



The influence of annealing on the properties of ZnO:Al layers obtained by RF magnetron sputtering

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ABSTRACT

Al doped ZnO has been explored as a viable alternative to indium thin oxide, which is usually used as transparent electrodes' coverage but is expensive. Homogenous and durable ZnO:Al layers on glass have been obtained in radio frequency magnetron sputtering system by adjusting optimized deposition parameters, using ZnO ceramic target with 2 wt% Al₂O₃. Then, after growth process, annealing treatment has been introduced in order to improve the quality of the layers. Structural, electrical and optical properties of the obtained ZnO:Al layers are presented and discussed. From the application point of view, the best results (sheet resistance of 24 Ω/sq and transparency well above 85%) were achieved after annealing in 300 °C.

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1. Introduction

Materials for thin transparent electrodes have been constantly drawing attention for their wide application area, e.g., in solar cells, light-emitting diodes (LEDs), organic light-emitting diodes (OLEDs), flat panel displays, touch screens and smart windows [1–3]. Semiconductors that play role of a transparent electrode are expected to exhibit low resistance, which is typical property of metals, and simultaneously high transmittance, which is characteristic for insulators. Since these two features are mutually exclusive of each other combining them in one material present a big challenge. The required sheet resistance of a thin transparent electrode should be lower than 500 Ω/sq but this value depends strictly on the type of application, e.g., for touch screens 200–500 Ω/sq is enough, for solar cells and OLEDs less than 50 Ω/sq is necessary together with transparency exceeding 80%.

In the role of thin films that cover electrodes and fulfill the requirements, transparent conductive oxides (TCO), e.g., indium tin oxide (ITO), fluorine tin oxide (FTO) are usually applied [4–6].

However, scarcity of indium and its increasing price is a motivation for searching of a substitute of a commonly used ITO, by developing investigations of other kinds of transparent conductive oxides and, also graphene which excellent mechanical strength and carbon abundance make it next generation alternative to ITO [7].

Among different TCOs, ZnO doped with III group elements such as Al, Ga, B, In [8–10] are valuable substitute to ITO since they are non-toxic, unexpensive, resistant to defects and, when properly prepared, merge good transparency and acceptable sheet resistance. Al doped ZnO (AZO, ZnO:Al) sputtered layers are widely investigated and have proven to work well [2]. TCO of this kind can be grown by different methods like pulsed laser deposition (PLD) [11], aerosol assisted chemical vapour deposition (AAVD) [12], vacuum thermal evaporation [13], spray pyrolysis [14], DC magnetron [15,16] and used in this work RF magnetron sputtering, which provides smooth, homogenous, durable layers that can be obtained on glass [17] or flexible substrates [18].

The quality and properties of the layers deposited in magnetron highly depend on parameters of the sputtering process such as: cathode power, deposition time, working pressure and distance between substrate and target [19,20]. Preparing of glass substrate (cleaning, etching), as well as after deposition treatments like heating can also be of highly importance influencing final results.

In the presented work we investigated structural, electrical and optical properties of ZnO:Al coatings grown by RF magnetron sputtering on glass substrates for photovoltaic applications. ZnO:Al layers were deposited at RT and then annealed in order to improve their quality.

2. Methods

ZnO:Al layers were deposited on a clean microscope soda lime glass using radio frequency (rf) magnetron sputtering system Alliance Concept AC 450. Glass substrates were prepared by clean-

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ing ultrasonically in acetone and ethanol and then dried in nitrogen. Ceramic target of high purity ZnO doped with 2 wt% Al_2O_3 was employed. According to our EDS study the composition of ZnO:Al layers was as follows: Zn w.% – 68.06, O w.% – 29.65, Al w.% – 2.29 [20]. In the system used, the target diameter equals 1016 mm and its distance to the substrate is fixed at 90 mm. After 5 min. pre-sputtering process deposition time was adjusted at 45 min. and magnetron power of 250 W. Base pressure in the magnetron chamber was $1 \cdot 10^{-2}$ Pa. During the growth of the layers pressure of high purity (99.99%) Ar gas was maintained at 0.283 Pa. ZnO:Al deposition process was performed at room temperature (RT) and then followed by annealing treatment at 200 °C, 300 °C, 400 °C by using resistance furnace in N_2 atmosphere.

The crystalline structure and orientation were analyzed by X-ray diffraction Empyrean PANalytical Diffractometer system. Scanning electron microscope FEI Quanta 3D FEG was used to obtain images of the samples surface. The sheet resistance of ZnO:Al coatings was determined at RT using RM3000+ four point probe equipment from Jandel Engineering Ltd. The optical transmittance measurement was performed by Shimadzu UV–vis spectrophotometer. Positions of minima and maxima on the obtained transmittance curve (v.i.) served to estimation of layers thickness by envelope method, which has proven to be very useful [21,22,17]. The envelope method is based on the following equation:

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)}, \quad (1)$$

in which λ_1 , λ_2 are the wavelength of two adjacent minima or maxima. Refraction index n_1 was determined according to the equations:

$$n_1 = [N_1 + (N_1^2 - s^2)^{\frac{1}{2}}]^{\frac{1}{2}}, \quad (2)$$

$$N_1 = \frac{2s}{T_m} + \frac{s^2 + 1}{2} \quad (3)$$

in which s is the refraction index of glass, T_m is the transmittance at a given maximum or minimum. Analogously, the refraction index n_2 was calculated. The thickness of ZnO:Al layers obtained at RT determined according to envelope method is equal to 2470 nm and decreases after temperature treatment leading to values of 2210 nm, 1720 nm and 1900 nm for samples annealed at 200 °C, 300 °C, 400 °C, respectively.

3. Results and discussion

3.1. Structural properties of AZO films

To study the crystalline quality of the deposited and then annealed ZnO:Al layers XRD analysis (Fig. 1) was performed. The intensity and the full width at half maximum (FWHM) of X-ray diffraction patterns provide information necessary to evaluate crystalline quality of ZnO:Al structures. The layers are found to have a wurtzite hexagonal polycrystalline structure with (002) plane as a preferential growth plane due to its low surface free energy. Other diffraction peaks characteristics for ZnO such as (102), (103) are also observed, which suggests that Al^{3+} dopant ions substituting Zn^{2+} in regular sites do not change hexagonal wurtzite structure.

Before annealing, in XRD spectrum ZnO:Al exhibits peak at 34.64° and an additional peak at 33.79° coming probably from crystallites containing more Al dopant in which Al^{3+} ions occupy interstitial sites. Annealing treatment results in an increase of kinetic energy, which enhances mobility of Al^{3+} ions that can substitute Zn^{2+} ions. After annealing Al^{3+} ions' substitute Zn^{2+} ions in the regular positions in a crystalline lattice and as a consequence only peaks at angle higher than 34° are observed since Al^{3+} ions

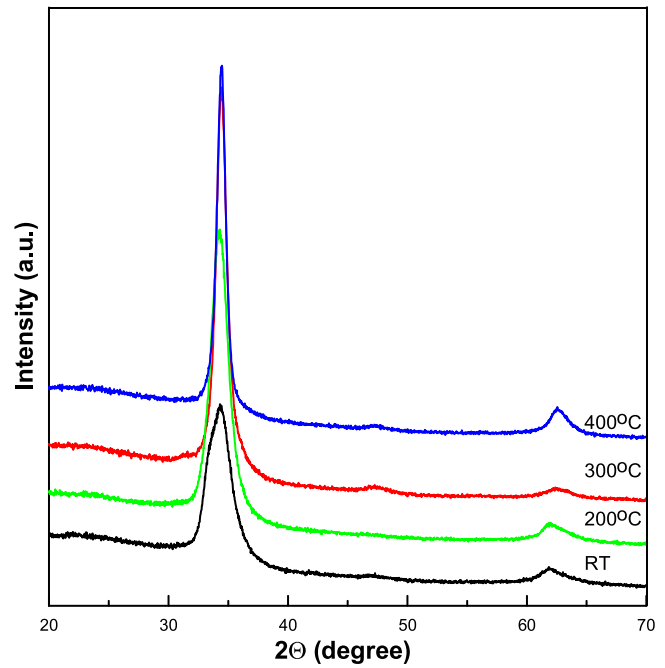


Fig. 1. XRD diffraction spectra of ZnO:Al layers obtained at RT and then annealed.

(radius of 0.54 Å) are smaller than Zn^{2+} ions (radius of 0.74 Å) [23]. Finally, interplanar spacing and lattice constant (see Table 1) have smaller values than that observed at 33.79° but still higher than for pristine ZnO ($c = 5.204$ Å), which means that not all Zn^{2+} ions are substituted by Al^{3+} [24]. The overall amount of Al in deposited layers estimated by EDS method in our previous studies (submitted) equals 2% and is determined by the composition of the sputtering target.

After annealing at 200 °C and 300 °C, the increase in an intensity of (002) peak is observed probably owing to the fact that structure quality improvement occurred as a result of atoms' mobility enhancement in higher temperature. Gaining additional energy by atoms allows for decreasing of defects' density and achieving better internal order. However, at higher annealing temperature of 400 °C the (002) peak intensity decreases. Similar dependence observed by Fang [25] may be attributed to the appearance of porosity in the layer structure.

The full width half maximum of (002) peak decreases after annealing (Table 1) comparing to film grown at RT without temperature treatment. It indicates that annealing enhances crystalline ordering by removing the defects such as vacancies and lattice disorders. From the FWHM of (002) diffraction peak the grain size of the crystallite can be determined according to Scherrer formula [26]:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (4)$$

in which $\lambda = 1.54$ Å is the wavelength of the X-rays used, β is the broadening of diffraction line measured at the half of its maximum intensity in radians and θ is the angle of diffraction. The crystallite sizes, reported in Table 1, consequently increase as a function of annealing temperature and change from 42 Å to 127 Å.

It is important to notice that all above mentioned parameters derived from X-ray diffraction pattern are related to the presence of stress and strain in the growing film structures. Stress occurring in ZnO:Al deposited layers has two components: thermal and intrinsic stress. The mismatch in the thermal expansion coefficients ($9 \cdot 10^{-6}/\text{K}$ for soda lime glass and $5\text{--}6 \cdot 10^{-6}/\text{K}$ for ZnOAl hexagonal crystals) [27–30] is the reason that evokes thermal stress. Intrinsic

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