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Influence of Annealing Temperature on the Structural and Optical Properties of Tellurium-Doped ZnO Thin Films for Optoelectronic Applications

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The structural, morphological and optical properties of Te-doped ZnO thin films prepared on microscopic glass substrates using the sol-gel technique were investigated. Zinc acetate dihydrate and tellurium tetrachloride as starting precursors, 2-methoxy ethanol as solvent were used to prepare the gel solution. Deposited films were post-annealed at different temperatures and characterized by X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and UV-VIS Spectrophotometer for studying structural, surface morphological and optical properties. Energy dispersive analysis by X-ray (EDAX) shows the incorporation of Te content into ZnO. XRD spectrum confirmed that the deposited Te-doped ZnO films are hexagonal. The crystallinity of films was found to be increased with an increase in post-annealing temperature. The optical band gap of Te-doped ZnO annealed films was found to be increased from 3.225 to 3.281 eV. Photoluminescence (PL) intensity of ultraviolet and blue emission measurements of the thin films was obtained in the spectral range from 350 to 600 nm.

Keywords: Sol-gel, XRD, FESEM, EDAX, UV-VIS.

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1. INTRODUCTION

Zinc oxide (ZnO) is one of the most promising materiali because of its superior optoelectronic properties. ZnO is a direct wide bandgap semiconductor material (E_g = 3.37 eV) with transparency in the visible blue and UV wavelength region. It has high exciton energy of 60 meV, efficient excitonic emission at room temperature and hexagonal crystalline structures [1]. It is superior for optical properties in wide range of application such as light-emitting diodes, photodetectors, transparent thin-film transistors and solar cells [2]. The dopants affect the electrical, physical and optical properties of ZnO thin film [3]. ZnO with suitable doping elements create localized impurity levels. Dopants for ZnO materials may substitute either oxygen or zinc.

These dopants cause variations in physical and optical properties for ZnO, after different treatments of oxygen and zinc. One of the suitable dopants is Tellurium (Te) [4]. Te is a group VIA (Oxygen, Sulphur, Selenium and Tellurium) chalcogen family element. Te has attractive potential characteristics in different optoelectronics devices like sensors, energy technologies nanodevices [5]. Tellurium is an anionic dopant element that can be substituted with oxygen in the ZnO lattice, causing changes in electronic band structure of ZnO [6].

Several fabrication techniques have been used for doping ZnO thin films such as electrochemical deposition [7], magnetron sputtering, sol-gel and spray pyrolysis [8]. Sol-gel technique has many advantages such that low cost, large-area deposition, precise microstructural and chemical control for the film properties. The sol-gel spin coating method is a scalable technique used in the preparation of high-quality ZnO thin films [9].

In this paper, we have synthesized high quality ZnO films for five atomic percentage (5 at. %) Te-doped ZnO on the microscopic glass substrates using sol-gel technique. The effects of different post-annealing temperatures on films have been studied and their structural, surface morphological and optical properties have been compared.

2. EXPERIMENTAL DETAILS

All the chemicals and materials used in this experiment are higher purity. Zinc acetate dihydrate ($C_4H_6O_4Zn$ $2H_2O$) and tellurium tetrachloride ($TeCl_4$) were used as the starting precursors and 2-methoxyethanol ($C_3H_8O_2$) was used as the solvent. Ethanolamine ($H_2NCH_2CH_2OH$) was used as the reacting reagent for the preparation of gel solution. Two separate 0.5 M solutions were prepared, first solution used in 20 ml 2-methoxy ethanol dissolving in 2.7438 g powder of zinc acetate dihydrate and second solution used 5 ml 2-methoxy ethanol dissolving in 0.1372 g powder of tellurium tetrachloride (5 at. % Te). Both solutions were stirred on a magnetic hot plate at ~ 80 °C for 30 min. Few drops of ethanolamine are added to the prepared solution. After few minutes, tellurium tetrachloride solution is added dropwise to zinc acetate dihydrate solution. The mixture of the solution was stirred on a magnetic hot plate at the same temperature for an hour, the solution became transparent and finally aged for eight hours at room temperature. The prepared transparent homogenous solution was used for deposition on the 5 at. % Te-doped ZnO films. Before deposition glass, the substrates were cleaned with chromic acid, acetone and deionized water. The films were deposited on the microscopic glass substrate using a homemade spin coater. The speed of spin coater was maintained at 2000 rpm for 30 s. The coating procedure was repeated for twelve times to achieve the desired film thickness. After each coating, the films were preheated at 215 °C for 5 min to evaporate the solvent. Finally, samples

were post annealed at temperatures of 250 °C, 300 °C, 350 °C for one hour in the furnace.

The effect of three different post-annealing temperatures of Te-doped ZnO thin films were studied. The optical and crystalline structural properties of deposited film samples have been studied by by Shimadzu UV-2600 spectrophotometer and Rigaku Miniflex 600 X-ray diffractometer (XRD) respectively using Cu-Ka source operating with a wavelength 1.54059 Å. Energy dispersive X-ray gives clear insight of Te incorporation in ZnO films. The surface morphological and elemental composition of deposited films were studied by using Carl Zeiss sigma FESEM.

3. RESULTS AND DISCUSSION

3.1 Structural Properties (XRD)

The crystal structures of deposited films were observed at different 2θ values from scanning range 20°-80°. XRD spectra of Te-doped ZnO thin films at the three different post-annealing temperatures are shown in Fig. 1. The film's XRD peak position are at (100), (002), (101), (102), (110), (103) and (112) at approximately oriented 2θ values at 31.77°, 34.42°, 36.25°, 47.53°, 56.60°, 62.86° and 67.96°. These XRD spectra are matches with corresponding JCPDS card No. 36-1451 of films that have a polycrystalline and hexagonal structure. No other orientation peaks are visible in these XRD spectra. All the samples have a high (002) diffraction peak, indicating that all samples were strongly oriented along *c*-axis and most intense peak is observed at $2\theta = 34.42°$.

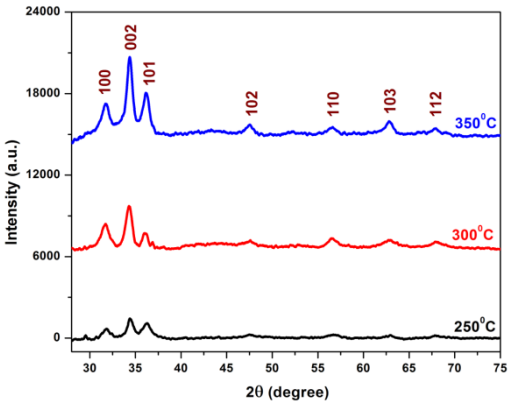

Fig. 1 – XRD spectra of 5 at. % Te-doped ZnO films at 250, 300, 350 °C annealing temperatures

However, the intensity peaks were found to be increased with increasing annealing temperature and it was greater for 350 °C. Also found high diffraction peak (002) shift at lower angle side with increasing annealing temperature. Due to the higher ionic radii of Te_2- (2.07 Å) ions than O_2- (1.40 Å) ions, the lattice parameters and induced stresses decrease with Te doping of ZnO film. The similar was reported by S.H. Park et al. for Te doping [10].

The lattice interplanar spacing '*d*' was calculated using Bragg's formula:

$$d = \frac{\lambda}{2\sin\theta},$$

where λ is the X-ray wavelength (X-ray source 1.54059 Å) and θ is the Bragg's angle. The value of d is related to the lattice constants a and c. The lattice parameters a and c for hexagonal ZnO structure are calculated by the following relation:

$$\frac{1}{d^2_{(hkl)}} = \left(\frac{4}{3}\frac{h^2+hk+k^2}{a} + \frac{l^2}{c}\right),$$

where h, k and l are the Miller indices. Table 1 shows the values of the calculated lattice constants a and c, $a = 3.2299$ Å and $c = 5.1755$ Å using diffraction peaks (100), (002) [11, 12].

The grain size of the Te-doped ZnO film was obtained by substituting the values of FWHM in Scherrer's formula [13]:

$$D = \frac{0.94\lambda}{\beta\cos\theta},$$

where D is the crystal grain size, λ is the wavelength, β is the full width at half maximum (FWHM) and θ is the Bragg diffraction angle at the peak (002).

The diffraction peak (002) increases with the post-annealing temperature. The grain sizes in Te-doped ZnO films were calculated as 14.01 nm, 14.97 nm and 15.79 nm for 250 °C, 300 °C and 350 °C, respectively. The FWHM values of the film are also decreased from 0.62 to 0.55° and the grain size was increased from 14.01 to 15.79 nm as shown in Fig. 2.

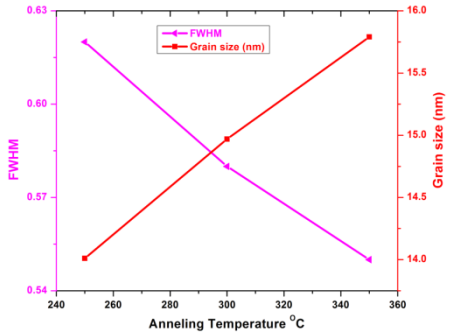

Fig. 2 – Changes in the FWHM and grain size of 5 at. % Te-doped ZnO films at 250, 300, 350 °C annealing temperatures

Table 1 shows detailed information about 2θ (°) values, FWHM, lattice parameter, grain size and optical energy bandgap for corresponding samples for post-annealing temperature.

Ann. temp. (°C)	2θ (°)	FWHM (°)	Lattice parameters (Å)		Grain size (nm)	Band gap (eV)
			a	c		
250	34.40	0.62	3.0075	5.2098	14.01	3.225
300	34.37	0.58	3.0100	5.2142	14.97	3.247
350	34.35	0.55	3.0117	5.2171	15.79	3.281

3.2 Surface Morphology Properties

The FESEM images of surface morphology of 5 at. % Te-doped ZnO films for different post annealing temperatures are presented in Fig. 3. The magnification of FESEM images was 180 kX times applied voltage at 100 nm. The incorporation of tellurium in ZnO films

morphology with growth in the crystal structure of the films can be observed in the surface images. The rate of growth is proportional to the annealing temperature on the entire surface of the substrate. As annealing temperature increases, the grain size increases. There were quite clear nanoparticles at surface nature of the films and was greatly affected by the variation of annealing temperature of Te-doped ZnO.

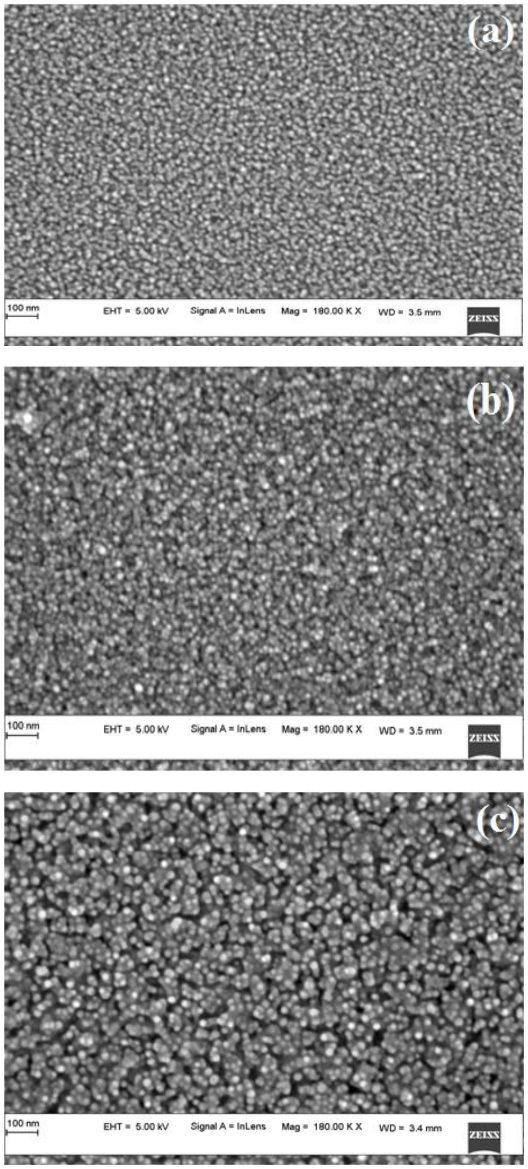

Fig. 3 – FESEM images of Te-doped ZnO film for 250 (a), 300 (b) and 350 (c) °C

The energy-dispersive X-ray spectrometer (EDAX) spectra for the samples in Fig. 4 shows that the Te has deposited successfully on ZnO film by using the sol-gel spin coating technique. The atomic concentration for the deposition of the films was taken 5 at.%. The visible elements are of O, Zn and Te in films. The spectrum Si is appeared due to glass substrate.

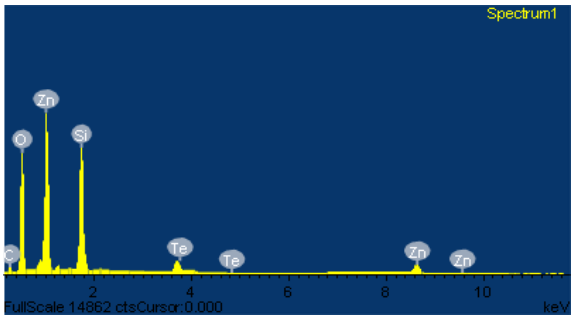

Fig. 4 – EDAX spectrum of 5 at. % Te-doped ZnO film at 350 °C annealing temperature

3.3 Optical Properties

Optical properties of transmission and absorption spectra recorded in the range of 300-800 nm at room temperature of deposited films. Transmission image of the 5 at. % Te-doped ZnO films deposited on the microscopic glass substrates at three different post annealed temperatures is depicted in Fig. 5. Deposited films were above ~ 90 % transparent in the visible region of 300-750 nm. It was found that with an increase in post-annealing temperature the absorption edge shifts to the lower side wavelength [14].

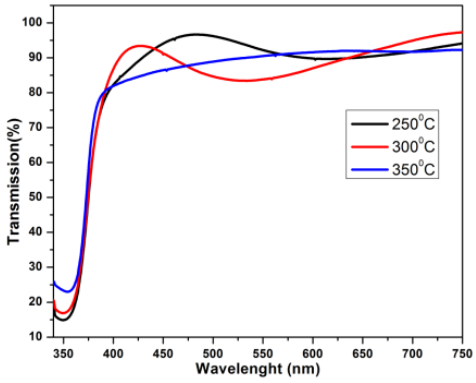

Fig. 5 – Transmission spectrum of 5 at. % Te-doped ZnO films at 250, 300, 350 °C annealing temperatures

The optical bandgap (E_g) of 5 at. % Te-doped ZnO films were measured from the absorption coefficient and the results of the post-annealing temperatures on band gap are specified and compared in Fig. 6. The absorption coefficient was calculated from the Tauc relation for direct transitions [15]:

$$(\alpha h\upsilon) = B\left(h\upsilon - E_g\right)^{1/2},$$

where α is the absorption coefficient, $h\upsilon$ is the photon energy and B is the constant. E_g is the optical bandgap. The computation of the graph gave the increased optical bandgap value of 3.225, 3.247, 3.281 eV for the post-annealing temperature at 250, 300, 350 °C, respectively.

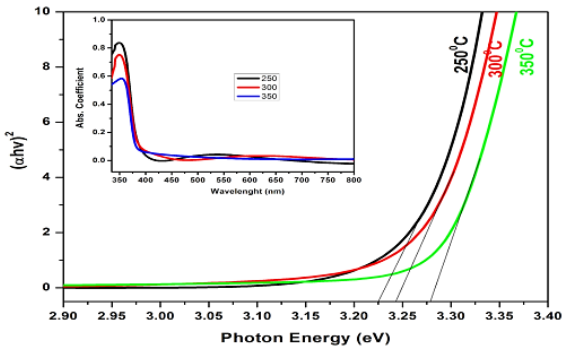

Fig. 6 – The optical bandgap of 5 at. % Te-doped ZnO films at 250, 300, 350 °C annealing temperatures

3.4 Photoluminescence

Another optical property of Te-doped ZnO thin films was examined by photoluminescence (PL). Fig. 7 shows the room temperature PL spectra of 5 at. % Te-doped ZnO thin films, in the excitation of 350 nm wavelength. All PL spectra of Te doped ZnO have two emission bands, first the ultraviolet emission peak is

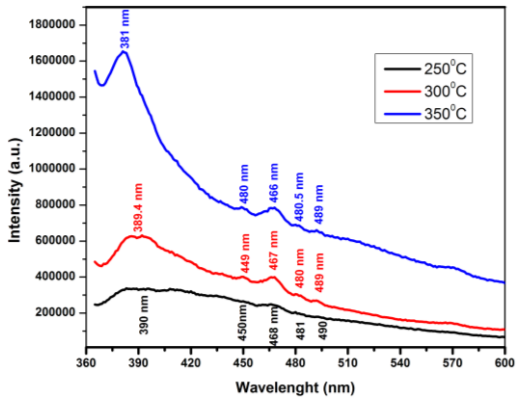

Fig. 7 – Room-temperature PL spectra of 5 at. % Te-doped ZnO films at 250°, 300°, 350 °C annealing temperatures

observed at 381 nm, which is assigned to the near band edge transition, specifically the recombination of free excitons. Second visible blue emission peaks in the range of 450-490 nm related to deep level defect transition. The results, from the recombination of electrons with holes trapped in the singly ionized oxygen vacancies and the associated deep level [16].

In the present study, the PL intensity of UV emission and blue emission are increased and shifted to lower side wavelength with the increase in annealing temperature [17]. From Fig. 7, it can be understood that the sample annealed at a temperature of 350 °C has the strongest UV emission, which is an indication that the sample has good crystalline quality [18].

4. CONCLUSIONS

The Te-doped ZnO films for 5 at. % have been successfully synthesized on glass substrate by a sol-gel spin coating method. The effect of different post-annealing temperature on the structural, surface and optical properties of deposited thin films was investigated. XRD analysis indicates the polycrystalline hexagonal structure for all samples. With increase in post annealing temperature, a significant shift of the diffraction peak (002) towards lower side angle was observed. The variations in morphology of FESEM images and increase in grain size have been found with increase in annealing temperatures. EDAX study confirmed incorporation of Te in ZnO. Optical properties of the transmittance were higher than 90 % in the visible region (300-750 nm) in all films and the bandgap increased from 3.225 to 3.281 eV with increase in temperature. The PL intensity of ultraviolet and blue emission is increased and a shift of it towards lower side is observed with increase in annealing temperature. The annealing temperatures of the Te doped ZnO based thin films growth technique was a good range of optical band gap energies that made it good for application in optoelectronics.

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Вплив температури відпалу на структурні та оптичні властивості легованих телуром тонких плівок ZnO для оптоелектронних застосувань

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Досліджено структурні, морфологічні та оптичні властивості тонких плівок ZnO, легованих Te, виготовлених на мікроскопічних скляних підкладках золь-гель методом. Для приготування розчину гелю використовували дигідрат ацетату цинку та тетрахлорид телуру як вихідні прекурсори і 2-метоксиетанол як розчинник. Осаджені плівки були потім відпалені при різних температурах, а їх властивості досліджені методами дифракції рентгенівських променів (XRD), скануючої електронної мікроскопії (FESEM) і UV-VIS спектрофотометра. Енергодисперсійний аналіз за допомогою рентгенівського випромінювання (EDAX) показує включення Te в ZnO. XRD спектр підтвердив, що нанесені плівки ZnO, леговані Te, мають гексагональну ґратку. Встановлено, що кристалічність плівок підвищується зі збільшенням температури відпалювання. Показано, що оптична заборонена зона відпалених плівок ZnO, легованих Te, збільшилася з 3,225 до 3,281 еВ. Вимірювання інтенсивності фотолюмінесценції ультрафіолетового та синього випромінювання тонких плівок було отримано в спектральному діапазоні від 350 до 600 нм.

Ключові слова: Золь-гель, XRD, FESEM, EDAX, UV-VIS.