Structural, electrical and optical properties of Gd doped and undoped ZnO:Al (ZAO) thin films prepared by RF magnetron sputtering

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Abstract

The influence of the gadolinium doping on the structural features and opto-electrical properties of ZnO:Al (ZAO) films deposited by radio frequency (RF) magnetron sputtering method onto glass substrates was investigated. X-ray analysis showed that the films were polycrystalline fitting well with a hexagonal wurtzite structure and have preferred orientation in [0 0 2] direction. The Gd doped ZAO film with a thickness of 140 nm showed a high visible region transmittance of 90%. The optical band gap was found to be 3.38 eV for pure ZnO film and 3.58 eV for ZAO films while a drop in optical band gap of ZAO film was observed by Gd doping. The lowest resistivities of 8.4 \times 10^{-3} \, \Omega \, cm were observed for Gd doped and undoped ZAO films, respectively, which were deposited at room temperature and annealed at 150 °C.

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Keywords: Zinc oxide; RF magnetron sputtering; Transparent conductive thin film; Optical and electronic properties

1. Introduction

Zinc oxide (ZnO) has a wide direct band gap of 3.37 eV and a relatively large exciton binding energy of 60 meV that makes it attractive for a variety of electronic and electro-optical applications [1]. For the band gap of ZnO is well above the visible range, prepared films are electrically conductive, which is leading to applications for transparent conducting oxides (TCO) thin films such as transparent electrodes for liquid crystal displays, solar cell, photo-thermal conversion system and so on [2–4]. The high quality of ITO films deposited by sputtering of oxide targets has already been successfully achieved on a commercialized production scale. However, both ITO target and its film contain a very high concentration of indium (90% In2O3 + 10% SnO2 in weight) that is a very expensive material. ZnO is considered as one of the most promising materials by taking the advantages of abundance in nature, non-toxicity and good stability in hydrogen plasma process. Moreover, though some dopant is very expensive, only a small amount of dopant can make ZnO film’s electrical and optical properties comparable to ITO film. This means that the cost price of doped ZnO film is still lower than that of ITO film. Based on the viewpoint that ZnO films are more potential than ITO films, we believe that it’s valuable for our further investigation about ZnO films [5,6]. The electrical conductivity and optical transmittance of ZnO are related to the free carrier density generated by dopant atom substitution of Zn atom (giving out one extra electron), and oxygen vacancies (acting as two electron donors).

A lot of studies have focused on changing various technics parameters and the dopant concentration to improve the performance of ZnO:Al (ZAO). Chung et al. [7] have researched working pressure effect on the physical properties of ZAO films. However, only a few studies on the effects of doping on the electrical properties and their dependence with the film structure have been reported. It is generally considered that the ion radii of dopants for transparent and conductive ZnO films should be small and close to that of...
Zn$^{2+}$. But the co-doping effect of a big ion radius rare earth impurity and Al$^{3+}$ has not been reported before. Gd$_2$O$_3$ has certain and useful physical property in optical applications, which was selected as dopant and expected to improve the transmittance for ZAO film. The aim of this work is to comparatively establish structural, optical and electrical property comparative relations between the undoped and Gd doped ZAO films.

2. Experimental

2.1. Ceramic targets preparation

The ceramic sputtering targets, of which raw materials were mechanical mixed powders, were fabricated by sintering in the air after die pressing and cold isostatic pressing. The following compositions were chosen: 97% ZnO + 3% Al$_2$O$_3$ and 97% ZnO + 2% Al$_2$O$_3$ + 1% Gd$_2$O$_3$ (in weight). Raw materials were commercially available ZnO, Al$_2$O$_3$ and Gd$_2$O$_3$ (99.99% in purity) powders. The linear shrinkage ratios of sintered targets reached to about 20%, as well as the relative density was over 90% (highest is 97.63%). The sintered circular ceramic targets with a diameter of 65 mm were used in thin films’ preparation.

2.2. Thin films preparation

Gd doped and undoped ZnO thin films on Corning eagle 2000 glass substrates were deposited at room temperature by ratio frequency (RF) magnetron sputtering. Glass substrates were thoroughly cleaned using acetone, ethanol absolute and water as solvents and ultrasonic technology, and then dried before loading it in the deposition chamber. The base pressure in sputtering chamber was about 2$\times$10$^{-4}$ Pa. A sputter-etch of 20 min was used to remove the target surface contamination. At last, argon was introduced, and the gas pressure was adjusted. The deposition conditions are shown in Table 1.

The thin film’s thickness was measured by elliptical polarization Instrument (Jobin-Yvon). Electrical properties of the films were measured by a dc four-point probe technique. The optical transmittances of the studied films were determined at room temperature for photon wavelengths ranging from 320 to 800 nm, using a UV-250 spectrophotometer. Crystallographic and phase structures were determined by an X-ray diffractometer (Rigaku) with Cu K$_\alpha$ radiation. The surface morphologies and thickness of the deposited films were investigated by a Cambridge S-360 scanning electron microscope (SEM).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Power mode</td>
<td>RF</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Deposition time (min)</td>
<td>17</td>
</tr>
<tr>
<td>Partial pressure of O$_2$ (Pa)</td>
<td>0.45</td>
</tr>
<tr>
<td>Target–substrate distance (mm)</td>
<td>119</td>
</tr>
<tr>
<td>Pressure (Pa)</td>
<td>10$^{-4}$</td>
</tr>
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</table>

3. Results and discussions

3.1. Structural characterization

Fig. 1 shows the X-ray diffraction patterns for the Gd doped and undoped ZAO thin films deposited at room temperature. The (0 0 2), (1 0 2), (1 0 3) peaks are observed. The results of the films were in good agreement with those reported in the PDF for ZnO (PDF75-576, $a = 3.24270$ Å, $b = c = 5.19480$ Å), and the peaks correspond to a hexagonal wurtzite structure with no additional peaks of gadolinium and aluminum phases [8]. The (0 0 2) reflex for both films is dominating in the XRD spectra. For both films, the crystalline granule grew along its c-axis and perpendicular to the surface of the substrate. There was no any peak shift of Gd doped film as compared with ZAO film, which indicates that gadolinium atoms doping did not distort the original crystalline structure [9,10]. It was same with the report by Lin et al. [11] who studied heavily Al doped ZnO films by simultaneous rf and dc magnetron sputtering methods. The crystal size $g$ can be estimated using Scherrer formula:

$$ g = \frac{0.94\lambda}{\Delta(2\theta)\cos\theta}, $$

where $\lambda$ is the X-ray wavelength, $\theta$ the Bragg diffraction angle in degrees and $\Delta(2\theta)$ is the FWHM in radian [12–14]. The crystal size is in the 28–42 nm range.

Fig. 2 illustrates the surface morphology of Gd doped and undoped ZAO thin films deposited at room temperature. The films show different morphology of surface grains, which are dependent on the deposition temperature and addition of dopants [15]. For the obtained ZAO thin films, uniform and dense surface with small grain size is observed. For gadolinium oxide doping, the surface morphology shows a noticeable variation of the film surface with appearing of some big grains. It indicates that, during deposition of Gd doped ZAO film by sputtering onto substrates the growth has taken place by
nucleation and coalescence process. Randomly distributed (0 0 2) oriented nuclei may have first formed and these nuclei then have grown to form observable islands. As islands increase their size by further deposition and come closer to each other, the larger ones appeared to grow by coalescence of smaller one. Flattening of islands to give increased surface coverage of the clusters follows this step [8,16].

3.2. Optical and electrical properties

The transmittance of the Gd doped and undoped ZAO films of thickness 170 nm is depicted in Fig. 3. The transmittance of all deposited films at $\lambda = 550$ nm is better than 87.0%. In the visible region, the undoped ZAO film shows the transmittance of the order of 87% while that of Gd doped ZAO film was of the order of 92%. Al doping affects the transmittance of ZnO films a little. It’s noticed that the additional Gd doping improves the optical properties. This attributed to decrease in free carrier absorption due to the elevated carrier mobility of the film [17]. The absorbance has slightly increased after Gd doping, which is related to the introduction of the Gd defect states within the forbidden band leading to absorption of incident photons. In the ultraviolet region, the optical transmittance of the film falls sharply due to the onset of the fundamental absorption in this region. The absorption edge of the Gd doped ZAO film appeared to shift towards the longer wavelength side. The optical absorption coefficient provides information on the band structure. $\alpha$ is given by the formula [18]:

$$\frac{T}{1 - R} = \exp(-\alpha t),$$

where $T$ is the optical transmittance, $R$ the optical reflectance, $\alpha$ the absorption coefficient and $t$ is the film thickness. The optical band gap, $E_g$, can be determined from the experimental spectra of the absorption coefficient, $\alpha$, as a function of the photon energy, $h\nu$, using the following equation [19,20]:

$$\alpha h\nu = C(h\nu - E_g)^{1/2},$$

where $C$ is a constant dependent on the electron–hole mobility. Plot of $(\alpha h\nu)^2$ as a function of photon energy against $h\nu$ of undoped and Gd doped ZAO films is shown in Fig. 4. The values of the optical energy gap determined by extrapolating the linear portion of the curves to $\alpha = 0$ are in agreement with those reported in the literature [21–23]. The optical band gap was found to be 3.37 eV for pure ZnO film and it increases to 3.58 eV for ZnO:Al films. The widening of optical band gap may be attributed to Moss–Burstein shift effect [24]. This effect is due to that the conduction band filling in highly degenerate semiconductor makes the Fermi level exceed the conduction band minimum. The band gap was found to be decreased to 3.45 eV for Gd doped ZAO film (1 wt.% Gd doping concentration), which is similar to the report of Kim and Park [25] who
observed the band gap shift from 3.25 to 3.13 eV for Co doped ZnO film (8% doping concentration). Resistivity of doped and Gd doped ZAO films deposited at room temperature and annealed at different temperature is illustrated in Fig. 5. The lowest resistivities of 8.4 \times 10^{-3} and 10.6 \times 10^{-3} Ω cm are observed for Gd doped and undoped ZAO films, respectively, deposited at room temperature and annealed at 150 °C. Gd doped ZAO films exhibit a sensitivity to the different annealing temperatures from 20 to 300 °C. For Gd doped and undoped ZAO films, the electrical resistivities are decreasing with increasing of the annealing temperature from 20 to 300 °C and exhibit a minimum of resistivity value at approximately 150 °C. Raising the annealing temperature, the atoms receive energy and migrate to relative equilibrium positions. This induces a series of effects, for example, reducing the lattice strain and the oxygen defect levels, appearing a more perfect crystallite, pilling up of donor, weakening the grain boundary scattering and increasing the number of current carrier [26,27]. However, excessive annealing temperature causes coarsening of grain, deteriorating of crystal orientation and bringing overmuch defects at grain boundary, which are closely related to the increase in resistivity. After doped Gd, ZAO thin film has an obvious increase in resistivity under the same deposition condition. This is similar to the results of Shinde et al. [8] and Han et al. [28].

4. Conclusions

Gd doped and undoped ZAO films on glass substrates grown by RF magnetron sputtering method at room temperature annealing at different temperature from 20 to 300 °C. A small amount of Al and Gd impurities in the films did not alter the wurtzite structure of ZnO. All of the deposited films demonstrated a c-axis preferred orientation with grain size ranging from 28 to 42 nm. Among all the studied films, ZAO films (3 wt.% deposited at room temperature annealing at 150 °C have the most interesting and useful properties, which are equal to the application in solar cell. They have a transmittance to visible light above 87% and an electrical resistivity of the order of 8.4 \times 10^{-3} Ω cm. Moreover, the electrical properties of Gd doped ZAO films (2 wt.% Al and 1 wt.% Gd) films deposited at room temperature are very sensitive to the annealing temperature. This feature is not obviously exhibited by ZAO and pure ZnO films. The optical band gap of pure ZnO film is 3.37 eV and it increases to 3.58 eV for ZnO:Al films, which is generally attributed to Burstein–Moss effect. The optical band gap was found to be decreased from 3.58 to 3.45 eV by Gd doping for ZAO films. The electrical conductivity of the studied Gd doped ZAO films has been correlated to the existence of Gd and Al atoms in the ZnO matrix and the role of Gd doping effect in the grain growth process by crystallite aggregation. The grain size coarsening for the Gd doped ZAO films deposited at room temperature leads to considerable grain boundary effects, which distributes their electrical properties.

References