fibers of 200 mm diameter (6 illumination fibers around 1 read fiber).

The electrical characterization of the films was carried out in a tube furnace by monitoring the variation of electrical resistance (R) as a function of temperature (T) using conventional DC two-probe technique. The range of temperature investigated was 300-450 K with a control accuracy of (±)1 K. Approximately 30 mm long silver (Ag) contacts, separated by 7 mm, were made on ZnO films for electrical measurements.

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