Chapter 32

Influence of the Concentration of Ga-doped on the Structural and Optical Properties of ZnO Thin Films

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Abstract. Gallium (Ga) doped zinc oxide transparent conductive films were deposited on corning glass by homemade DC magnetron sputtering. Influence of Ga-doped concentration on the structural and optical properties of ZnO:Ga thin films were studied by XRD and UV-Vis spectrometer. The XRD pattern demonstrated that crystallinity of the film was improved with increasing Ga-doped concentration from 1 to 2%, but the peak (002) intensity of the samples deposited at Ga doped 3% significantly decreased with increasing Ga-doped concentration. The optical transmittance of ZnO films with 1 and 2% Ga-doped concentration are about 85% in the visible range and the films deposited at 3% Ga-doped concentration is about 70%. Band gap of the ZnO thin films are 3.28, 3.25 and 3.22 eV for 1, 2 and 3% Ga-doped concentration respectively.

Keywords: ZnO, Ga-doped, DC magnetron sputtering

I. Introduction

Transparent conductive oxide (TCO) thin film materials such as zinc oxide (ZnO) and indium tin oxide (ITO) have been widely to used as transparent electrodes, window materials for display and solar cells. These materials have received much attention because their interesting optical and electrical properties [1]. ZnO is a promising alternative to ITO in TCO applications, due to inexpensive, non toxic, relatively low deposition temperature and chemical stability [2], and wide band-gap (3.4 eV) [3]. However, the properties of the pure ZnO are unstable [4]. Therefore, to enhance these properties, ZnO can be doped with some dopants. The group III such as B, Al, Ga, and In have been doped to ZnO crystals [5]. The atom dopants replace the Zn site in the ZnO crystal. In this case, more one free electron has been generated.

From all dopant elements, Ga is the most effective for ZnO [4] because the covalent bond length of Ga-O (1.92 Å) and Zn-O (1.97 Å) is similar. Therefore, the doping of Ga to the ZnO crystal can be reduced the deformation of the ZnO crystal structure.

ZnO films have been grown by many methods. Among the preparation techniques, sputtering method is promising with several advantages. The films can deposit in large area and the growth rate is high enough [6]. Also, sputtering method is low cost of the source materials [2]. In this study, ZnO:Ga thin films with different Ga concentration were fabricated by using homemade dc magnetron sputtering. The structural and optical properties of ZnO:Ga films were investigated

II. Experimental Procedure

A homemade dc magnetron sputtering system was employed for the deposition of ZnO:Ga thin films on corning glas substrates at substrate temperature at 400^{o}C. A sintered targed with a mixture of ZnO (99.999 % purity) and Ga_2O_3 (99.999 % purity) was employed as the source materials. The target diameter was 2.5 cm with total mass of 10 gram. The amount of Ga_2O_3 added to the target was varied at concentration 1 and 3 (wt. %) respectively. The dc sputtering power was kept constant at 30 watt. The ultrasonic bath was used to clean corning glass substrates with aceton and methanol solution for 15 minutes. All the films were deposited at 60 minutes deposition time.

The structural properties were analyzed with X-ray diffractometer (XRD) with $Cu - K_\alpha$ radiation (1.5406 Å).

The optical transmittance measurement was done by UV-Vis spectroscopy. The samples were characterized at room temperature. The characterization results have been compared with the properties of ZnO:Ga (2%) in the previous work [7].

III. Results and Discussions

Fi. 1 shows the XRD spectrum for ZnO:Ga thin films at 1 and 3% Ga-doped concentration. The spectrum has been compared by ZnO:Ga (2%) XRD spectrum in the previous work [7]. As shown in Fig. 1, a strong (002) peak is observed at 2θ = 34.4 and a weak (004) peak for all samples. These crystalline dimension along *c*-axis

is 34.57, 34.44 and 34.05 for 1, 2 and 3 % Ga concentration respectively, as estimated by Scherer formula. These peaks indicate that the crystal structure almost independent of the Ga-doped concentration. Only the films deposited with 3% Ga-doped concentration showed a weak (101) peak. It reveal that all of the obtained ZnO thin films were polycrystalline with the hexagonal wurzite structure and had a preferred orientation with *c*-axis perpendicular to the substrates [8]. These films showed that no Ga_2O_3 phase was found from the XRD patterns, which implies that Ga atoms substitute Zn atom in the hexagonal lattice or probably segregate to the non crystalline region and form Ga-O bond. Ma *et al.* [2] believed that much of Ga is able to ionize into Ga^{3+} and substitute Zn^{2+}, so that it can contribute a free electron from each Ga atom.

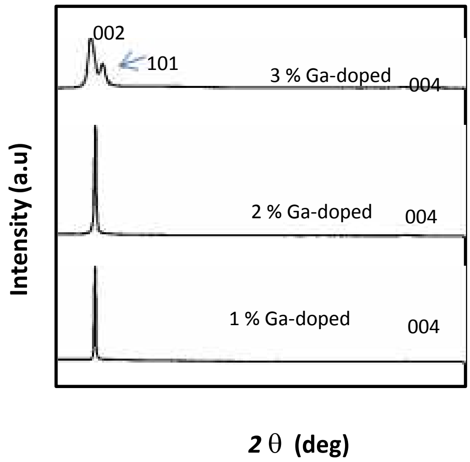


Fig. 1. X-ray diffraction patterns for ZnO:Ga thin films deposited at different Ga concentrations.

As the deposition Ga concentration doped increases, the diffraction angle does not change significantly and the intensity of of the (002) peak becomes more intense and sharper at 2% Ga concentration. However, when the Ga concentration at 3 %, the intensity of the (002) peak becomes very weak, which can be indicated to degraded the crystallinity of the samples. This is could occur because the number of Ga nuclei increase during the deposition process so that the distribution of crystallities became more random [9]. Thus, the XRD pattern demonstrated that crystallinity of the film was improved with increasing Ga-doped concentration from 1 to 2%, but the peak (002) intensity of the samples deposited at 3% Ga-doped concentration significantly decreased with increasing Ga concentration.

TABLE I
STRUCTURAL PARAMETERS OF GALLIUM DOPED ZINC OXIDE THIN FILMS DEPOSITED AT DIFFERENT ARGON CONCENTRATION

Sample	2θ (^{o})	Lattice constant *c* (Å)	Crystal size (nm)	d-spacing (Å)
1% Ga-doped ZnO	34.57	0.519	42	2.59
2% Ga-doped ZnO [7]	34.44	0.520	24	2.60
3% Ga-doped ZnO	34.05	0.526	12	2.63

Table I shows structural parameters of the ZnO:Ga thin films deposited. It clearly shown that the Ga concentration has a great influence on ZnO:Ga crystal size. These parameters reveal that increasing of the Ga- doped concentration reduces crystal size. However, the *c*-axis lattice constant, increased from 0.519 to 0.526 Å with increase in the Ga concentration. The increase in the *c*-axis lattice occurs probably due to the increase in substitution of Ga^{3+} ions, so that increase the repulsive force total. Crystal size decrease from 42 to 12 nm with increasing Ga concentration showed that ion Ga^{3+} more random distribution.

TABLE II
LATTICE STRAIN AND STRESS VALUE OF GALLIUM DOPED ZINC OXIDE THIN FILMS DEPOSITED AT DIFFERENT ARGON CONCENTRATION

Sample	Lattice strain	Stress (GPa)
1% Ga-doped ZnO	0.1555	- 36.2234
2% Ga-doped ZnO	0.2068	- 48.2022
3% Ga-doped ZnO	0.5791	- 134.9198

Table II shows lattice strain and stress value of ZnO thin films with different Ga concentration doped. Lattice strain and stress values can be analyzed from XRD spectra. Lattice strain value of the ZnO:Ga films can be found with tangent formula [10]

$$\varepsilon = \frac{\beta}{4\tan\theta} \qquad (1)$$

Where ε is lattice strain, β is full width half maximum (FWHM) and θ is diffraction angle. Stress of the films is given by Eq.2.

$$\sigma_{film}^{XRD} = -233\varepsilon \qquad (2)$$

Where σ_{film}^{XRD} denotes thin film stress.

Fig. 2 shows the optical transmittance spectra for the ZnO:Ga thin films fabricated with 1 and 3% Ga-doped concentration. The spectrum of optical transmittance of the samples were compared with optical transmittance of ZnO:Ga (2%) spectrum also. The transmittance of the ZnO thin films with 1 and 2% Ga concentration were 85% in the visible region. This value is similar with the transmittance spectrum of the ITO thin films [5]. However, transmittance of 3% Ga-doped ZnO only reached about 70%. It occurs probably due to related with the degraded the crystallite structure of ZnO thin films.

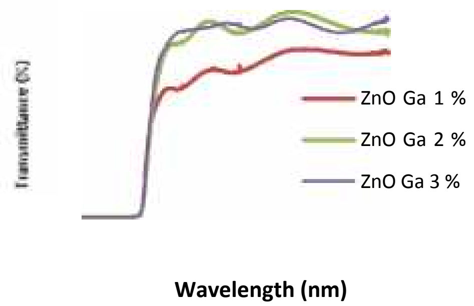
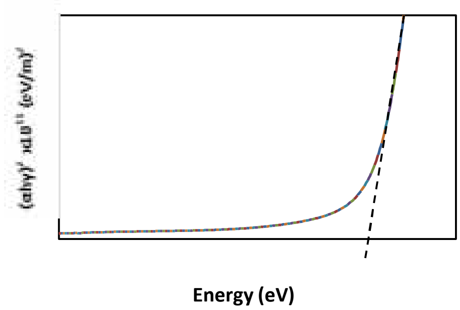
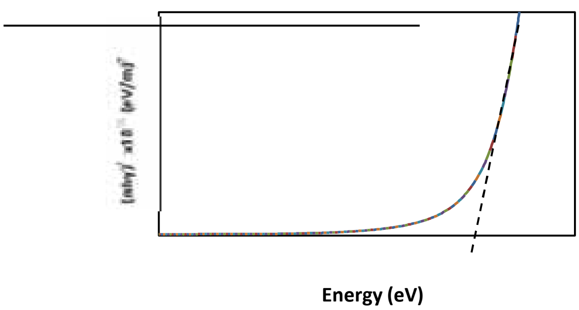


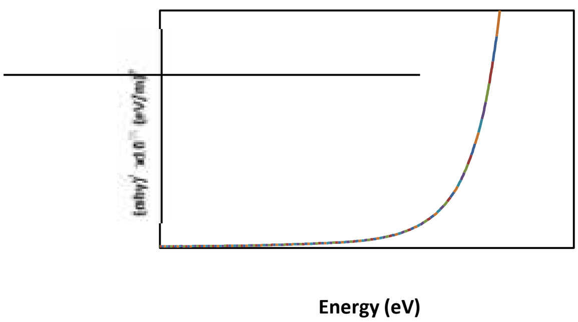
Fig. 2. Transmittance spectrum of ZnO:Ga thin films prepared at different Ga-doped concentrations.



(a)



(b)



(c)

Fig. 3. Optical band gap (E_g) of ZnO thin films at different Ga-doped concentration: (a) 1%; (b) 2%; and (c) 3%.

ZnO:Ga thin films have a direct band gap, so that the absorption edge for interband transition is given by Eq. 3.

$$(\alpha h\nu)^2 = A(h\nu - E_g) \tag{3}$$

where α denotes the absorption coefficient and A denotes the constant for a direct transition. The E_g of the films is obtained by plotting α^2 vs. $h\nu$ and extrapolating the straight line portion of this plot to the energy axis as shown in Fig. 4. As the Ga concentration increases from 1 to 3%, the band gap E_g of the ZnO:Ga thin films decrease from 3.28 to 3.22 eV, which is sorter than that of undoped ZnO (~3.3 eV) [5]. This deviation may be due to the structural defects takes place at deposition process [11]. The decrease of band gap occurs probably due to correlate with the crystal size and lattice strain of the films. Furthermore, the decreasing band gap can be due to the carrier concentration effect [12]. In previous work, Shin *et al.*[5] reported that the optical band gap would decrease with decreasing carrier concentration. On the other hand, Lin *et al.* [9] also reported that the carrier mobility dropped when Ga was between 3.0 and 10.0 at%

IV. Conclusions

Gallium doped ZnO thin films were fabricated on corning gas substrates at different Ga concentration 1, 2 and 3% (wt) by homemade DC magnetron sputtering. All films deposited are polycrystalline with the hexagonal wurzite structure and had a preferred orientation with *c*-axis perpendicular to the substrates. The Ga-doped concentration has a great influence on film structural. As the deposition Ga-doped concentration increases, the diffraction angle does not change significantly and the intensity of of the (002) peak becomes more intense and sharper at 2% Ga concentration. However, when the Ga-doped concentration at 3 %, the intensity of the (002) peak becomes very weak, which can be indicated to degraded the crystallinity of the Ga-doped ZnO thin films. The optical transmittance of ZnO films with 1 and 2% Ga-doped concentration are about 85% in the visible range. However, transmittance of the films deposited at 3% Ga-doped concentration is about 70%. Band gap of the ZnO thin films are 3.28, 3.25 and 3.22 eV for 1, 2 and 3% Ga-doped concentration respectively. The optical band gap of the ZnO:Ga deposited are shorter than of pure ZnO (~3.3 eV).

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