The Effects of Gamma Radiation on Structural and Surface Properties of ZnO Thin Films Deposited on n-Si Substrate

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Abstract— In this research, we have investigated the structural and surface properties of ZnO thin films before and after ^{60}Co gamma (γ)-ray source irradiation with the total dose range of 0-500 kGy at room temperature. The effects of gamma radiation on structural and surface properties of thin films were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM) methods. The crystal grains sizes, size of particles of crystals, D- spacing and full width at half maximum (FWHM) were determined by means of XRD method. Atomic surface structure and surface topography were measured by AFM. Surface morphology is carried out by SEM. Experimental results with before and after gamma radiation of prepared thin films was compared.

Index Terms— Structural properties, Surface properties, Thin film, γ- irradiation, Zinc oxide (ZnO).

1 Introduction

II-VI group elements give rise to binary compounds. Zn, II group element and O, VI group element constitute ZnO compound semiconductors [1]. When we look at the devices used in optoelectronic and photoelectric applications, we see the importance of the II-VI group compounds and ZnO thin films in this group. Thin film-based materials have a very important place in the metal-semiconductor contacts in today's electronic circuit elements industry. Direct-pass zinc oxide is a material with a high energy dissipation temperature [1, 2] and an energy band gap of Eg ~ 3.37 eV at room temperature [3-5]. These materials can be used in high temperature, high frequency, high power circuits. Because they are highly resistant to high-energy electron radiation when compared to other semiconductors, high particle radiation is used in some experiments, so zinc oxide has proved to be suitable for space research [7-9]; they can also be used in terrestrial applications such as nuclear power plants [1].

Semiconducting thin films also have a great proposition in terms of optical applications. These optical coatings have economical marketability and wide range of products due to their wide usage areas [1]. It is hoped that the broad bandgap ZnO, can withstand radiation more than compound semiconductors such as GaAs. But the end results ZnO is greater resistance to electrons, protons and heavier ions radiation more than GaN [8, 10-12]. This result can also be dependent on the rate of defect losses in ZnO partially [8]. But the different fluxes encountered in space may lead to differences in the formation of defects and in the rate of annealing.

It is most important to understand the manner in which radiation interacts with matter and transfers its energy. Energy from radiation is transferred to matter in two ways: Ionization and Excitation. Ionization is the process of removal of an electron from an atom leaving the atom with a net positive charge.

In excitation, the energy of incoming radiation raises an outer electron to a higher energy state from which it returns very rapidly (10^{-8} s) to its original state emitting a photon of light in the process. The effects of ionizing radiation on metal oxide thin films depend on both the radiation dose and the parameters of the films including the film thickness. It is already an established fact that the degradation is quite serve for higher radiation doses and thinner films [13].

The interaction of different incident particles with the electrons of the crystalline lattice leads to a change of electron energy. The change is not permanent, and the thermal equilibrium of the electron within the crystal lattice is restored in a few milliseconds. This is not the case if the particle energy is transferred to an atomic nucleus. If the imparted energy is less than a binding energy of the nucleus in the lattice, the atom is elastically displaced from its site and the displacement is not permanent. If the transferred energy is higher than the binding energy of the atom, it is permanently removed from the site. This results in a vacancy at the original site with simultaneous appearance of a surplus atom in an interstitial position between the atoms. This is a Frenkel-type lattice effect. The vacancy behaves like an acceptor; the surplus atom behaves like a donor. Therefore, new energy levels appear in the crystal under the action of radiation.

Gamma radiation is a type of electromagnetic wave that interacts with matter via and the Photoelectric Effect, Compton Scattering and Pair Production described below. The aim of this work is to evaluate the effect of gamma radiation on structural and surface performance of the ZnO/n–Si diode which is experimental.

2 Experimental

Substrates used in this study were chosen to have n-type Si crystals with a thickness of 400 μm and with 1-10 Ωcm resistivity. Firstly, the wafer was sequentially cleaned with trichloroethylene, acetone and methanol ultrasonically for 3 min respectively and then rinsed in deionized water of 18 MΩ and dried with high purity N_2. The Si wafer were chemically cleaned using the RCA cleaning procedure (i.e, 10 min boiling in $NH_3+H_2O_2+6H_2O$ followed by 10 minutes in

$HCl+H_2O_2+6H_2O$ at 60°C) before making contacts. Preceding each cleaning step, the samples were rinsed thoroughly in deionized water of 18,2 MΩ cm resistivity with ultrasonic vibration for 5 min and were finally dried by high purity nitrogen (N_2) atmosphere.

ZnO thin film with a power of 60W were grown on n-type Si semiconductor substrates, which had been previously cleaned, by RF magnetron sputtering system and using the ready ZnO target. The n-Si substrats prepared to perform this operation were placed on the circle. The samples were then heated at a substrate temperature of 200°C. Argon gas was introduced into the system at a flow rate of 205 sccm. The plasma was then created in the main chamber at a power of 60 Watt. This was kept for 5 minutes to clear the ZnO target surface. This also ensures that the heat is stabilized. After 5 minutes of spraying, the ZnO target lid is opened and growth can begin with continued sample conversion for homogeneity. ZnO accumulation was achieved at a power of 60 Watt at a rate of about 0.4 nanometers per minute. After reaching the desired growth period, the ZnO target trap was turned off and the plasma turned off. The room heater was then turned off and the samples were cooled to room temperature before being removed from the hoop. The samples were then removed from the hoop and ZnO/n-Si/Au-Sb structures were obtained.

Surface and structural characteristics of thin films were investigated. The prepared interface-layered (ZnO/n-Si) diodes were exposed to gamma radiation for 5 minutes at different energies (barium, amersium and cobalt). After radiation, surface and structure studies were performed again and the results were compared with the results before radiation.

2 Results and Discussions

Exposure of solid materials to ionizing radiation such as gamma rays (γ) produces changes in the microstructural properties, which in turn affects the optical and other physical properties of the solid materials [14]. The effects of the gamma irradiation on the thin films of metal oxides have been studied to find out the suitability of these thin films in post- exposure and real – time gamma radiation dosimetry.
Naturally, a deep understanding of the effects of gamma irradiation on different physical properties of these thin films is quite vital from the viewpoint of the physics of metal oxides as well as from the design and development of novel radiation sensors and dosimeters.

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The XRD, SEM and AFM measurements taken before and after exposure of the prepared ZnO/n-Si samples to different energies (barium, amersium and cobalt) gamma radiation were compared comparatively. Fig. 1 (a-c) and Fig. 2 (a-c) show the XRD of ZnO thin film before and after irradiation. X-ray measurements were made at 10 - 90 degrees depending on the angle. X-ray diffraction analysis shows that the polycrystalline hexagonal structure for the non-irradiated and irradiated film exhibits a good c-axis orientation perpendicular to the substrate surface.

From the XRD pattern, the polycrystalline structure of ZnO films is clearly visible. Deposited films exhibit (002), (101), (102), (110), (103), (112) diffraction peaks, indicating that deposited films have a hexagonal wurtzite structure. The XRD pattern shows six peaks indexed for ZnO wurtzite type hexagonal structure. No peaks from other ZnO phase or other compound are observed, suggesting that high-purity ZnO wurtzite phase was obtained. Correspondingly, the full width at half-maximum (FWHM) of these peaks increases after gamma radiation.

Peak position is well suited to that given by the JCPDS card number 36-1451. Moreover, no other peak implying that the thin film prepared was pure ZnO was not detected. The sharp and strong peak (002) observed at 2θ = 34.40 (D = 2.60 Å) and 2θ = 34.53 (D = 2.57 Å) for the unirradiated and irradiated film respectively is shown in Table 1 which are consistent with the ASTM standard value [15]. Where D is the planar spacing and (hkl) Miller indices. The D can be calculated using the equation of $2D\sin\theta = \lambda$, where λ is used as the X-Ray wavelength (λ = 1,5406 Å), and θ Bragg angle at the half maximum peak of the XRD pattern. Grain size of the films, was found to be decreasing after radiation as seen from Table 1. Due to irradiation, grain size and peak position were affected.

The calculated values were found to be in good agreement with the standard values for the ZnO wurtzite structure [15]. The crystallite size of the particles in the films is calculated by the Sherrer formula [16].

$$L = 0.94\,\lambda/\mathrm{FWHM}\cos\theta \quad (1)$$

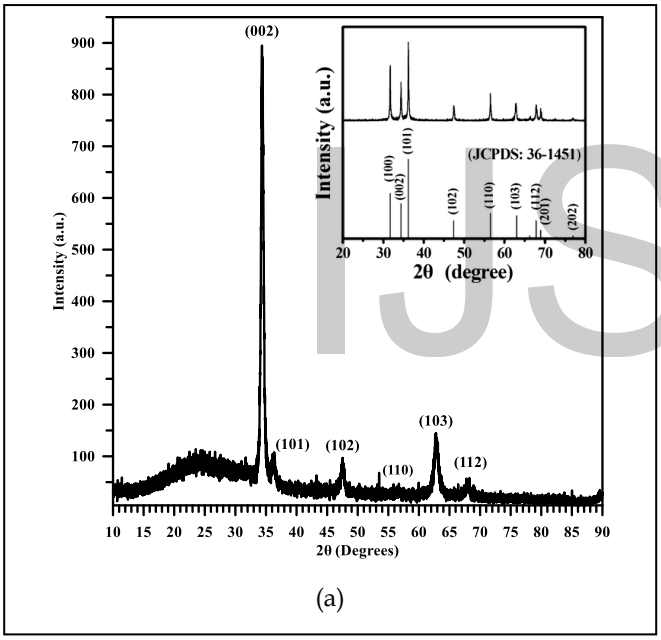
Where FWHM is the full width. The crystallite sizes in the c-axis, calculated using Scherrer's formula are in the range (203,943 to 109,795 nm). The peak position of films shifts from 34.40 for before radition to 34.31 for after gamma radition in (002) orientation.

Table 1 shows the calculated parameters at 2θ angle of each plane forming ZnO thin films using Bragg reflection and Scherrer approximation. Here, the basic characteristic for the XRD peak of ZnO, especially at 2θ = 3440 °, is the dominant peak, indicating that it is hegzagonal. The differences between the planes are also attributed to the defects in the structure. It can be said that the magnitude and the crystal structure of the enlarged films are directly related to the intensity and FWHM values of the peaks of the parmeters such as quality and grain size. Accordingly, the particle sizes are inversely proportional to the half maximum peak width of the diffraction peak obtained with XRD.

As shown in Fig.1 (a-c), the diffraction peaks of the ZnO thin films before the gamma radiation are quite dense and the diffraction peaks are very narrow, which allows the particle size to be large. Accordingly, it can be said that crystal structure of the film produced is of good quality. When gamma radiation is applied to these obtained thin films, FWHM value increases and particle size decreases.

TABLE 1
PARAMETERS CRYSTAL STRUCTURE OF THIN FILM ZNO

	UNIRRADIATED		IRRADIATED	
ZNO	D (Å)	L (Å)	D (Å)	L (Å)
(002)	2.60	203.943	2.57	201.844
(101)	2.47	196.594	2.43	191.750
(102)	1.91	190.526	1.88	187.532
(110)	1.63	155.699	1.60	150.792
(103)	1.47	140.582	1.42	133.487
(112)	1.37	112.685	1.36	109.795



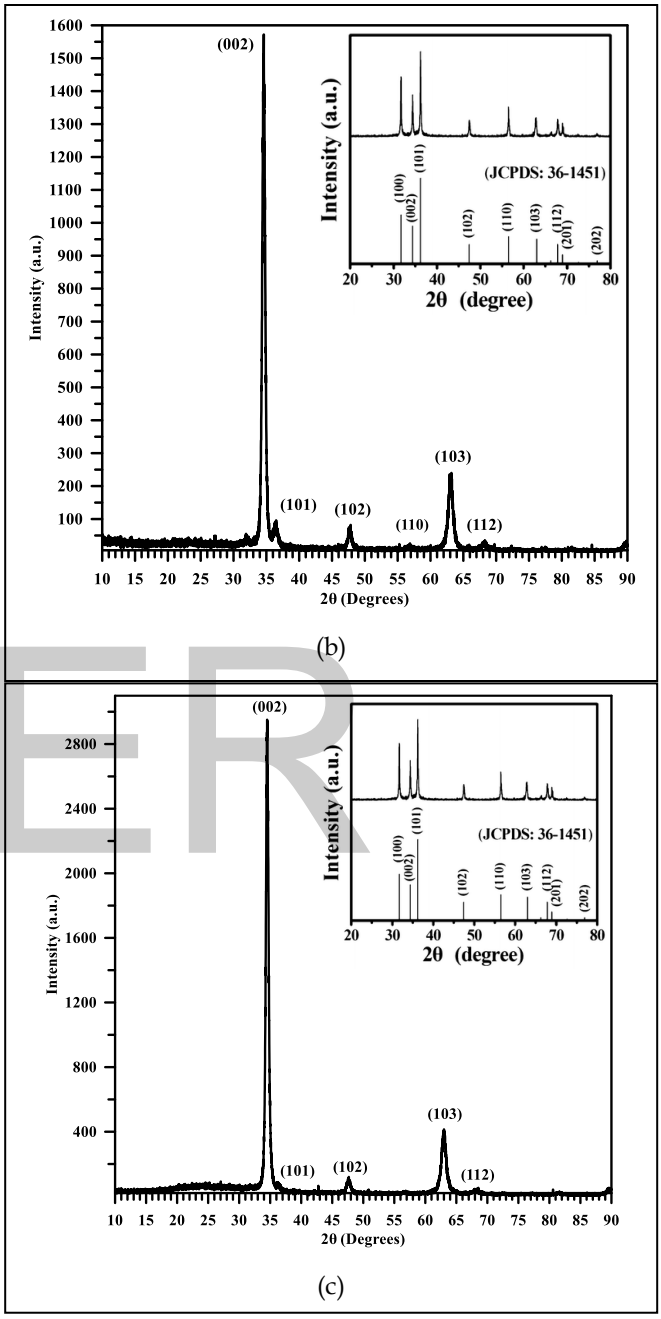
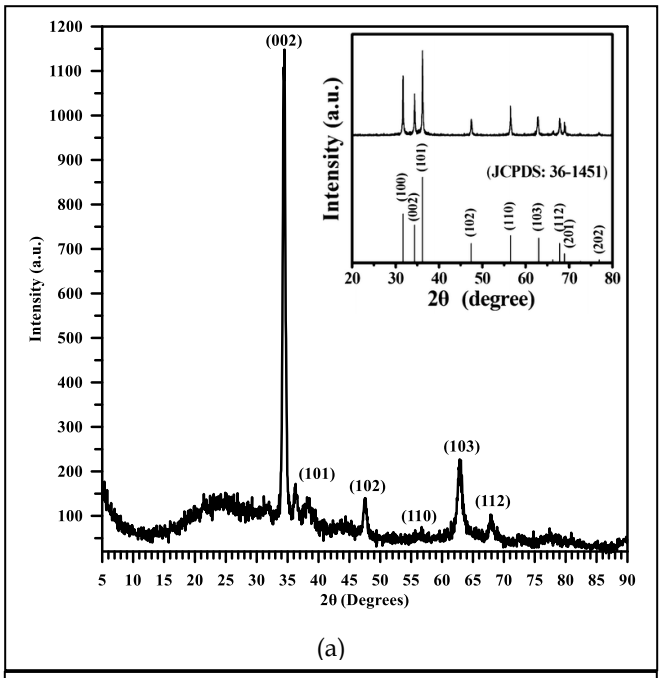
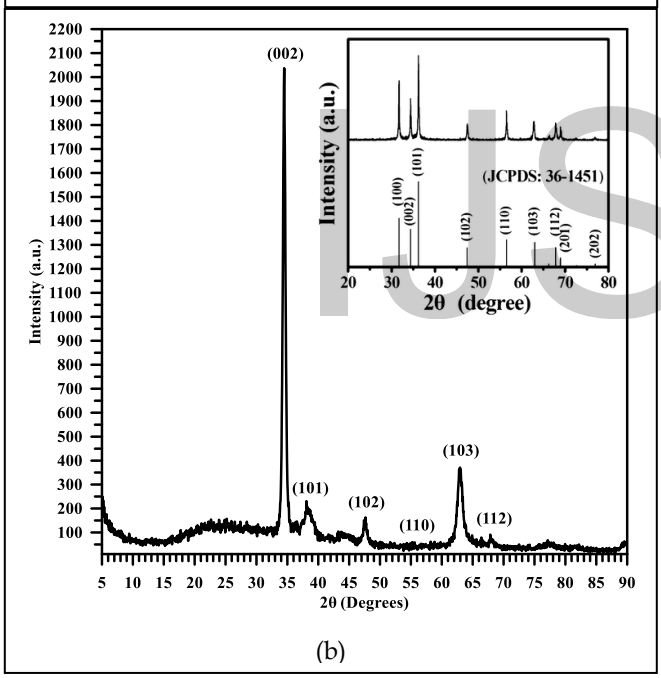


Fig. 1. a) barium b) americium c) cobalt, X-ray diffraction patterns before radiation.



(a)



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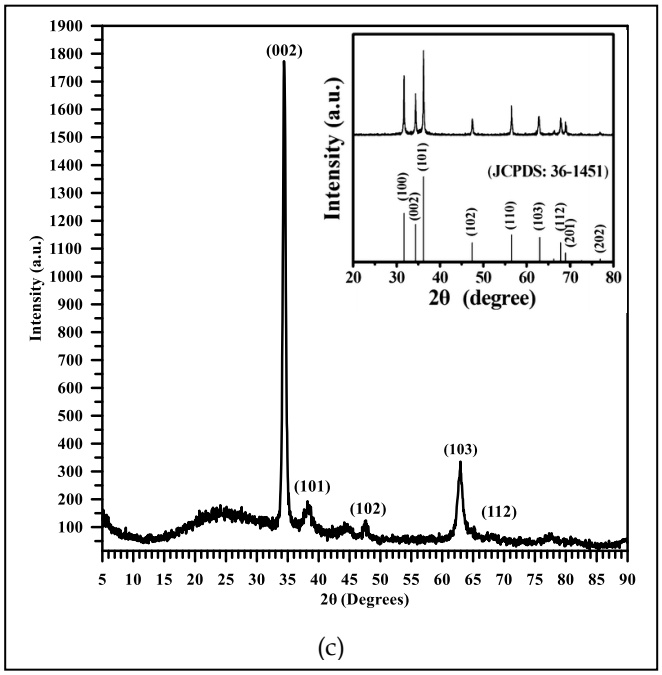


(c)

Fig. 2. a) barium b) americium c) cobalt, X-ray diffraction patterns after radiation.

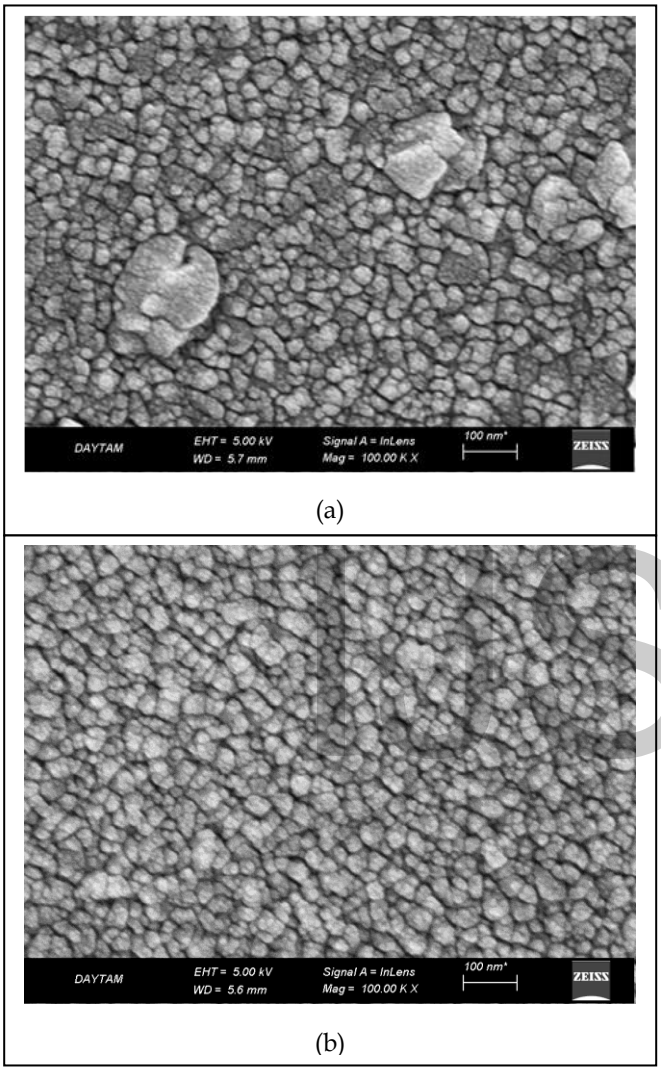
Morphological analysis of ZnO thin films was performed using scanning electron microscopy (SEM). SEM micrographs of unirradiated and irradiated gamma radiation at different energies are shown in Fig. 3 (a-c) and Fig. 4 (a-c) for ZnO thin films. The ZnO films magnified by RF sputtering technique on the shiny surface of the ohmic contact n-Si semiconductors is shown in Fig.3 (a-c) before irradiation by 10000 magnified SEM images. SEM images will work best when the vibration noise is kept to a minimum. A 5kV acceleration voltage was applied to obtain the film image. In Fig. 3 (a-c) and Fig. 4 (a-c), the SEM photograph shows a certain cross-sectional area seen with a 100 nm scaling.

As can be seen in Fig. 3, the grains fill the surface homogeneously, without accumulation and voids. These regular crystal particles show that the growing film crystal structure is of high quality. Thus, films show polycrystalline structure in favorable orientations. ZnO thin film consists of dense packed and random orientation nanostructures. The results obtained from SEM images are consistent with the observations of XRD.

As seen in these figures, after radiation, the size of the grain is reduced and it is piled up in different shapes. The same results were obtained in the literature [17]. SEM micrographs are clearly indicating the formation of controlled size and regular shaped nanoparticles. Therefore, it is possible to control size and shape using the gamma irradiation. It indicates that the nanoparticles with aligned orientation and the high degree of crystallinity in the sample by high dose [18].

SEM micrographs of the diodes irradiated at different energies of gamma radiation are shown in Figure 4 (a-c). In the micrograph, it is clear that the grain size decreases as a result of irradiation and is stacked in different shapes. The same results have been observed in the literature [17].

After radiation, the films exhibit nanocrystalline depositions with smaller dense structures and smaller particles. ZnO nanostructures have different orientations with decreasing particle size as a function of radiation. SEM images show that grain size decreases after gamma coalescence.



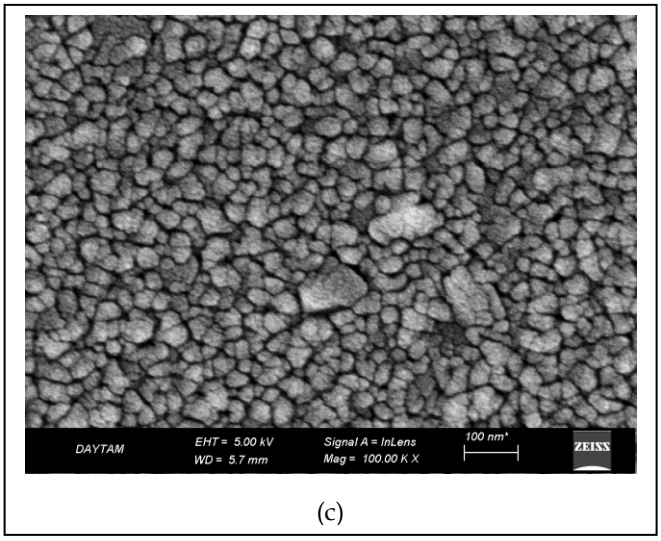
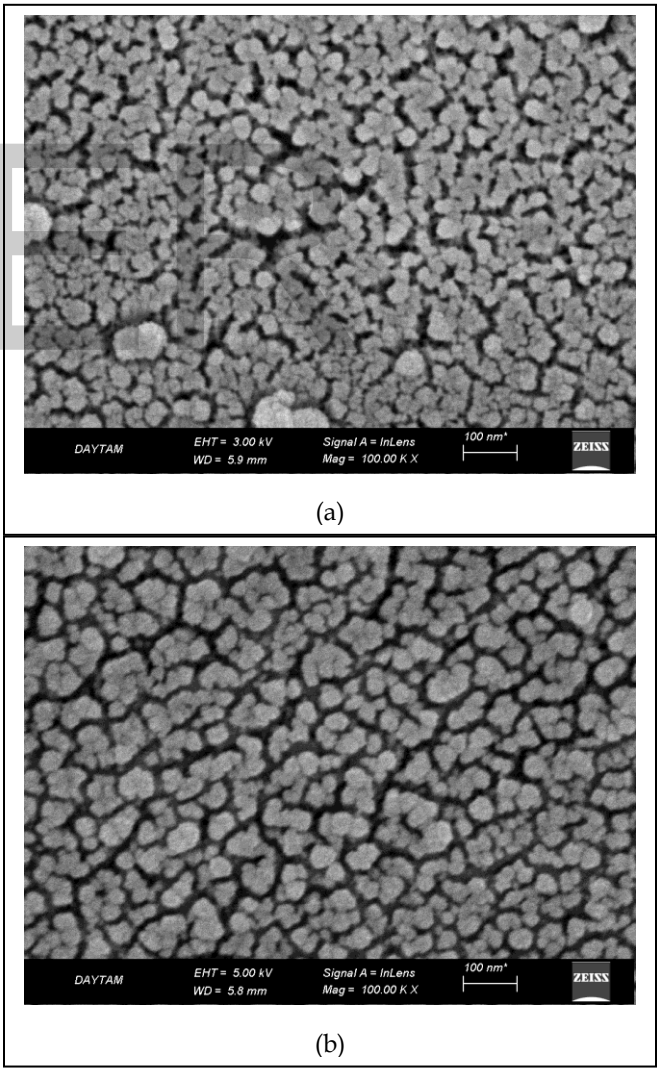
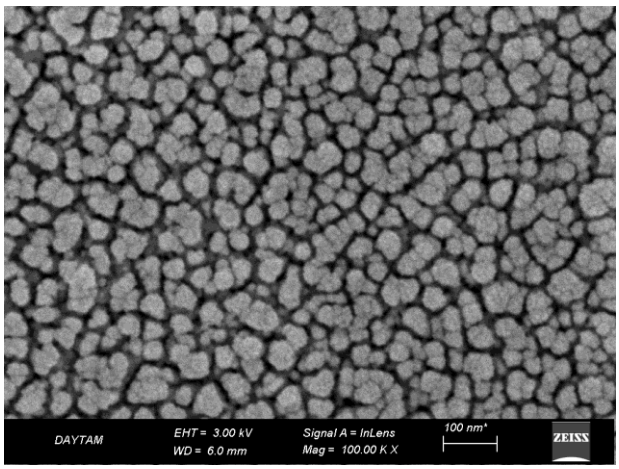


Fig. 3. The SEM micrographs of ZnO thin films before of (a) barium, b) americium and (c) cobalt radiations.





(c)

Fig. 4. The SEM micrographs of ZnO thin films after of (a) barium, b) americium and (c) cobalt radiations.

Unirradiated and irradiated AFM images are shown in Fig. 5 (a-c) and Fig. 6 (a-c) for ZnO thin films. The surface morphology and surface roughness of the films were also examined using an AFM technique. Surface roughness is one of the important properties of the ZnO thin film for many optoelectronic applications, because the level of surface roughness will do minate the carrier mobility and light scattering [19]. The scan speed is synchronized to a speed of 2 MHz to obtain the desired image of the grain particles on ZnO thin film which can be visual- ized clearly. All films show a smooth surface morphology. For the 5x5μm² scan area, the root mean square (RMS) of the mean surface roughness for all samples was determined for the change in surface morphology. AFM 2D images reveal modification of the ZnO films surface roughness after irradiation.

2D AFM images irradiated (Fig. 6) (a-c) samples clearly depicted the change in surface morphology due to the irradiation. AFM image of samples before irradiation showed a typical three dimensional growth structure with irregular grains of nearly same sizes and a surface roughness (RMS), 17.77 nm for barium, 4.60 nm for americium and 28.29 nm for cobalt. After gamma irradiation, RMS roughness of ZnO thin films has a decrease and these values for different energies of gamma were 9.27, 4.23 and 3.056 nm respectively. Previous studies have mentioned that the increase of grain crystal size will cause enhancement in surface roughness of ZnO thin [20]. Therefore, the small of the crystal grain size causes the roughness to decrease.

The films irradiated show a transition region at the interface between the irradiated and non-irradiated zone with R_{rms}= 4.60 -28.29 nm and inside the irradiated area, R_{rms}= 3.056- 9.27 nm in the localized zones containing clusters. The grains and the clusters on the ZnO films surface could be attributed to thermal annealing effect resulted by energy transfer from the incident particles, due to inelastic collisions.

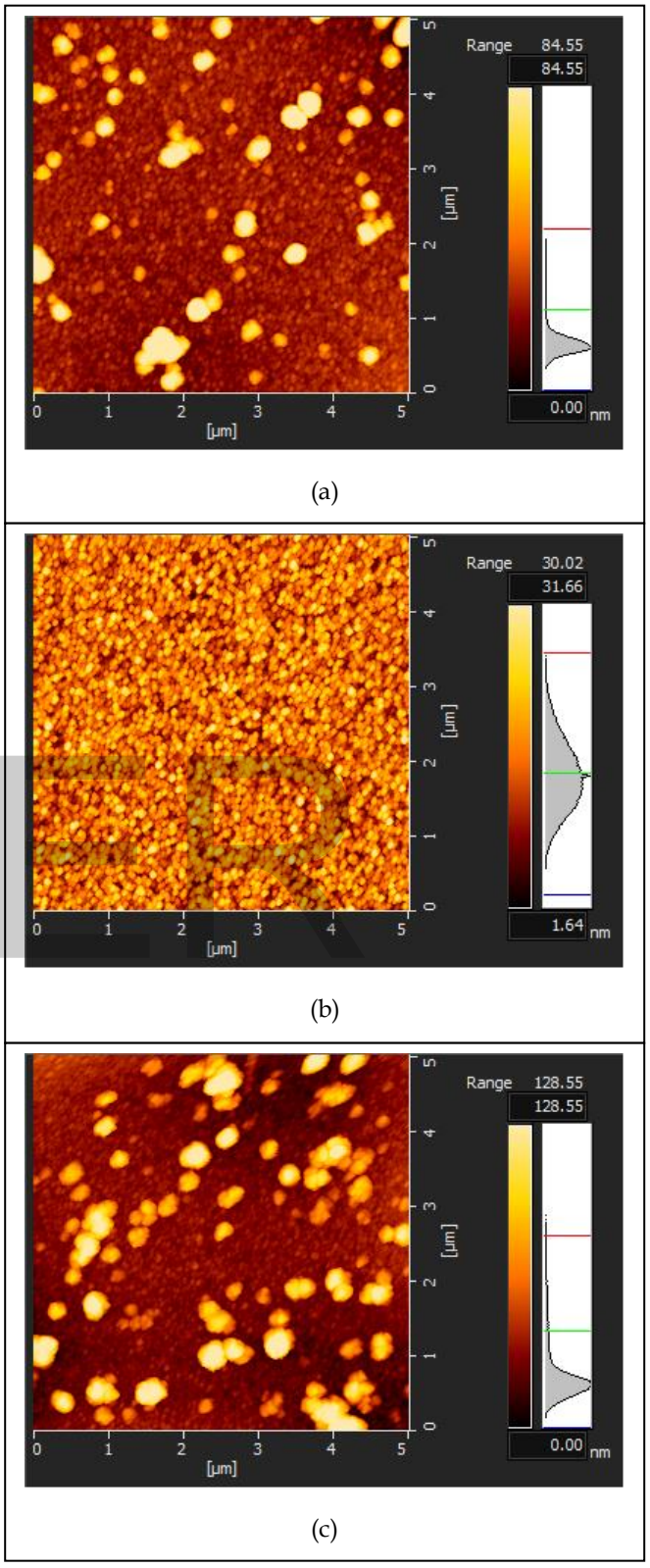


Fig. 5. AFM images of ZnO thin films before of (a) barium, b) americium and (c) cobalt radiations.

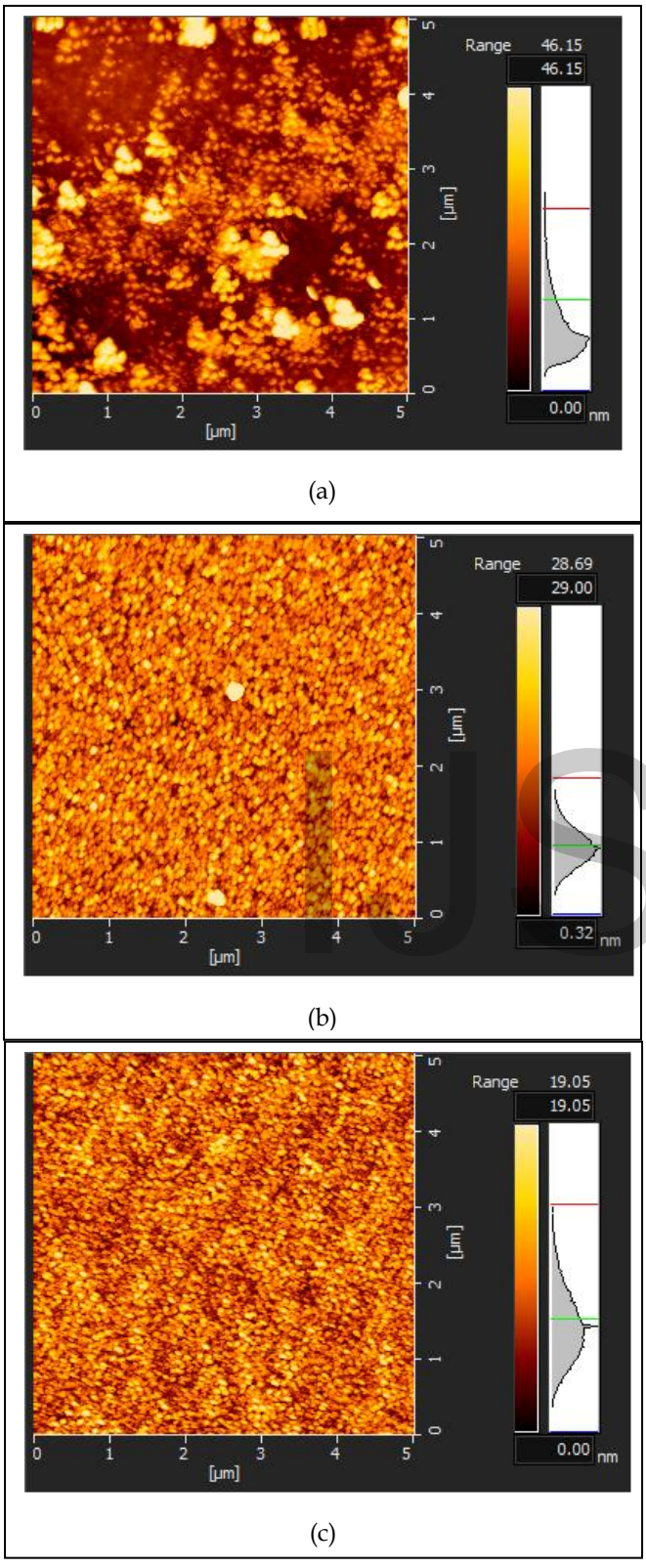


Fig. 5. AFM images of ZnO thin films after of (a) barium, b) americi um and (c) cobalt radiations.

4 Conclusion

ZnO thin films were deposited by a RF magnetron sputtering technique; effects of gamma radiation on the structural and surface properties were investigated. Based on the correlation, combination and integration of the results from different measurements leads to the following conclusions.

The XRD patterns of the ZnO thin films show broad peaks at various positions such as, 34.40° (002), 36.26° (101), 47.50° (102), 56.54° (110), 62.99° (103), and 67.97° (112). All the diffraction peaks are found in good agreement with the file for ZnO reported by the Joint Committee on Powder Diffraction Standard (JCPDS 36-1451, a = 3.249 Å, C = 5.206 Å). There observed no special peak associated with impurities and all the peaks can be indexed to ZnO nanostructures. All films are polycrystalline single phase of hexagonal (wurtzite) crystal structure. In general, there is no change in crystal structure but there is variation in the degree of preferred orientation and diffraction line profile. From these observations, it might be concluded that the grain size of ZnO film was getting smaller after irradiation. There was a small shift in the peak position in the XRD pattern, after irradiation. The calculated value of the grain size, and planar spacing of un-irradiated and irradiated thin films are given in table 1, it is clear from the table, that the grain size for un-irradiated samples is greater than irradiated one. This can be attributed to strong effect of gamma irradiation on the structure of the investigated samples.

The XRD data point out that the irradiation with gamma determines a decrease in crystallite size in the films volume, besides of the grains at the film surface and grains agglomeration, as observed in the AFM images. As a result, the damage to the structure is increased by irradiation. In other words, when the intensity of the radiation dose increases, it causes defects. The effect of the irradiation of gamma rays on the structural and surface properties has been investigated. XRD data shows the reduced particle size after gamma-ray irradiation. SEM images show that the grain size is reduced after gamma irradiation.

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