THE EFFECT OF ANNEALING ON THE PROPERTIES OF ZNO:AL FILMS GROWN BY RF MAGNETRON SPUTTERING

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ABSTRACT

The effect of annealing temperature ranged from 200 to 600 °C on the structural, optical and electrical properties of aluminum doped zinc oxide (ZnO:Al) films was reported. The thin films were deposited on glass and silicon substrates by rf magnetron sputtering method using ZnO target (diameter 7,5 cm) mixed with 2 wt.% Al_2O_3. It has been found that the crystal structure of ZnO:Al films is hexagonal with c-axis preferential orientation. With an increase in the annealing temperature the intrinsic compressive stress was found to decrease, and near stress-free film was obtained after annealing at 600 °C. A resistivity of $1.25x10^{-3}$ Ωcm and an average transmittance above 90 % in visible range were obtained for films prepared at room temperature.

KEYWORDS: magnetron sputtering, Al doped ZnO, annealing temperature, properties.

1 INTRODUCTION

Generally, optical transparent oxides tend to be electrical insulators because of their large optical band gap (≥ 3.1 eV). However, ZnO is one of the few metal oxides, which can be simultaneously optically transparent, and electrically conductor. Zinc oxide thin films have attracted much interest and are used in many applications: as optically active layers in solar cells, transparent electrodes for flat panel displays, energy windows, varistors, gas sensors,…[1- 4], due to their important properties characterized by a high transparency, a low electrical resistivity, a good adhesion to substrate, a good thermal stability against hydrogen plasma, non toxicity and an easy fabrication[5,6] .

Several methods are adopted to fabricate ZnO thin films, such as sputtering [7,8], plasma enhanced chemical vapor deposition (PECVD) [9], pulsed laser deposition [10], sol-gel [11] and spray pyrolysis [12,13].

The physical properties of ZnO films prepared by rf magnetron sputtering depend mainly on the sputtering parameters such as sputtering power, argon gas pressure, substrate temperature and the target-substrate distance. In this paper, thin films of ZnO:Al are prepared by magnetron sputtering system. The mutual dependence of structural, optical and electrical properties of the samples as function of annealing temperature is investigated.

2 EXPERIMENTAL PROCEDURE

ZnO:Al films were deposited in magnetron sputtering system using a ZnO target (diameter 7.5 cm) mixed with 2 wt.% Al_2O_3. Prior the deposition, the base pressure in the chamber was $5x10^{-7}$ mbar. The target-substrate spacing, the sputtering power, and argon gas pressure were kept constant at 2.6 cm, 200 W and $2x10^{-3}$ mBar respectively. All the films were deposited at room temperature on glass and monocrystalline silicon (100) substrates. In order to investigate the influence of annealing in air on the ZnO:Al properties, the annealing temperature was varied from 200 to 600 °C.

Film thickness and substrate curvatures were measured with a stylus profilometer DEKTAK 3030. As most commonly used, the stress in our films has been calculated by the bend-bending method, where the radius of the coated substrate curvature is determined and used to calculate the residual stress. The internal stress in the deposited film is calculated from the change in the substrate curvature from $1/R_0$ for the uncoated substrate to $1/R_e$ after film deposition, with the following Stoney's formula [14]:

$$\sigma = [(E_s e_s^2) / (6(1-\nu_s)e)][(1/R_e)-(1/R_0)]$$

where R_0 is the radius of curvature of the Si substrate, R_e is the curvature radius after film deposition, E_s and ν_s are, respectively, the Young's modulus and Poisson ratio of the substrate, e_s and e are the thickness of the substrate and the film, respectively. The crystal structure of the films was studied by x-ray diffraction technique using a Siemens D 5000 system with Cu K_α (λ= 0,15406 nm). The structural investigation was also performed using a Jeol 6400 Scanning Electron Microscope (SEM). A CARRY UV-Vis-NIR scanning spectrophotometer was used to record the optical transmittance. The optical band gap of the films is determined by applying the Tauc model [15], and the Davis and Mott model [16] in the high absorbance region:

$$(\alpha h\nu) = A\,(h\nu - E_g)^n$$

Where ($h\nu$) is the photon energy, Eg the optical band gap, and A is a constant. For n = 1/2 the transition data provide the best linear curve in the band-edge region, implying the direct transition. The band gap of the films can be deduced from a plot $(\alpha h\nu)^2$ versus photon energy ($h\nu$) and extrapolating the straight line portion of this plot to the energy axis. The localised state near the band edge causes the appearance of band tails in material band diagram. This band tail states are the responsible of the absorption in the low energies range. In this range the absorption coefficient is given as [17]:

$$\alpha(h\nu) = \alpha_0 \exp\,(h\nu/E_U)$$

Where α_0 is the pre-exponential factor, $h\nu$ the photon energy and E_U is the band tail width or energy of disorder commonly called Urbach tail [17]. E_U can be estimated from the inverse slope of the linear plot between $\ln(\alpha)$ versus $h\nu$.

The dc electrical resistivity measurement is achieved at room temperature with four-point probe, with the appropriate correction factors.

3 RESULTS AND DISCUSSIONS

X-ray diffraction patterns of the ZnO:Al films annealed at different temperature (200 to 600 °C) are shown in figure 1. All the films are found to have the hexagonal wurtzite structure. A prominent (002) peak indicates that the crystallite structure of the films is oriented with their c-axis perpendicular to the substrate plane. The increase in intensity of the diffraction peak and also the narrowing of the peak, i.e., decrease in the full width at half maximum (FWHM) of the peak, with the increase in annealing temperature indicate the improvement in crystallinity of the films. By considering the (002) peak position in the standard data as reference position, we found that the peak position shifts towards lower angle value, this indicates the clear evidence of the existence of compressive stress in the film network. Figure 2 shows the stress versus annealing temperature, the stress is compressive and varies from 1.1 (GPa) to nearly free of stress when the annealing temperature increases from 200 to 600 °C. This is attributed to the improvement in crystallinity. A similar value of stress was reported in the literature [8, 18].

The morphologies of the films were evaluated by the SEM micrographs. Figure 3 shows a typical surface SEM image of the film deposited at room temperature and annealed at 600 °C in air. The film displays a granular surface, uniform grain size and void free. We can clearly see that the film surface after annealing shows similar observations to the as-deposited film, except the evidently bigger grains sizes.

In figure4 we have reported the optical transmittance spectra for ZnO:Al films as-deposited and annealed at various temperature, the fluctuation in the spectra is principally due to the interface effect owing the reflexion at interfaces. Sharp fundamental absorption edges are observed in all the spectra corresponding to the ZnO:Al films. These films have a high transmittance (>92%) in visible regions and high absorption (near 100%) in ultraviolet regions. As the annealing temperature decreases, the average transmittance of the films reduces slightly. It would be noted that the film as-deposited becomes nearly opaque to near infrared region. This is due to the highest carrier concentration, which absorb photons. The blue shift of the absorption edge with decreasing annealing temperature is mainly attributed to the Burstein-Moss effect [19,20], since the absorption edge of degenerate semiconductor is shifted to shorter wavelength with increasing carrier concentration [21]. This decrease in the band gap energy with increasing annealing temperature is confirmed by the decrease in band tail width figure 5. The value of E_U obtained for undoped ZnO prepared by sol-gel [22] and CVD techniques [23] is reported to be in the range of 0.07 – 0.10 eV. The larger values of E_U (0.15 – 0.18 eV) obtained in the present study indicates the presence of a large concentration of localised donor states in the band gap.

Figure 6 also illustrates the resistivity of ZnO:Al films as a function of annealing temperature. As seen, low values of the resistivity ($\sim 1.25 \times 10^{-3}$ Ωcm) can be obtained for as-deposited films. Moreover, we can observe that the resistivity increases significantly with increasing annealing temperature. This variation of resistivity with annealing temperature could be attributed to the change in carrier concentration and/or mobility which also characterize the film microstructure. It is possible to observe a decrease in the free carrier concentration; this could be explained by the absorption of oxygen in the grain boundaries which act as traps for the carriers, leading to a decrease in the carrier's concentration when the annealed treatment is performed in oxidant.

4 CONCLUSION

In summary, highly transparent and lower resistive ZnO:Al films were deposited at room temperature on silicon and glass substrates using rf magnetron sputtering technique. A systematic study was made on the influence of annealing temperature, on the structural, optical and electrical properties of our films.

X-ray diffraction studies indicated that the films were polycrystalline in nature with (002) orientation axis perpendicular to the substrate surface. The FWHM of the films decreased from 21° to 19° with increasing annealing temperature.

The increase in the annealing temperature leads to a decrease of the compressive stress. The decrease in the intrinsic stress is probably the raison for the observed improvement of film crystallinity.

All films have a high transmission greater than 90% in visible region. However, the as-deposited film is nearly opaque in near infrared region. This is due to photons absorption by the large concentration of free electron present in film network; this is consistent with the low measured electrical resistivity (~1.25×10^{-3} Ωcm) in as-deposited film. The optical band gap shifts towards lower energy with an increase of annealing temperature.

From the study performed it is possible to conclude that the annealing treatment in air leads to the significant improvement on the structural and optical properties of ZnO:Al films, however we observed an increase in resistivity by more than three orders of magnitude.

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FIGURES CAPTION

Figure 1: X- ray diffraction patterns of as-deposited ZnO:Al film and annealed at different temperature.

Figure 2: Variation of FWHM and intrinsic stress with annealing temperature.

Figure 3: SEM images of ZnO:Al film deposited at room temperature (a), annealed at 400 °C (b) and 600 °C (c).

Figure 4: Optical transmittance of as-deposited ZnO:Al film and annealed at various temperature.

Figure 5: Variation of band gap and band tail width with annealing temperature.

Figure 6: Dependence of electrical resistivity in ZnO:Al film on annealing temperature.

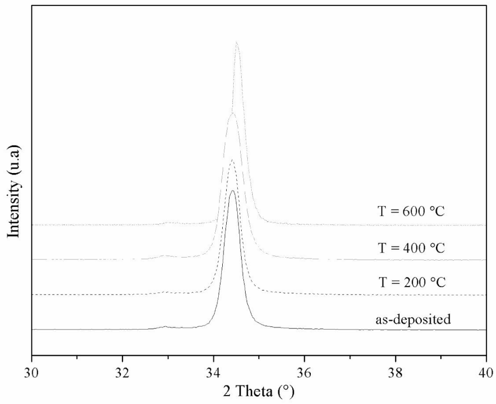

Figure 1

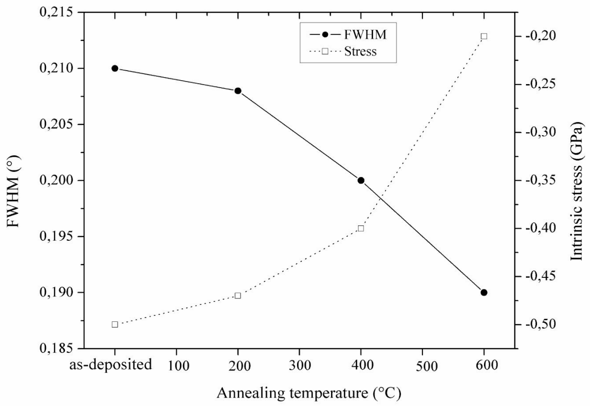

Figure 2

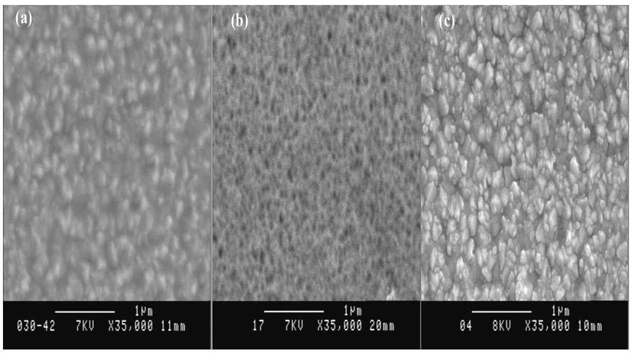

Figure3

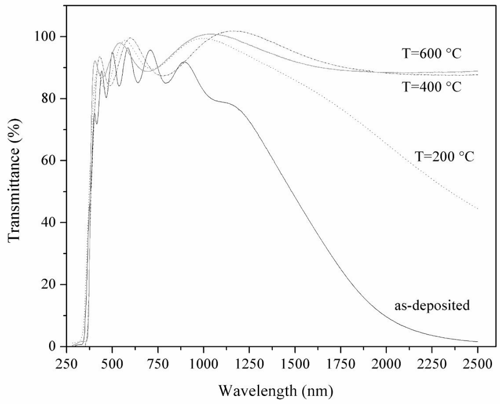

Figure 4

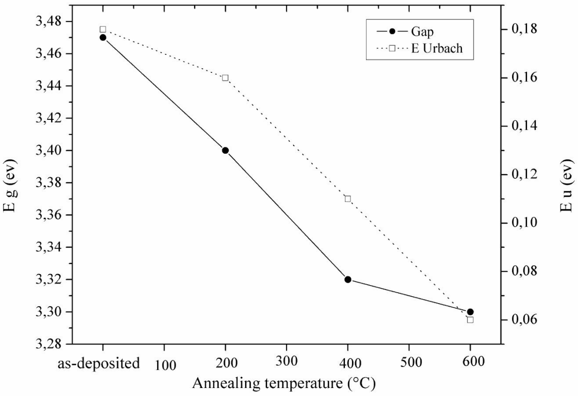

Figure 5

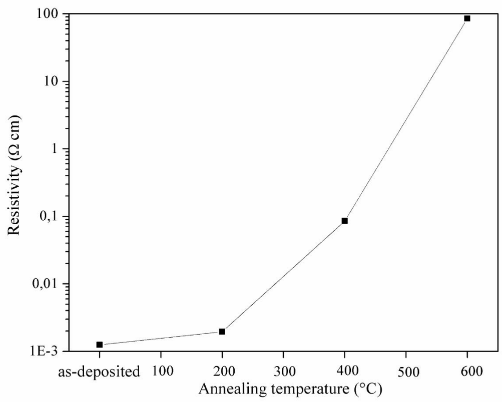

Figure 6