Effect of Gallium incorporation on the properties of ZnO thin films

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Abstract: Ga doped ZnO thin films were formed by the Ultrasonic Chemical Spray Pyrolysis method onto substrates using zinc acetate and gallium (III) nitrate hydrate as precursors. The structural, optical, surface and electrical properties were studied as a function of increasing Ga doping concentration from 0 to 6 at %. Structural studies revealed that films were polycrystalline with hexagonal wurtzite crystal structure. The transparency in the visible range was around ~85% for thin film deposited using 6 at % Ga doping. With the aim of determining surface images and surface roughness of the films atomic force microscope images were taken. The Ga additive to ZnO thin films significantly reduced surface roughness. Electrical resistivity was determined by four point method. The resistivity 2 at % Ga doped ZnO film was the lowest resistivity of 1.7 Ωcm. In the photoluminescence measurements of the films, existence of UV and defect emission band were observed. As a result, Ga doped ZnO films have advanced properties and promising materials for solar cells.

Keywords: Ga-doped ZnO; chemical spray technique; XRD; AFM; Optical properties; Electrical properties.

1. Introduction

Transparent conductive oxide (TCO) thin films have a very important place in optoelectronic applications. The most developed TCO technology for practical applications is based on indium tin oxide (ITO) [1]. Recently, zinc oxide (ZnO) has emerged as an important transparent conductive metal oxide capable of replacing commonly used expensive ITOs. ZnO is a transparent semiconductor material composed of II-VI type with natural n-type conductivity. ZnO is a non-toxic material found abundantly in nature. It has also emerged as one of the most promising materials due to its optical and electrical properties. [2]. Group III A elements Al, In, Ga and B have been frequently used as n type dopants for ZnO [3]. Ga-doped ZnO (GZO) has also drawn attraction in the recent times as well as doping-free ZnO [4-7]. GZO is more stable due to high electronegativity of gallium [8]. GZO with low electrical resistance and high optical transparency in visible region is one of the most suitable candidates for alternative TCO films. [9]. In order to obtain Ga-doped ZnO films, various thin-film production techniques such as magnetron sputtering [10-13], chemical spray pyrolysis[14-21], sol-gel [22-24], chemical vapour deposition (MOCVD) [25,26], pulsed laser deposition (PLD) [27-29] and ion plating with DC are discharge [30,31] are used. The chemical spray technique among these techniques is widely used thanks to its advantages in terms of that the films produced have wide surfaces
as well as that it is economic and simple. In this paper, undoped and Ga-doped (2,4 and 6 at %) ZnO films were produced by using Ultrasonic Chemical Spray technique (USP) and their electrical, optical, structural and surface properties were researched.

2. Experimental Details

USP technique is a low-cost, non-vacuum required, way to synthesize materials in the form of powders and films [32]. The films were produced on glass substrates with USP technique. Zn(CH$_3$COO)$_2$·2H$_2$O was used as Zn source and Gallium (III) nitrate hydrate [Ga(NO$_3$)$_3$·xH$_2$O] was used as Ga source in order to obtain the films. All the films were produced at a substrate temperature of 350 ± 5 °C, and the substrate temperature was measured using an iron-constantan thermocouple. Totally 100 cc of solution was sprayed onto pyrex glass substrates during 20 min. The solution flow rate was kept at 5 cc min$^{-1}$ and controlled by a flow meter. Air (1 bar) was used as the carrier gas. The production parameters and codes of the films were given in Table 1. In order to examine the structural properties of the films, XRD patterns were taken at 30° ≤ 2θ ≤ 70° by “Rigaku X-Ray Diffractometer” with the powder method by using Cu$K_x$ radiation (λ = 1.5406 Å). With the "Park Systems XE 100 model", the surface properties of the films were taken. Also, rms ($R_q$) and average ($R_a$) roughness values were determined. Thicknesses of the films ($t$), Δ values, refractive indexes ($n$) and extinction coefficients ($k$) were determined by “OPT-S9000 Spectroscopic Elipsometer (SE)” with 250-2300 nm measuring range. Transmittance ($T$) spectra were taken by “Shimadzu-2550 UV-Vis Spectrophotometer” with 300-900 nm measuring range. Also, optical band gaps ($E_g$) of all films were determined by the optical method. “Keithley 2601A LUCAS Labs PRO4” device was used to determine the electrical resistivity of the films. Also, photoluminescence spectra (PL) of the films were taken by “Perkin Elmer LS55 Fluorescence Spectrometer”.

Table 1. Codes and production parameters of GZO.
| Film          | Code | Molar | Spraying Time | Substrate Temperature |
|--------------|------|-------|---------------|------------------------|
| ZnO          | Z0   | 0.1 M | 20 min        | 350±5 °C               |
| ZnO:Ga %2    | GZO-2| 0.1 M | 20 min        | 350±5 °C               |
| ZnO:Ga %4    | GZO-4| 0.1 M | 20 min        | 350±5 °C               |
| ZnO:Ga %6    | GZO-6| 0.1 M | 20 min        | 350±5 °C               |

3. Results and Discussions

3.1. Structural properties

Fig.1 shows XRD patterns at various Ga doping concentrations (0 to 6 at. %). Several peaks were observed which corresponds to (0 0 2), (1 0 1), (1 0 2) and (1 0 3) planes that are all indexed to the hexagonal wurtzite structure of ZnO. The presence of peaks of different densities and widths is an indication that films are formed in polycrystalline structures [33]. It is seen that the crystallinity of Z0 film is better than that of the other ones. In other words, the crystallinities of the films are spoiled with increasing Ga concentration. This is due to the stresses caused by the difference in the ionic radii of zinc and gallium. In Table 2, it draws attraction that \( 2\theta \) and \( d \) values belonging to the films show difference in accordance with the values given in Joint Committee for Powder Diffraction Standards (JCPDS) (00-036-1451) [34]. As shown in Table 2 that the refractive peak (002) is shifted to higher angles when Z0 film is compared with other films. This indicates that Ga\(^{+3}\) (0.62 Å) having a small ionic radius took the place of Zn\(^{+2}\) (0.74 Å) ion having a bigger ionic radius [35]. Grain size (\( D \)) values can be calculated using the Debye-Scherrer formula given below:

\[
D = \frac{0.94 \lambda}{\beta \cos\theta}
\]

where \( \lambda \) is the x-ray wavelength (1.5405 Å) used, \( \beta \) is the full-width at half maximum (FWHM) of the diffraction peak and \( \theta \) is the Bragg’s angle, \( d \) the interplanar spacing, and \( d_0 \) the interplanar spacing without deformation [36, 37]. In Table 2, it is seen that the Ga additive disrupts the crystal structure.
Figure 1. The XRD patterns of GZO films.
Table 2. The data and structural parameters belonging to XRD patterns of GZO films.

| Film  | \(2\theta^o\) | \(d (\text{Å})\) | \(d_0 (\text{Å})\) (JCPDS) | (hkl) | \(D \text{ (nm)}\) |
|-------|----------------|-----------------|--------------------------|-------|---------------------|
| \(Z0\) | 34.22          | 2.618           | 34.42 (002)              | 35    |
|       | 36.06          | 2.489           | 36.25 (101)              | 30    |
| \(GZO-2\) | 34.48          | 2.599           | 34.42 (002)              | 29    |
|       | 36.42          | 2.477           | 36.25 (101)              | 24    |
| \(GZO-4\) | 34.40          | 2.605           | 34.42 (002)              | 18    |
|       | 36.20          | 2.479           | 36.25 (101)              | 18    |
| \(GZO-6\) | 34.54          | 2.595           | 34.42 (002)              | 26    |
|       | 36.36          | 2.469           | 36.25 (101)              | 26    |

3.2. Optical properties

The thicknesses and optical constants of the films are determined by SE. The polarization state of the electromagnetic wave is given by \(\Psi\) and \(\Delta\), which are known as ellipsometric parameters. Thus, information about the sample that changes the polarization state is obtained. \(\Psi\) and \(\Delta\) parameters are measured as wavelength function in SE measurements [38]. Elipsometric data analysis requires an optical model (Cauchy-Urbach model) that defines the layer thickness and optical constants of the sample. The Cauchy model is suitable for areas where the extinction coefficient is zero. The Urbach equation represents the extinction coefficient of the region where the material has little absorption [39]. Cauchy-Urbach model is used for fitting the experimental data. SE measurements have been taken at a wavelength range of 1200-1600 nm.

In order to determine the thickness of all films with high precision, polarized light are sent at different angles (60°, 65°, 70°) on the material, and \(\Delta\) spectra are taken. The best angle for \(\Delta\) spectra was determined as 70°. \(\Delta\) spectra of the films are shown in Fig. 2. A good fit was found between experimental and theoretical data using Cauchy-Urbach model. But in the films, it draws attraction that there are deviations at experimental and theoretical \(\Delta\) values. These may be related to the production technique used in the preparation of films. Also, such a deviation may have been occurred due to the data taken in spectroscopic elipsometer technique which is sensitive to surfaces of the films. Another reason of the deviation may have been the grain boundaries. It is previously seen that there is a decrease at crystallization level with addition of
Ga element. Fitting the experimental ellipsometric spectra allowed us to determine the thickness ($t$), refractive index ($n$) and extinction coefficient ($k$) for all films. The thickness values of ZnO films and ellipsometric data are given in Table 3. It is noteworthy that the thickness values decrease with Ga incorporation.

**Figure 2.** $\Delta$ spectrums of GZO films.
Table 3. Thicknesses ($t$) Cauchy-Urbach model parameters, the average refractive index ($n$) and extinction coefficient ($k$) values of GZO films.

|   | $t$ (nm) | $A_n$ | $B_n$ (nm)$^2$ | $C_n$ (nm)$^4$ | $A_k$  | $B_k$ (eV)$^{-1}$ | $n$  | $k$  |
|---|---------|-------|----------------|----------------|-------|-----------------|------|------|
| Z0 | 135     | 1.914 | 0.0100         | 0.011          | 0.29  | 1.09            | 1.922| 0.0233 |
| GZO-2 | 39     | 2.201 | 0.0106         | 0.0014         | 0.35  | 1.386           | 2.206| 0.0135 |
| GZO-4 | 59     | 2.079 | 0.0102         | 0.0015         | 0.36  | 1.386           | 2.085| 0.0136 |
| GZO-6 | 51     | 2.031 | 0.0100         | 0.002          | 0.36  | 1.385           | 2.037| 0.0139 |

Figure 3 shows transmittance spectra of the films. The films are seen to be transparent and homogeneous [14]. This is also confirmed by transmittance spectra of the films. The transmittance in the visible area is approximately % 80. The regions with sharp decrease in transmittance are the fundamental absorption regions. It is clear from the inset of Fig. 3 that the absorption edge of Ga doped ZnO thin films shifts toward lower wavelengths with the increase in Ga content. Another important point in Fig. 3 is the increase of transmittance values of ZnO films in visible region with the addition of Ga into the structure. Ga doped samples exhibited increased optical transmission, in the visible area and this is good for device application.
Figure 3. Transmittance spectra of GZO films. 

$(\alpha h\nu)^2 - h\nu$ plots of GZO films are given in Figure 4. Optical band gap values of the films have been determined by optical method [40]. Optical band gap values of the films Z0, GZO-2, GZO-4 and GZO-6 have been calculated to be 3.27, 3.28, 3.28 and 3.28 eV, respectively. All films have direct band gap transitions [5, 7, 14].

Figure 4. $(\alpha h\nu)^2 - h\nu$ plots for GZO films.

PL spectroscopy is an important tool to characterize defects in semiconductors [41]. PL spectrums of the films taken with 3.82 eV excitation energy at room temperature are given in Figure 5. ZnO films have two variety emissions according to literature: (i)
The UV emission observed at 380 nm depends on the crystal quality and (ii) visible deep level emissions which is observed at 450-730 nm and these emissions are due to various nature defects in the structure of ZnO. [42-45]. When PL spectrums are examined, it is determined that UV emission are at ~390 nm (3.18 eV) (1\textsuperscript{th} peak); blue emission is at ~440 nm (2.76 eV) (2\textsuperscript{nd} peak); green emission is at ~490 nm (2.5 eV) (3\textsuperscript{rd} peak); yellow-orange emission is at ~550 nm (2.25 eV) (4\textsuperscript{th} peak) and orange emission is at ~590 nm (2.11 eV) (5\textsuperscript{th} peak) [46, 47]. The intensity of the 1\textsuperscript{st} peak known as UV emission decreases when the Ga additive increases. But, the intensity of 1\textsuperscript{st} and 2\textsuperscript{nd} peaks in the GZO-2 increased compared to others. It was resulted from the interstitial zinc (Zn\textsubscript{i}) [19, 20]. 3\textsuperscript{rd} peak corresponding to the green emission in PL spectra is an indicator for existence of oxygen vacancies (V\textsubscript{o}) that act as a deep visible trap in the structure [14]. The increase in the intensity of this peak draws attraction especially in GZO-2 films. 4\textsuperscript{th} and 5\textsuperscript{th} peaks that show yellow-orange and orange emissions are indicators of interstitial oxygen (O\textsubscript{i}).
3.3. Surface properties

Figure 6 shows the atomic force microscope images of the Ga-doped ZnO thin films. There are randomly distributed particle formations on the surface with different sizes that can be distinguished from each other [40]. Ga doping concentrations affected the surface roughness levels of the films. This is probably a result of uncompleted reactions because of high Ga content exceeding for this samples. The $R_q$ (rms) and $R_a$ (average) roughness values of the GZO films are listed in Table 4. It is seen that roughness decreased in Ga-doped films.

![AFM images of GZO films](image)

**Table 4.** Roughness values of GZO films.

| Film  | Z0  | GZO-2 | GZO-4 | GZO-6 |
|-------|-----|-------|-------|-------|
| $R_a$(nm) | 26  | 4     | 10    | 7     |
| $R_q$(nm)  | 32  | 5     | 12    | 10    |
3.4. Electrical properties.

Resistivity values of the films ZO, GZO-2, GZO-4 and GZO-6 have been determined to be 29.4, 1.7, 1.9 and 3.0 Ωcm, respectively. The resistivity of the ZO is higher than that of the Ga doped films. GZO-2 has the lowest resistivity value among others. This may be related to the increasing amount of Ga and Zn interstitials which in turn increases the carrier concentration.

In sample GZO-4, we haven’t obtained the expected decrease in resistivity. Sample GZO-6 has the highest resistivity value among Ga doped samples. A further increase in the concentration of Ga, the increased energy formation can suppress ZnO films to form energy transition metal atom and oxygen gap defects. We think that the high crystal quality of this sample is due to the fact that Ga³⁺ behaves as a substituent with Zn²⁺ instead of playing an interstitial role. This will probably hinder the further decrease of electrical resistivity. Also, the defects such as interstitial Ga³⁺ or interstitial zinc (Zn_i) or oxygen vacancies(V_o) as well as Ga doping may take a role in the increase of carrier densities by playing a role in this case [48,49].

4. Conclusions

Ga doped ZnO films have been deposited onto glass substrates by USP technique. The Ga element doping procedure has been selected at three different rates of 2%, 4% and 6%. Structural, optical, surface and electrical properties of the films have been researched. The XRD patterns indicate that the GZO thin films have polycrystalline nature. X-ray diffraction studies showed that the crystallinity level has been impaired by the effect of Ga element. That is, successfully substitution of Ga³⁺ ions with Zn²⁺ ions has been applied. Spectroscopic ellipsometry technique is used to determine the thicknesses and optical constants of the films. It is seen that the optical permeability of the films is the contribution of gallium. It appears that Ga does not have an effect on the optical band gap values. The minimum resistivity was achieved for Ga doped ZnO thin films. As a result of the investigation of the optical, structural, surface and electrical properties of all the films obtained, it was determined that the amount of doping element significantly affected the physical properties of ZnO films. It was also concluded that the films may be used in solar cells as transparent front contact due to their opto-electric properties.
Acknowledgments

This study was supported by Eskisehir Osmangazi University BAP Commission (Grant No: 201219022).

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