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Optical and Structural characterization of low dose gamma irradiated Zinc Oxide (ZnO) thin films prepared by Electrostatic spray pyrolysis

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***Abstract*:** *Zinc Oxide (ZnO) thin films of 150 nm thickness were prepared by electrostatic spray pyrolysis and subjected to gamma irradiation of 5 Gy, 10 Gy and 15 Gy dose. The as-deposited and irradiated films were subjected to XRD, SEM and UV-VIS spectrophotometer characterizations. XRD pattern of as-deposited and irradiated ZnO thin films were amorphous hexagonal wurtzite structure with preferred orientation along (100) plane. The SEM images exhibited aggregated nanosized particles with visible voids and the exposed ZnO thin films become more and more uniform with fewer voids. The optical band gap and energies band tail of localised states of ZnO thin films decreases with increase in gamma irradiation dose.*

***Keywords*:** *Thin films, Zinc Oxide, Gamma Irradiation, Dosimetry, Optical Band Gap*

I. Introduction

The exposure of every solid material to ionizing radiations produces changes in the microstructural properties of the material, which in turn affects the optical, electrical and other physical properties of the material [1-5]. Several studies have been made on thin films made up of metal oxides and their mixtures for their use in radiation dosimeters, sensing and memory cells [6]. The observed changes in structural, electrical, optical and other physical properties of thin films of metal oxides due to the exposure to ionizing radiations clearly revealed that thin films of metal oxides can be used in radiation dosimetry.

Zinc oxide (ZnO) is a Transparent Conductive Oxide with excellent characteristics. It is inexpensive, versatile n-type semiconducting material that has a large transparency in the visible region. It has wide direct band gap energy of 3.27eV, large exciton binding energy, benign and abundant in nature [7-10]. Most prominent crystalline structure of ZnO is hexagonal wurtzite type, although, it also exists in the cubic zinc blende and rocksalt structures. In wurtzite type, each Zn ion is surrounded by a tetragonal coordination. This gives rise to polar symmetry along the hexagonal axis, which is responsible for a number of properties of ZnO [11]. It has many potential applications such as light emission display devices, piezoelectric transducers, surface acoustic devices, optoelectronic devices and solar cells [10].

Thin ZnO films have been produced using a variety of techniques such as RF Magnetron Sputtering [9], Spin coating [12], Sol-gel [7,8], Spray pyrolysis [10,13], Thermal evaporation [1,4-5], Electron beam evaporation [3] Among these methods, the spray pyrolysis technique has several advantages such as simplicity, safety and low cost of the apparatus.

The influence of radiation depends on both the dose and the parameters of the films including their thickness however; the degradation is more severe for the higher dose and the thinner films [1-6]. The aim of this study is to investigate the changes in the microstructure, structural and optical properties of ZnO thin film structures under the influence of low dose gamma irradiation.

II. Experimental

Electrostatic spray pyrolysis deposition process was used to deposit Zinc Oxide (ZnO) thin films on soda lime glass slides with home-made electrostatic spray pyrolysis system. Before the deposition the glass slides were washed with detergent, rinsed with distilled water and finally cleaned by ethanol. Zinc Acetate dehydrate (99.99%) of 2.20g was dissolved in 15ml of deionized water. A 5ml of acetic acid was added to assist in the complete dissolution of zinc acetate. Concentrated ethanol and acetone were added to aqueous solution at volume of 30ml and 50 ml respectively. The prepared aqueous solution of Zinc acetate was pumped into a spray nozzle by means of a syringe pump electronically controlled by asynchronous motor that moves forward and backward. The substrate temperature was maintained at 300 ^{0}C and solution flow rate was 0.08 cm^3/minutes.

The nozzle to substrate distance was 11 cm and spraying time was 30 minutes. Electrostatic force at high voltage (5- 17 kV) was used to atomize the aqueous solution through a spray nozzle into fine uniform droplets on the heated substrate. The deposited thin films were annealed in open air at 300 ^{0}C for two hours.

A Cobalt-60 radiation source (Gamma Beam X200) was used to expose the thin film samples to gamma radiation at room temperature. The samples were subjected to a total dose of 15 Gy in steps of 5 Gy by the gamma source at a dose rate of 30 mGy/sec. X-ray diffraction (XRD) (XPERT-PRO PANalytical) characterization were carried on samples, Transmission and Reflection measurements were carried out using Ultraviolet-Visible (AVASPEC 2048) spectrophotometer and Scanning Electronic Microscope (SEM) (Model_Phenom ProX) measurement were carried for irradiated and non-irradiation samples. The thicknesses of thin films were measured by profilometer (VEECO DEKTAK 150) and found to be of 150 nm thicknesses.

III. Results and Discussion

3.1 X-ray diffraction Analysis

Fig. 1 shows XRD spectra of the as-deposited and irradiated ZnO thin films. The as-deposited ZnO thin film shows a more pronounced crystalline diffraction peak along preferred orientation (100) plane. X-ray diffraction analysis for irradiated ZnO thin films at 5 Gy of radiation dose indicates decrease and almost near absence of crystalline peak along preferred orientation (100) plane.

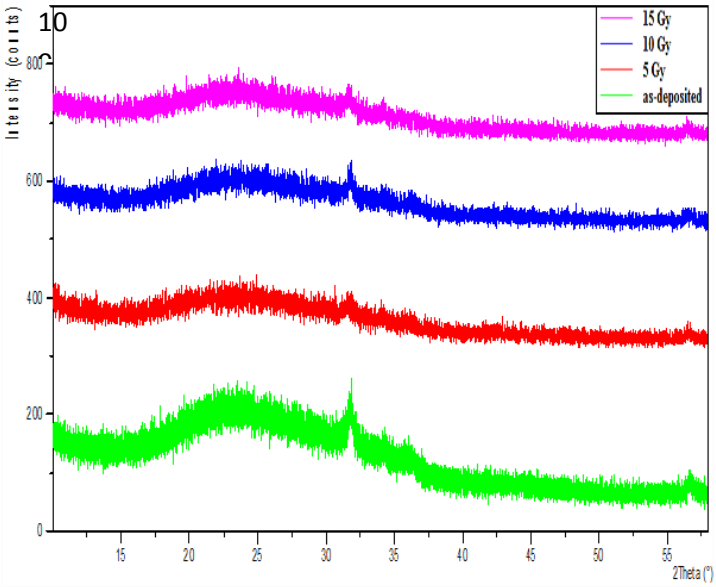

Figure 1: XRD patterns for as-deposited and irradiated ZnO thin films.

For 10 Gy irradiated ZnO thin film, X-ray diffraction analysis indicates decreased in peak compared to as-deposited ZnO thin film along preferred orientation (100) plane. At 15 Gy of irradiation of ZnO thin film, X-ray diffraction analysis show decrease in crystalline diffraction peak compared to 10 Gy irradiated ZnO thin film. The X-ray diffractions spectra show that the irradiated films are amorphous and have preferred orientation in the (100) plane.

The grain sizes (D) of the ZnO films were calculated by using Scherrer's formula [11].

$$D = \frac{0.9\lambda}{\beta cos\theta} \tag{1}$$

β is the full width at half maximum, λ is the wavelength of the X-radiation used (1.54060 Å) and θ is the angle at which the maximum intensity was observed.

The strain in the films were determined based on the bixial strain model [15]. The strain (ε) of the films is determined with the use of the following formula [14]:

$$\varepsilon = \left|\frac{Co - C}{Co}\right| x\ 100\% \tag{2}$$

where c_0 is the strain-free lattice parameter measured from ICSD ZnO powder sample and c are estimated lattice paremeter of the ZnO films.

The stress of the film parallel to the film's surface is determined using, the following formula [15], which is valid for a hexagonal lattice:

$$\sigma = \left(\frac{2c_{13}^2/2c_{13} - c_{33}(c_{11}+c_{12})}{2c_{13}}\right)\varepsilon \quad (3)$$

where c_{ij} are elastic stiffness constant for ZnO. The elastic constants used were: c_{11}=208.8 GPa, c_{33}=213.8 GPa, c_{12}=119.7 GPa, and c_{13}=104.2 GPa [20].

TABLE 1 shows the estimated lattice parameters c and d of as-deposited and irradiated films, the grain sizs D, the strain ε and stress σ. The c-spacings of the as-deposited and irradiated films were higher compared to ICSD value of 5.2151 Á. The calculated value of grain size for as-deposited ZnO thin film is 5.72 nm and decreased to 2.86 nm at 5 Gy irradiation film, then increased to 11.44 nm at 10 Gy of irradiated ZnO thin film and decreased again to 2.86 nm at 15 Gy of irradiated ZnO thin film. This show a non-linear relation between gamma irradiation doses and grain size, a linear relationship was reported for gamma irradiated tin oxide films [3]. The estimated strain value of 8.01 for as-deposited ZnO film increased to 8.37 at irradiated dose of 5 Gy, then decreased to 7.77 at irradiated dose of 10 Gy and increased again to 8.01 at irradiated dose of 15 Gy. The strain also exhibits a non-linear relation with dose. The negative sign for the calculated stress of the films indicate that the lattice constant c are elongated as compared to the unstressed ICSD ZnO pattern.

Table 1: Values of Grain Size, Strain and Stress of the Films

Sample	c spacing (Å)	d (Å)	D (nm)	strain	Stress (GPa)
5.6329 Å	5.6329 Å	2.8190 Å	5.72	8.01	-0.471
5.6329 Å	5.6329 Å	2.8281 Å	2.86	8.37	-0.492
5.6515 Å	5.6515 Å	2.8121 Å	11.44	7.77	-0.457
5.6205 Å	5.6205 Å	2.8281 Å	2.86	8.01	-0.471

3.2 UV-Visible- NIR Analysis

3.2.1 Transmittance (T)

Optical Transmittance (%T) spectrum of as-deposited and irradiated thin films is shown in Fig. 2. In the visible region as-deposited and irradiated ZnO thin films had an optical transmittance greater than 70%. Beyond transmission edge, in the wavelength range of 395 nm to 553 nm, the as-deposited ZnO thin film has highest transmittance at 88% while the film irradiated at 10 Gy has lowest transmittance at 75% in this range. Beyond 553 nm of wavelength, all the films had an almost equal transmittance at higher wavelength.

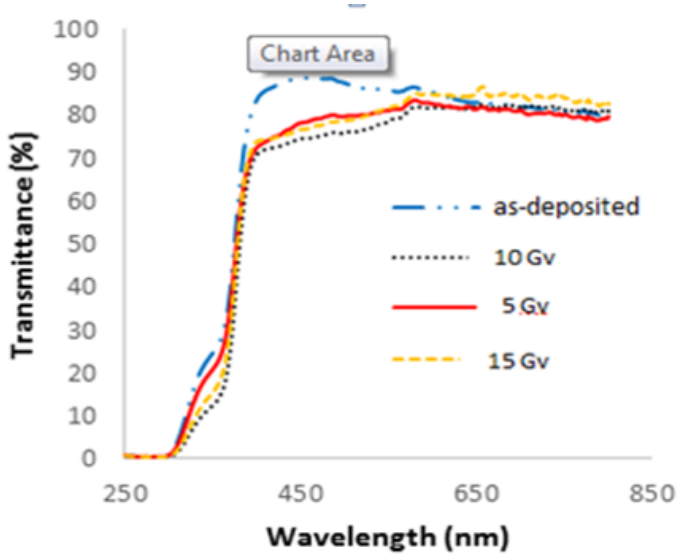

Figure 2: Optical transmittance (%) spectra of as-deposited and irradiated ZnO thin films

3.2.2 Optical band gap

The optical band gap energy (E_g) were calculated using the Mott and Davis' model [2]

$$hv = B(hv - Eg)^{1/2} \quad (4)$$

where B is a constant, hv is the energy of incident photon and α is optical absorption coefficient. The optical band gap (E_g) of the films were determined by extrapolation of the straight linear portion to the energy axis (hv) in the plot of $(\alpha hv)^2$ against hv in Fig. 3.

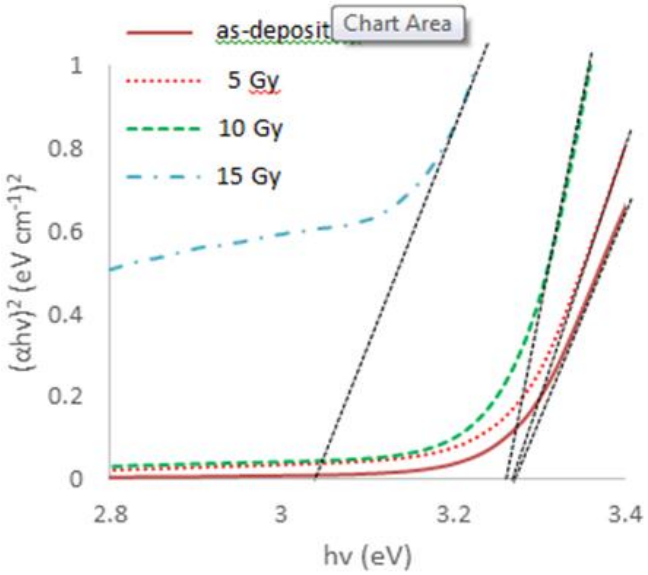

Figure 3: Plots of $(\alpha hv)^2$ against *hv* for as-deposited and irradiated ZnO thin films.

TABLE 2 shows the values of optical band gap for as-deposited and irradiated ZnO thin films.
The value obtained for optical band gap for as-deposited ZnO thin film was found to be 3.28 eV and decreases with increase in gamma dose

Table 2: Values of Optical Band gap of As-deposited and Irradiated ZnO Thin Films.

ZnO thin films	Optical band gap (E_g) eV
As-deposited	3.28
5 Gy	3.27
10 Gy	3.26
15 Gy	3.04

The decrease of the optical band gap is basically due to the increase in the energy width of band tails of the localised states. During gamma irradiation, the defects are created within the thin film. At the same time, the defects also get annihilated even under the normal room temperature conditions [1, 4-6]. This creation and annihilation of defects coexist together and, at higher gamma radiation doses, the number of defects created due to irradiation becomes much more than the number of defects annihilated. The recombination of defects in the film increases the density of localised states in the band gap and consequently decreases the energy band gap [13]. A similar decrease in the optical band gap of the ZnO thin film of 800 ± 10 nm thickness from 3.25 to 3.20 eV with active radiation (0.36μci) and gamma emission energy of 0.662MeV for 21 day at room temperature was also reported [14]. The decreases in the optical band gap from 3.80 to 2.95 eV for the TeO_2 thin films of 100 nm thickness exposed to the gamma radiation dose of 60 Gy has also reported. Beyond 60 Gy, optical band gap was found to increase with increase in gamma radiation dose [3,5, 15].

The dose dependence of the optical properties of the ZnO thin films, described above, is quite similar to the dose-response of the most materials used in thermoluminescence dosimerty [5]. These materials usually show a linear, then super-linear, followed by saturating response and further increase in the radiation dose

results in the high structural disorder. The high structural disorder at very high radiation doses reduces the sensitivity of material parameters to further exposure of radiation [1, 5].

At the absorption edge, the absorption coefficient exhibits an exponential dependence on photon energy in accordance with Urbach's formula [4]

$$\alpha = \alpha_0 ln\, e^{(h\nu/\Delta E)} \quad (5)$$

Where α_0 is a constant and ΔE is energy width of the band tails of localized states.

A band tail of localised state is created due to irradiation. Based on density-of-state model, optical band gap decreases with an increase in degree of disorder of the amorphous phase [2]. The decrease in optical band gap leads to a shift in the band tail of localised state (ΔE) towards the higher energy region. Thus the calculated value of ΔE is expected to increase as the radiation dose is increased. Normalized energy width of the band tails of localized states (ΔE_N) is also expected to increase as the radiation dose is increased and the values can be obtained by this equation given below [5]:

$$\Delta E_N = (\Delta E - \Delta E_0)/\Delta E_0 \quad (6)$$

where ΔE_0 is band tail of localized states of as-deposited ZnO thin films. The values of ΔE were calculated from the slopes of linear low wavelength parts of $ln\alpha$ versus $h\nu$ in figure 4.

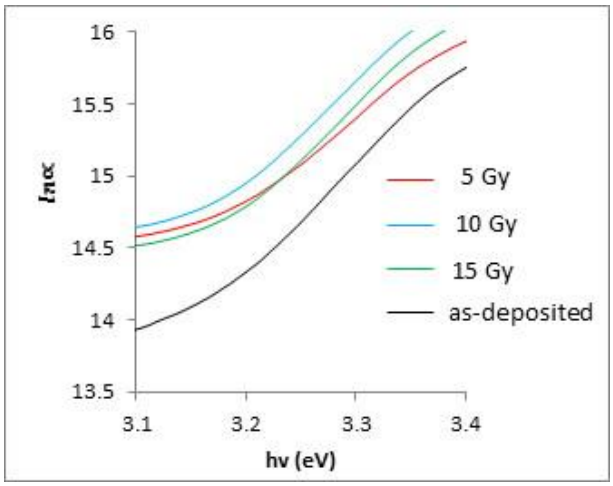

Figure 4: Graphs of $ln\alpha$ versus $h\nu$ of the films

The results of the band tails obtained are shown in the TABLE 3.

Table 3: Values of ΔE and (ΔE_N) of As-deposited and Irradiated ZnO Thin Films.

Sample	ΔE (eV)	ΔE_N (eV)
As-deposited	5.5	0.0
5 Gray	6.0	0.1
10 Gray	7.0	0.3
15 Gray	7.5	0.4

It is observed from the values showed in TABLE 3, ΔE and ΔE_N for irradiated thin films linearly increase with increase in radiation dose in agreement with theoretical considerations.

In the normal dispersion region the dispersion of refractive index was analyzed using the single oscillator model. The refractive index in the normal dispersion region according to the single-effective-oscillator model is [14]:

$$n^2(\lambda) - 1 = \frac{E_d E_o}{E_o^2 - E^2(\lambda)} \quad (7)$$

where n(λ) is the refractive index at a wavelength λ, E_o is the average electronic energy gap for transition (average excitation energy) known as the oscillator energy, and E_d is the dispersion energy (average strength of interband optical transition) called the oscillator strength. By plotting $(n^2-1)^{-1}$ versus E^2 as in figure 5 and fitting a straight line, the values of the parameters E_o and E_d were calculated from the intercept (E_o/E_d) and the slope $(E_oE_d)^{-1}$ of the plot [14].

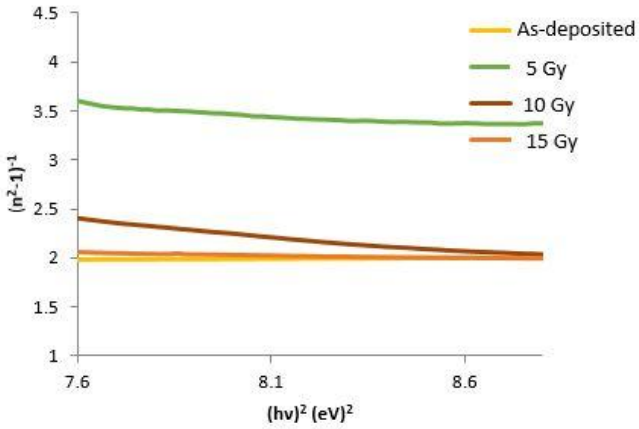

Figure 5: Plot of $(n^2-1)^{-1}$ versus $(hv)^2$ of as deposited and irradiated ZnO thin films

TABLE 4 shows the values obtained for E_o and E_d of as-deposited and irradiated ZnO thin films. The static refractive index n_o is deduced from the dispersion relation

$$n_0^{\,2} = 1 + E_d/E_0 \tag{8}$$

Which is related to the static dielectric constant ε_0 by [16]

$$\varepsilon_0 = n_0^2 \tag{9}$$

Table 4: Values of E_o, E_d, n_o, and ε_0 of as-deposited and irradiated Zinc Oxide thin films.

Samples (Gy)	E_o (eV)	E_d (eV)	n_0	ε_0
As-deposited	6.63	3.35	1.23	1.51
5	4.38	1.22	1.13	1.28
10	2.81	1.17	1.19	1.42
15	6.22	3.02	1.22	1.49

The values of E_o and E_d of irradiated films show significant decrease compared to that of as-deposited film. However E_o and E_d show non linear relation with irradiation dose as they both show an increase in value from an irradiation dose of 5 Gy to 10 Gy but then decrease at 15 Gy irradiation compared to that of 10 Gy. The oscillator energy E_o is an average energy gap and can be related to the optical band gap. The oscillator energy E_o in a close approximation, is related to the optical band gap by $E_o = 1.5E_g^{opt}$ as suggested by WD model [14]. The determined E_o values of the films related empirically to the optical band gap by $E_o \approx 2.03E_g$ for as-deposited ZnO thin film, $E_o \approx 1.34E_g$ for irradiated ZnO thin films at 5 Gy, $E_o \approx 0.86E_g$ for irradiated ZnO thin film at 10 Gy and $E_o \approx 1.90E_g$ at an irradiation of 15 Gy. Both n_0 and ε_0 show increase in value with increase in irradiation dose.

3.3 Microstructure Characteristics

SEM images and corresponding 3D topographical maps of as-deposited and irradiated thin films of different levels of gamma dose are shown in figure 6. In Fig. 6(a), the microstructure of as-deposited ZnO thin film show evidence of aggregated small nano-sized particles with visible voids. In this case, intrinsic defects are

formed during the film deposition. In Fig. 6(b), the microstructure of irradiated ZnO thin film at 5 Gy exhibited aggregation of nano-sized particles such that they are closely packed together to form clusters with fewer voids.

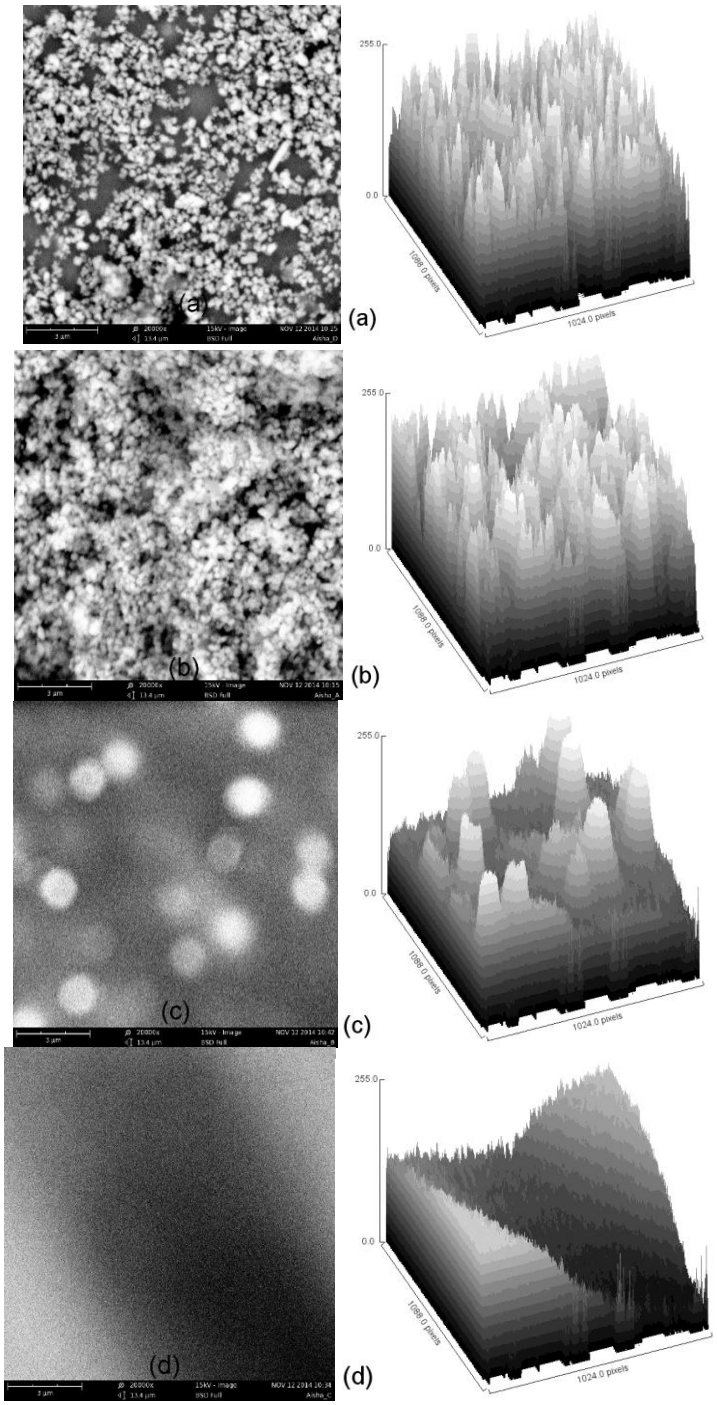

Figure 6: SEM images and 3D topographical maps of ZnO thin films (a) as-deposited, (b) 5 Gy gamma irradiated, (c) 10 Gy gamma irradiated and (d) 15 Gy gamma irradiated.

In Fig. 6(c) and 6(d), the microstructure of irradiated ZnO thin film at 10 Gy and 15 Gy exhibited fine homogeneous grain structure with smooth and uniform surface structure. The SEM micrograph and 3D topographical maps indicates the surface morphology is influenced by gamma fluence. This is evident from the decrease in porosity and disappearance of contrast peaks.

IV. Conclusion

The effect of gamma irradiation on microstructual, structural and optical properties of ZnO thin film deposited by elctrostatic spray pyrolysis deposition technique has been investigated. The XRD results show that

the irradiated ZnO thin films are amorphous hexagonal wurtzite structures with preferential growth in the (100) plane. The UV-Vis spectrophotometer results show that the as-deposited and irradiated ZnO thin films showed high transparency at visible region greater than 70%. Optical band gap values showed a decrease and values of energies of band tail of localised states showed an increase as a result of increase in gamma radiation dose. The SEM micrograph show that irradiated ZnO thin films are uniform and grains are closely packed together to formed clusters with fewer voids as a result of disorder of the film structure. At 15 Gy of absorbed dose, irradiated ZnO thin film surface become smooth which attributed partly to the healing effect and the lowering of the optical band gap as a result of increase in disorder of the structure of the film. The observed changes indicated that ZnO thin film can be used in real-time dosimetry.

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