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RESEARCH PAPER

Preparation and Characterization of ZnO Thin Layers with Various Percentages of Gallium Impurities

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ABSTRACT

In this study, thin films of pure ZnO and doped ZnO with different percentages of gallium (0.5, 1, 2 and 4vt. %) on the glass substrates were deposited by using sol-gel method via spin coating technique at 2500 rpm, and all layers were annealed at 200°C for 1h and then Were examined their electrical, optical and structural properties. Concentration of all solution was 0.1M. The results show that the optimized layer is 0.5% GZO. By examining the transmittance spectrums we find that by doping the transparency of samples were improved and all samples in the visible areas 400-800nm are transparent. The electrical conductivity of all samples has been measured by four-point probe technique. The electrical conductivitys of pure ZnO sample and 0.5% GZO are 910^{-5} S/cm and 110^{-4} S/cm respectively. It can be a good choice for optoelectronic applications. Also X-ray diffraction results showed that diffraction peaks of 0.5% GZO sample have a small changes towards lower angles compared to the diffraction peaks of ZnO.

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INTRODUCTION

In recent years, the transparent conductive thin films, have attracted much attention. This layers has a high electrical conductivity and high optical transparency in the visible region and also have high reflectance in the infrared region [1]. By having these properties, these layers have many applications in many parts of electro-optics, gas sensors, pressure sensors, the optic's cumulative, solar cells and etc [2,3]. Among these materials the ZnO is relatively cheaper than other materials and non-toxic, so is considered as an important technological material. The ZnO is a compound semiconductor with wide band gap about 3.4 eV, hexagonal crystalline structure, mechanical stability, relatively cheap, high thermal and chemical reactivity that in construction of optoelectronic components has been highly regarded [4]. The properties of these semiconductors by adding impurities can change significantly [5]. Gallium is trivalent element that with entry to the ZnO lattice can be changed the carrier concentrations so it's electrical and optical properties can be improved [6]. In this study, gallium impurity was added into the ZnO lattice and were examined it's structural, optical and electrical properties. To the manufacture of thin films of ZnO nano particles, there are a lot of chemical and physical methods such as; sputtering [7], molecular beam deposition [8], spray [9], pulsed laser [10] and sol-gel [11]. Sol-gel method are used more than other technique because

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of simple, being cheap, no need for vacuum equipment, high-purity materials, possibility of accumulation of thin layers with low thickness and etc [12]. Layers that obtained from sol-gel method, are uniform and chemical characteristics. In this report, layers with different concentrations of gallium impurities were prepared by sol-gel method via spin coating technique and then their properties were studied.

EXPERIMENTAL

Zinc acetate dehydrate (0.216gr), 2-propanol (10cc) and mono ethanol amine (1cc) as Precursor, solvent and stabilizer respectively in order to homogenization were placed on a magnetic stirrer in 70°C temperature for an hour to prepared the Intended sol. In the obtained sol there was no precipitate and sol was very stable. The Gallium (III) solution made from gallium nitrate (0.212gr) and ethanol (10cc) with different percentage (0.5, 1, 2 and 4vt. %) was added to the ZnO solution and for 20min were stirred that we achieved the completely transparent solutions of gallium-doped ZnO with different percentages. Glass substrates after washing with distilled water, acetone and isopropanol alcohol by Ultrasonic for 10 minutes, respectively and by argon gas were dried. Then by using spin coating technique with speed of 2500 rpm were deposited for 25s and were annealed in the 200°C for 1h.

RESULTS AND DISCUSSION

Transmission spectrum

Fig.1 shows the transmission spectra of GZO samples with different percentage. That by examining this spectrums we can find that all samples in the visible areas 400-800nm are transparent and by doping it turns out improved the transparency of samples. Table.1. shows the average and maximum of transmittance percentage of samples in the 300-800 nm wavelength. That also be observe 0.5% GZO doped sample have higher transmittance, and best performance. The results show that the layers are containing applications as transparent electrode in the optical devices.

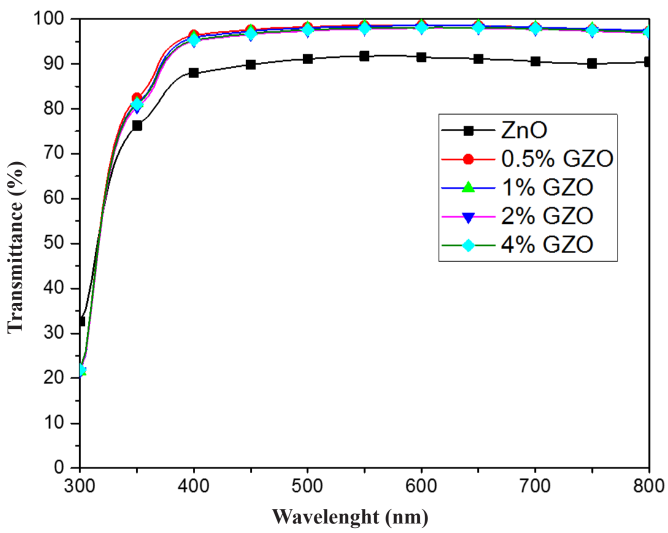

Fig. 1. Optical transmittance of 0 - 4% Ga doped ZnO thin films.

Table 1. Average and Maximum transmittance of 0 - 4 at. % Ga doped ZnO thin films at 300 – 800 nm.

Sample	Dopant ratio (%)	Average Transmittance (%)	Maximum Transmittance (%)
1	0	86.46	91.78
2	0.5	93.15	98.63
3	1	92.86	98.51
4	2	92.27	98.00
5	4	92.51	98.22

SEM spectra

The roughness of the interface are one of the very important basic features in the thin film technology because the surface roughness, effect on physical and chemical properties of layers, directly. Fig. 2. and Fig. 3. shows the SEM images of pure ZnO and optimized of 0.5% GZO thin layers respectively. As can be seen, the particles are spherical and have a very good homogeneity. The average size of grains is measured between 20-50nm in both of figure. Also, it can be observed that by doing doped the average size of particles were smaller and layer have better homogeneity.

X-ray diffraction spectra

Fig.4. shows the X-ray diffraction pattern of pure ZnO and samples of optimized of Ga-doped ZnO nanocrystalline thin films. It can be seen that there is strong diffraction peaks at 31.65°, 34.35° and 36.15° which correspond to the [100], [002] and [101] plates, respectively. And 0.5% GZO sample correspond to the ZnO structure have also wurtzite hexagonal structure. It is observed that diffraction peaks of 0.5% GZO sample have a small changes towards lower compared to the diffraction peaks of ZnO, this shows that the location of the Zn ions is occupied by the Ga ions, successfully. So, this changes of the diffraction peaks due to the occupation of Ga ions is in the place of Zn ions. Doping of Ga ions in ZnO does not cause structural metamorphosis, but since Ga3+ have ionic radius larger compared to Zn2+, by replacing Ga atoms with Zn atoms, will fallow the reduce of the lattice constant. Diffraction peak intensity of ZnO films by doing decreased, as it is seen, compared to corresponding peak of pure ZnO films. Full width at half maximum of all peaks in GZO pattern, is wider than ZnO. Similar to the results that observed by M. Thambidurai et al. [6] and R. Ebrahimifard et al. [28].

Calculation of the energy band gap

To calculate the energy gap from equation (1) is used:

$$\alpha h\upsilon = A\,(h\upsilon - E_g)^n \quad (1)$$

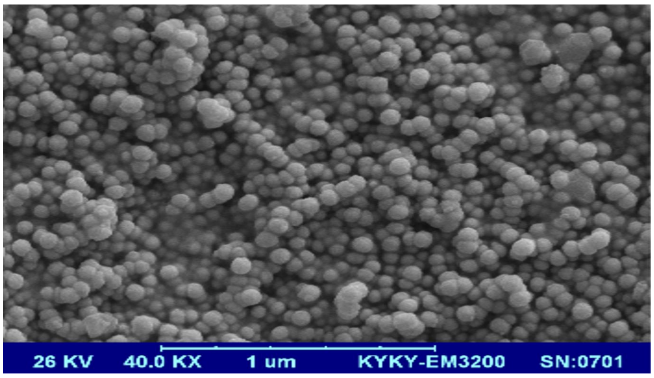

Fig. 2. SEM image of pure ZnO thin film.

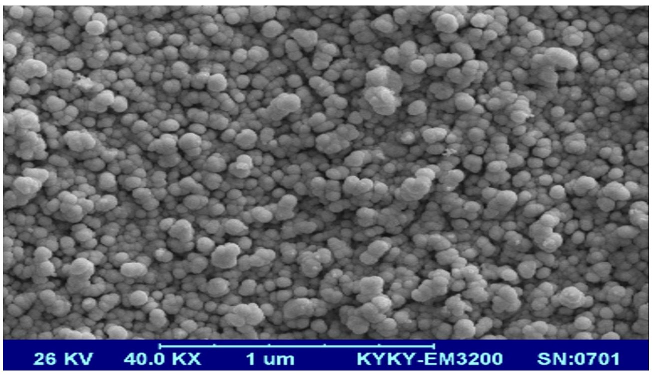

Fig. 3. SEM image of 0.5% GZO thin film.

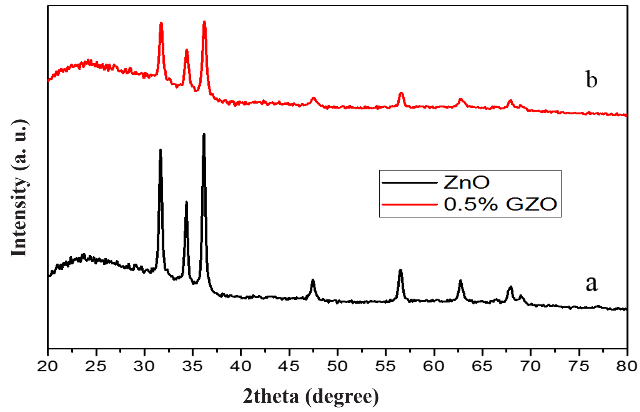

Fig. 4. X-ray diffraction pattern of ZnO and 0.5% GZO thin films.

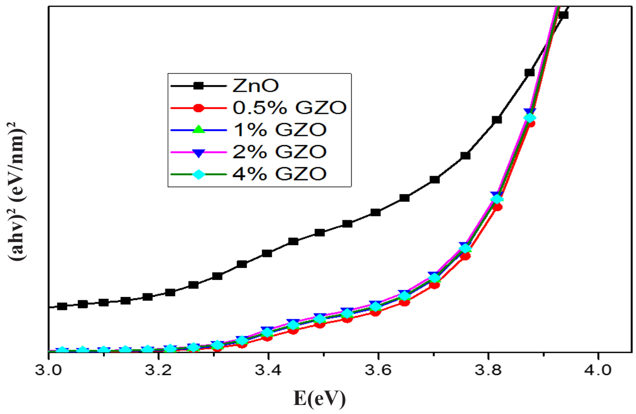

Fig. 5. Optical band gap of Ga doped ZnO thin films with various gallium content.

Were Eg is the band gap, A is the constant, α is the absorption coefficient, hυ is incident photon energy and n=2 is for indirect gap and n=0.5 for direct gap. Using the tangent line to curve changes of nth (αhυ) and along that up to the energy axis and cut it, can be found the energy band gap related to each samples with respective impurities that were showed in Fig. 5.

Table.2 according to Fig.5 shows the samples energy band gap with percentage of different doped, that 0.5% GZO has the highest band gap.

Electrical conductivity

In this study, the intrinsic donors were oxygen vacancies, and extrinsic doping involved the substitution of Ga^{3+} ions for Zn^{2+} sites in the ZnO structure. Therefore, one free electron was produced by the replacement of one Zn atom. As has been reported in many sources, resistance depends on the carrier concentration and mobility. The Zn atoms with Ga atoms has been replaced. So, the free electron density is increased and therefore, the doped films have lower resistance compared to the un-doped films. The electrical conductivity of all samples has been measured by four-point probe technique. Measured conductivity for pure ZnO sample was 9×10^{-5} S/cm and also for 0.5% GZO was 1×10^{-4} S/cm. The lower resistivity of the film after doping with the optimum Ga content can be explained by the fact that Ga atoms substitute for Zn atoms in the crystal lattice and behave as donors and

Table.2 Optical band gap of 0 – 4% Ga doped ZnO thin films.

Sample	Dopant ratio (%)	Band Gap (eV)
1	0	3.47
2	0.5	3.71
3	1	3.69
4	2	3.63
5	4	3.67

induces native n-type conductivity in ZnO film and also reduction of oxygen vacancy [6].

CONCLUSION

In this research, pure ZnO and Ga-doped ZnO thin films with different percentages of doping (0.5, 1, 2 and 4vt.%) were prepared by using sol-gel method via spin coating technique. The results of transmission spectrum show that all layers have optical transmittance top of 90% in the visible region that most optical transmittance is for 0.5% GZO sample so for optical applications is very appropriate. The results of image of scanning electron microscope is represents good quality of the layers, better homogeneity and shrinking particle size of optimized sample. The 0.5% GZO has the highest band gap. The results of X-ray diffraction show that Ga atoms placed instead of Zn atoms successfully and lattice structure of layers is wurtzite. So, with surveys conducted, the sample of 0.5% GZO can be appropriate option for electro-optical applications such as dye-sensitized solar cells.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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