Effect of Substrate Temperature on the Properties of Nanostructured ZnO Thin Films Elaborated by Sputtering RF-Magnetron

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Abstract- Thin zinc oxide doped with gallium layers were prepared by rf-magnetron sputtering from nanoparticles synthesized by sol-gel method. Increasing the deposition temperature has resulted in a change of preferred orientations of (002) with an intermediate step-like structure of powder. The films showed different morphologies of the surface of the grains that are dependent on the deposition temperature. This result is interpreted by a coalescence of small grains is favored by accoaisement the substrate temperature. The optical measurements showed that the films have a maximum transmission at about 90 %. Thin films of GZO, have a low resistivity, with a minimum value of $2.20 \times 10^{-4}$ Ω.cm deposited at a substrate temperature of 200 °C with a small thickness of about 300 nm. We found that the resistivity decreases with increasing substrate temperature the decrease is caused by the improvement of crystallinity, concentration and mobility of charge carriers.

Keywords- Thin films, Zinc oxide, rf-magnetron sputtering, optical and electrical properties

I. INTRODUCTION

Zinc oxide (ZnO) is a semiconductor with wide direct gap material and it is currently one of the most studied materials due to its broad potential application. These optical properties are by far those who give him the most important. ZnO is a material whose use has increased in many areas of applications such as piezoelectric transducers [1], the optical waveguides, acousto-optic, other photo-electronic devices [2] and transparent electrodes [3,4]. This is a degenerate semiconductor n-type conductivity is large produced by an excess of zinc in the ZnO layers. To further enhance the conductivity of ZnO layers, it is possible to dope these layers. The mechanisms of doping may be deviating from the stoichiometry of ZnO, mainly by the introduction of excess zinc atoms in interstitial position, or by the creation of oxygen vacancies (the centers created then behave as electron donors) [5], or by substituting zinc atoms or oxygen atoms by foreign network different valence. Various methods of thin film preparation have been used for the growth of ZnO; like evaporation [6], Chemical vapour deposition (CVD) [7, 8], spray pyrolysis [9], magnetron sputtering [10-12] and pulsed laser deposition (PLD) [13]. In this paper, transparent conducting GZO films deposited on glass substrates by rf magnetron sputtering technique are reported using a nanocrystalline powder synthesized by the sol–gel method. The effects of substrate temperature on structural, electrical and optical properties for the GZO films are investigated in detail.

II. EXPERIMENTAL TECHNIQUES

Nanocrystalline GZO aerogels were first prepared by sol–gel method using 10 g of zinc acetate dehydrate [Zn(CH3COO), 2H2O] as a precursor in 70 ml of methanol. After 30 min under magnetic stirring at room temperature, an adequate quantity of gallium nitrate [Ga(N3O9)], corresponding to [Ga]/[Zn] atomic ratios of 0.03 was added. After 30 min under magnetic stirring, the solution was placed in an autoclave and dried in a supercritical condition of ethanol (EtOH) Tc = 243 °C, Pc = 63.3 bars). Then, the GZO films were deposited on glass substrate by rf-magnetron sputtering (13.56 MHz- Cezar Rf-power Generator). Before each deposition, the sputter chamber was evacuated to a base pressure of about 10-5 mbar. After introducing the sputtering Argon gas with 99.9999 % high purity without oxygen, the sputtering deposition was carried out at pressure of 10-3 mbar. The sputtering targets were prepared from the aerogel powders of GZO. During the sputtering process, the target-to-substrate distance is 75 mm, the rfd power is 60 Watts and the substrate temperature is between room temperature to 300 °C.

The structural, morphological, electrical and optical properties were studied in this work. The crystal structure was characterized by X-ray diffraction (XRD) using CoKα radiation (1.78901 Å) .The GZO nanoparticles were also characterized by transmission electron microscopy (TEM)
using JEM-200CX. The composition studies were performed by Energy Dispersive X-ray Spectroscopy (EDS) using a scanning electron microscope JEOL JSM 5410 type with a probe. Surface morphology and roughness were measured using atomic force microscopy (AFM, Topo Metrix). Electrical resistivity, Hall mobility and carrier concentration were measured at room temperature by a Hall measurement system with the Van der Pauw method. The optical transmittance of the films was determined using a Shimadzu UV-3101 PC spectrophotometer in the wavelength range from 200 to 3000 nm.

III. RESULTS AND DISCUSSION

Fig. 1 shows the XRD spectrum of GZO nanoparticles elaborated in the first step. It was found that the sample has hexagonal wurtzite structure according to the JCPDS card number 36-1451. Three pronounced ZnO diffraction peaks, (100), (002) and (101) appear at 2θ = 36.84°, 39.98° and 41.35° respectively, which are very close to wurtzite ZnO ones [14]. This result indicates that GZO aerogel powder has a polycrystalline hexagonal wurtzite structure. Diffraction lines of ZnO were broad, and diffraction broadening was found to be dependent on Miller indices of the corresponding sets of crystal planes. The average grain size was calculated using Scherrer’s formula [15]:

\[
G = \frac{0.9\lambda}{B \cos \theta}
\]

where \(\lambda\) is the X-ray wavelength (1.78901 Å), \(B\) is the maximum of the Bragg diffraction peak (in radians) and \(\theta\) is the full width at half maximum (FWHM) of the XRD peak. The average grain size of the basal diameter of the cylinder-shape crystallites varies from 14 to 20 nm, whereas the height of the crystallites varies from 25 to 34 nm.

The EDS analysis shown in Table 1 confirmed the presence of gallium in the matrix of ZnO and absence of other impurities. From these analyses, we can conclude that the GZO nanoparticles are homogeneous and quasi-stoichiometric.

Fig. 2 shows TEM and SEM photographs of the aerogel powders of GZO as prepared by sol-gel method. It is shown that very small particles of GZO are present in this powder. The crystallites present a very similar prismatic shape with a narrow particle size distribution. The majority of ZnO particles present in this powder have a size between 20 and 32 nm, this result is comparable to that obtained by XRD.

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We report in Fig. 3 the XRD patterns of GZO thin films deposited on glass substrates at different rf power values. All films have 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 [16]. The films are developed without any second phase, indicating that they have a high quality crystalline structure. It is also clearly observed that the intensity of the (002) XRD peak increases with increasing in the substrate temperature. On the other hand, the variation in positions of the (002) peak intensity as a function of substrate temperature observed in Table 2. As Ts increases from RT to 300 °C, the average crystal size increases from 29.20 to 32.20 nm, indicating that a high substrate temperature can improve the crystallinity of the GZO film. The crystal size increased with the increase of substrate temperature, but decreased slightly at 300 °C.

Fig. 2. Typical TEM photograph (a) and SEM showing (b) the general morphology of GZO aerogel nanoparticles.

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Fig. 3. XRD patterns of GZO thin films deposited at various substrate temperatures.

From the XRD results, it can be concluded that the film properties are strongly dependent on substrate temperature. The lattice constant \(c\) can be calculated by the formula [17]:

\[
d_{\text{st}} = \left(\frac{4}{3} h^2 + k^2 + l^2 / a^2 + c^2 \right)^{-1/2}
\]

where \(a\) and \(c\) are the lattice constants and \(d_{\text{st}}\) is the crystalline plane distance for indices (hkl). According to
Eq. (2), the lattice constant c is equal to 2 $d_{hl}$ for the (002) diffraction peak. The values of $d_{hl}$ and c are listed in Table 2. All the values of $d_{hl}$ are larger than that of standard ZnO powder (2.603 Å), indicating that the crystalline plane distances of GZO films are lengthened by imperfections such as lattice strains and interstitial defects. Table 2 shows that the increase of substrate temperature results in the reduction of $d_{hl}$, which may be due to the decrease of imperfections and increase in the number of substitutional Ga$^{3+}$ ions for Zn$^{2+}$ ions.

**Table 1: Atomic compositions of GZO nanoparticles.**

<table>
<thead>
<tr>
<th>Chemical composition in at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
</tr>
<tr>
<td>47.12</td>
</tr>
</tbody>
</table>

**Table 2: Variation of the (002) peak positions, β, grain size, intertericular distance ($d_{hl}$) and lattice parameters of GZO films deposited at various substrate temperatures.**

<table>
<thead>
<tr>
<th>T</th>
<th>RT</th>
<th>100 °C</th>
<th>200 °C</th>
<th>300 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(002), 2θ (deg.)</td>
<td>40.04</td>
<td>40.00</td>
<td>40.05</td>
<td>40.04</td>
</tr>
<tr>
<td>β(deg.)</td>
<td>0.337</td>
<td>0.326</td>
<td>0.305</td>
<td>0.338</td>
</tr>
<tr>
<td>Grain size (nm)</td>
<td>29.20</td>
<td>30.10</td>
<td>32.20</td>
<td>29.06</td>
</tr>
<tr>
<td>$d_{hl}$ (nm)</td>
<td>0.2615</td>
<td>0.2613</td>
<td>0.2612</td>
<td>0.2614</td>
</tr>
<tr>
<td>c (Å)</td>
<td>5.230</td>
<td>5.226</td>
<td>5.224</td>
<td>5.228</td>
</tr>
</tbody>
</table>

The substrate temperature dependence about crystallite sizes for GZO films was also revealed by the AFM micrographs. Fig. 5 shows the surface morphologies of the films deposited at various substrate temperatures. With the AFM micrographs, we see an increase in grain size with temperature and the roughness decreases. All the film shows a uniform grain size and a smooth surface with a root mean square roughness of about 8 nm.

![Fig. 5: Surface morphologies for GZO 3at.% films deposited at various substrate temperatures.](image)

The optical transmittance and reflectance of GZO films deposited at various substrate temperatures. The optical absorption coefficient ($\alpha$) is calculated from the transmittance data, where the reflection losses are taken into consideration, by [18]:

$$\alpha = \frac{1}{d} \ln \frac{(1-R)^2 + 4TR}{2TR^2}$$

where $d$ is the thickness of the film and $R$ and $T$ are the reflectance and the transmittance, respectively. The optical energy band gap ($E_g$) of the ZnO thin films was calculated from Tauc plots [19]. The squared absorption coefficient was plotted versus photon energy, and the band gap was obtained by extrapolating the linear part of the curve intersecting with the photon energy axis (Fig. 7).

![Fig. 6: Transmittance (a) and reflectance (b) spectra of GZO films deposited at various substrate temperatures.](image)

The optical band gap for GZO 3at.% films deposited at RT, 100, 200 and 300 °C is 3.63, 3.57, 3.65 and 3.48 eV, respectively. All the values are larger than that of pure ZnO (3.30 eV). With increase in substrate temperature, the value of $E_g$ decreases first and then increases rapidly. This increase of the gap is caused by the Burstein-Moss effect [20, 21]. The blue shift of the top absorption layer of Ga-doped ZnO is...
related to the increased concentration of charge carriers blocking the lowest conduction band states (Burstein-Moss effect).

Semiconductor materials incorporated with dopants would induce the formation of band tailing in the band gap. The Urbach tail of the films can be determined by the following expression [22, 23].

$$\alpha = \alpha_0 \exp \left( \frac{h \nu}{E_u} \right)$$

where $\alpha_0$ is a constant and $E_u$ is the Urbach energy, which refers to the optical transition between occupied states in the valence band tail and the conduction band edge [22]. The $E_u$ values were obtained from the inverse of the slope of $\ln(\alpha)$ versus photon energy. The results are shown in Fig. 8. In increasing with the substrate temperature shows that the structural disorder decreases and improves the stoichiometry [24]. Natsume et al. [25] have proposed an explanation for this variation localized donor levels from interstitial zinc atoms states.

Zinc oxide is a transparent material whose refractive index in the massive form is 2 [26]. In the form of thin film, its refractive index and absorption coefficient varies depending on the conditions of preparation. The calculated refractive indices at different wavelength are shown in Fig. 9. It’s clear that the refractive index $n$ is in the range of 1.80 - 2.25 in the visible region decreases with the increase of the wavelength. These variations indicate that the refractive index increases with the substrate temperature. This growth of the refractive index can be mainly attributed to an increase in carrier concentration in the films Zn$_{0.97}$Ga$_{0.03}$O.

Fig. 10 shows the electrical resistivity ($\rho$), carrier concentration ($n$) and mobility ( $\mu$) as function of substrate temperature. All our Hall measurement results, show that GZO 3at.% films are with a resistivity in the range of $10^3$ $\Omega$.cm. The films deposited at room temperature exhibit a resistivity of $3.50\times10^3$ $\Omega$.cm. As the substrate temperature increases to 200 °C, the resistivity decreases to the minimum value of $2.20\times10^3$ $\Omega$.cm, and then slightly increased at 300 °C, which is due to the improved Ga substitution and ZnO crystallinity at higher temperature, as indicated by XRD results. At this temperature the mobility also undergoes a sharp increase, which results from the greatly weakened carrier scattering process due to the improvement of crystallinity. In addition, due to the polycrystalline nature of the film, higher substrate temperature can promote desorption of oxygen from the grain boundaries in grain boundaries, which helps to promote Ga substitution and provides more donor states, thus increasing the mobility.

The maximal mobility is 16.42 cm$^2$/V s, which are obtained at 200 °C. At this temperature the mobility also undergoes an increase, which results from the greatly weakened carrier scattering process due to the improvement of crystallinity. The increase in resistivity for temperatures above 200 °C corresponds to a decrease in mobility. The most likely phenomenon explaining the decreased mobility is
increased incorporation of impurities in the layers. The decrease in conductivity is attributed to an increase in chemisorbed oxygen, which acts as electron trap and results in the decrease of carrier concentration [27], while the decrease of carrier mobility may be related to the increase of grain boundary scattering for the free electrons. These results are in accordance with the theoretical explanation by Fu [28] and Hong et al. [29]. Results of this study indicated that the conductivity of ZnO/Ga film was closely related to the crystallinity. The electrons were resulted from little Ga donors (Zn. Ga). The electrical transport properties of ZnO/Ga films were dominated by the carrier concentration and mobility. V. Khranovskyy results [28] indicated that the conductivity was strongly dependent on the crystallinity of Ga doped ZnO film. However, the electrical transport properties of films were dominated by either carrier concentration or mobility. This is different from our results.

V. CONCLUSION

Transparent conductive GZO films were deposited successfully by RF magnetron sputtering on glass substrates, process using aerogel nanopowders prepared by sol-gel technique. An analysis of the effect of substrate temperature on the electrical, optical, structural characteristics was performed. ZnO:Ga films were deposited on glass substrates by RF magnetron sputtering. All the films were polycrystalline with the ZnO hexagonal wurtzite structure. However, the effect of Ts modifies the film growth process and, hence, affects the structure and surface morphology. The layers GZO, have a low resistivity, with a minimum value of 2.2 $10^{-3}$ Ω cm obtained by the sample deposited at a substrate temperature of 200 °C. We found that the resistivity decreases with increasing substrate temperature the decrease is caused by the improvement of crystallinity. In addition, all the layers are highly transparent in the visible range and with increasing optical gap. A blue shift of absorption edge occurred with increasing temperature. Based on the good conductivity and high transmittance, the GZO films prepared by rf- magnetron sputtering can be regarded as a transparent electrode.

REFERENCES