Effect of gamma rays on nanostructured TiO_2 thin film synthesized with sol gel method

W. A. FAROOQ[a*], SALAHUD-DIN KHAN[b*], SYED MANSOOR ALI[a], M. ASLAM[a]
[a]*Department of Physics and Astronomy College of science, King Saud University, Saudi Arabia*
[b]*Sustainable Energy Technologies Center, King Saud University, Saudi Arabia*

In this paper, nanostructured TiO_2 thin film has been investigated under gamma irradiation source(Co-60) at eight, sixteen and twenty four hours duration. The TiO_2 thin film was synthesized by spin coated sol-gel method. The irradiation was performed by using the facility of Gammacell-220 No.246 with cobalt-60 as gamma source. The structural morphology and modifications were analyzed with scanning electron mircroscopy(SEM) and X-ray diffraction(XRD) techniques. The results including the obsorption and emission spectra were acquired with JASCO spectrometer and flourospectrometer. The obtained data showed the decrease in particle size while increasing gamma irradiations exposure time at certain level of sixteen hours but then increase with further exposure upto twenty four hours duration.The analysis gives the understanding that the optical gap has decreased linearly with exposure time. This research predicts the variation in optical and morphological properties of TiO_2 thin films with gamma exposure and thus gives an indication of developing radiation shielding materials for nuclear applications.

(Received April 16, 2015; accepted August 3, 2016)

Keywords: Nanoparticles, Gamma radiation, Shielding, Sol gel

1. Introduction

The rapid advancements of techniques related to medical equipment using radiation shielding material increase number of space missions striving for the exploration of universe. Similarly, demand of nuclear power plants for electricity generation has prompted an increasing concern for radiation protection [1]. The major issue for personnel facing radiation equipment such as nuclear power plant engineers, spacecraft engineers and medical personnel is the radiation safety. Extensive work related with radiation environment in the hospital, nuclear power plants and the space mission could have detrimental effect on the environment and the people [2-4]. In addition, the long-term exposure to space radiation to both materials and humans is also of great concern. So far, lead has been used extensively for radiation protection from X-rays and Gamma rays due to its favorable properties mainly its high density [4]. On one side, it is comparatively cheaper, plentiful, and easily formable than other high density metals but on the other side, toxicity and the weight are the major concerns. With the growing utilities and easy transportation, an innovative idea for the replacement of lead to any lightweight material is desirable [5].Therefore, there is a need for development of smart materials that are light, flexible, robust and more resistive to the nuclear radiations [6-7]. Nowadays, there is boost of developing innovative materials in the field of nano-science like metal nano-particles, nano-fibers and polymer composite materials [8-10]. Some of these materials have shown their excellent applicability for shielding purposes.

Recently, gamma interaction with polymer materials in different forms has been extensively investigated for many applications. Gamma rays can also be used to induce chemical reaction in any form of mettle at different environment [11-14]. Many researchers have investigated the effect of gamma radiations on TiO_2 doped with other materials Sheng-ying et al [15], decomposes ethylene in plasma photocatalst process in which TiO_2/ACF was used and the sample was irradiated with gamma rays and observed the effects on the modification of these catalyst films. Ranveet et al in 2013 [16], developed cadmium based borosilicate glass by using quench method and find out the influence on the modification of CdO. F.H.Batal [17], used TiO_2 doped soda lime phosphate glasses under gamma irradiation and observe the effects on spectra with different techniques including UV-visible, infrared and Raman spectroscopy. M. S. Roy et al [18], monitored gamma radiation through thin film of CIAIPc doped with TiO_2 thin film and sandwiched device having ITO/CIAIPC and TiO_2/Ag by spin coating technique. J. Juarez et al [19], observed the radiolytical degradation of chlorophenol in the presence of TiO_2,Al_2O_3 and SiO_2 by irradiated with Co-60 and Cs-137 source. N. Ghoneim et al [20], did experiments on undoped and doped TiO_2 lithium phosphate glasses before and after gamma irradiation and have found that the lithium glasses show strong UV absorption while doped sample exhibits surplus broad visible bands. M. Todica [21], investigated the modification of PVA-TiO_2 membranes by gamma irradiation exposure using ESR and XDR methods. R. Kralchevska et al [22], studied the influence of gamma irradiation on the sorption characteristics of photo catalyst activity of commercially available TiO_2 Degussa P25. Some other recent studies of gamma radiation effects are presented in ref [23-27].

In the present work nanostructured TiO_2 thin film has been investigated under gamma irradiation at different exposure time. Structural morphology and modifications were analysed. The present study can be beneficial for the development of shielding materials and the usage of TiO_2 nanomaterials in the instruments being used in nuclear installation.

2. Experimental technique

2.1 Preparation of the sample

The sample was prepared from the paste of Titanium Oxide (mixture of rutile and anatase) nanoparticles purchased from Sigma Aldrich. This paste was further diluted with ethanol and was used for the film preparation on glass substrates by spin coating technique. Prior to deposition, the substrates were thoroughly cleaned using standard methods and dried by purging with oxygen free nitrogen gas. Spinning rate was kept at 3000 rpm. The film was annealed at 110 °C for 10 min and then allowed to cool at room temperature before next coating. The process was repeated for 10 times to get 200 nm thicknesses. The multilayer film obtained on the glass substrate was finally annealed at 450 ^oC for 1hr.

2.2 Sample irradiation with gamma rays and characterization

The prepared thin film samples were irradiated with Gammcell 220 No. 246 facility owned by King Saud University. This facility is loaded with source No. GS-415 containing 24910 curie of Cobalt-60.The dose rate at the center of chamber was 0.33Gry/sec. The samples were irradiated for 8, 16, and 24 hrs at the rate of 0.33Gry/sec.

Absorption of the samples before and after gamma irradiation was measured with JASCO UV/VIS/NIR spectrometer model V-670 in the wavelength range of 200–2500 nm. Photoluminescence measurement was carried out with JASCO spectrofluorometer model FP-8200. Microstructural changes were investigated with Scanning Electron Microscope (SEM) images and X-ray Diffraction (XRD) patterns. Images were taken with SEM model JSM-6380LA (JEOL, Japan) and XRD patterns were recorded with XRD (Bruker, D8 Discover) with Cukα source radiation.

3. Results and discussion

3.1 Structural modifications with Gamma irradiation

Effect of gamma ray exposure on structural changes were investigated using SEM images and XRD patterns. The fig 1(a to d) showed the XRD spectra of As deposited and gamma irradiated TiO_2 thin films in the range of $2\theta = 22^0 - 35^0$ respectively. It can be seen from fig.1 that As deposited TiO_2 thin films have anatase structure and after gamma irradiation, its anatase structure partially changed to the rutile phase. With increase in duration of gamma exposure, increase in conversion to rutile structure was observed which shows that after gamma irradiation, the film become more crystalline with mixed structure. We can see the existence of both structures in XRD pattern shown in fig.1.

The crystallites size of the grains in the films is estimated using the Scherrer's formula [28].

$$D = 0.9\lambda / \beta\cos\theta \quad (1)$$

Where λ is the wavelength of X-Ray used (λ=1.5406 Å), β the full width at half maximum peak of XRD pattern, and θ is the Bragg's angle. Estimated crystallites sizes of As deposited and gamma irradiated thin films are given in Table. 1.

Table 1. Estimated crystallites sizes of As deposited and gamma irradiated thin films.

	As deposited	**8 hrs**	**16 hrs**	**24 hrs**
FWHM (Degree)	0.56597	0.64819	0.7276	0.5616
Crystallite Size(nm)	17.87	15.83	13.43	17.40

The full width at half maximum of (101) peak increases up to 16 hours irradiation time and then decreases for further increasing the gamma ray exposure which indicates that crystalline size of the films first decreases up to 16 hrs exposure time and then increases with further exposure. It was noted that, intensity of the peak (101) increases with increasing gamma exposure. This result indicates some changes in microstructure of TiO_2 thin films with growth of the films along (110) direction.

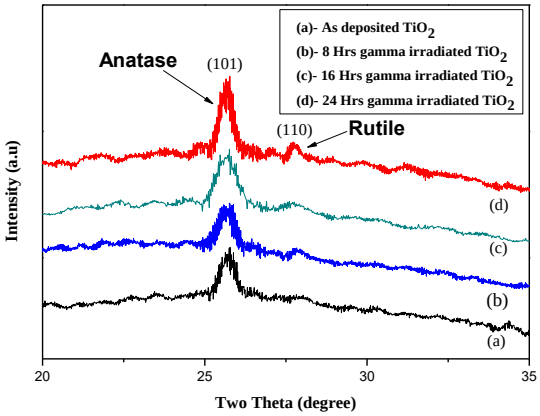
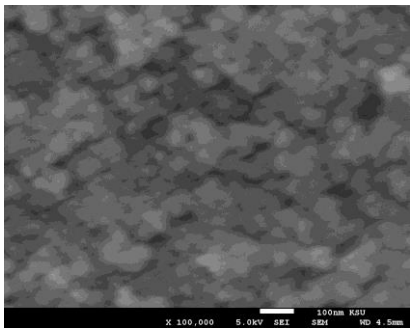


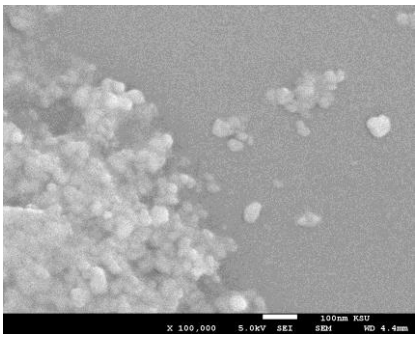
Fig 1. XRD spectra of As deposited and gamma irradiated TiO_2 thin films.

The SEM images of As deposited and gamma irradiated thin film samples at 8, 16 and 24 hours are depicted in fig 2 (a to d). The SEM images of As deposited thin film verifies the nanostructure of the film. It also showed that the size of the TiO_2 nanoparticles decreases with gamma exposure at 8 and 16 hours and then increases with further exposure to 24 hours. The decrease in the size might be due to continuous ionization of the material with continuous exposure. The increase in the size after 24 hours exposure might be due to agglomeration of the nano

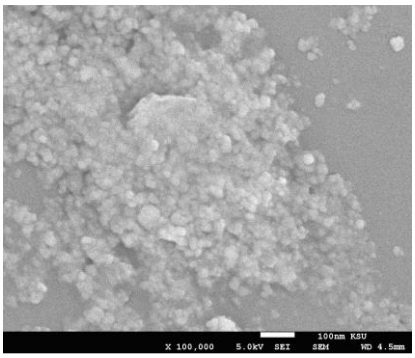
particles pointing out the thermal effect with gamma rays exposure for very long time. The variation in size has also been categorized with enhancing the interaction cross section by the interaction of photon with the material.



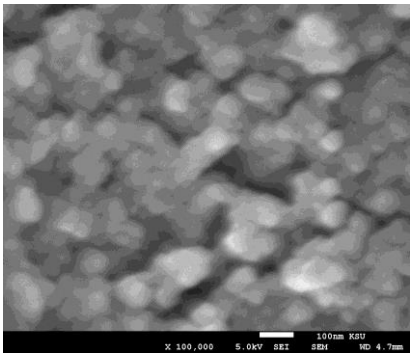
(a) SEM image of As deposited TiO_2 thin films



(b) SEM image of 8 hrs gamma irradiated TiO_2 thin films



(c) SEM image of 16 hrs gamma irradiated TiO_2 thin films.



(d) SEM Image of 24 hrs gamma irradiated TiO_2 thin films.

Fig 2. (a): SEM image of As deposited TiO_2 thin films (b): SEM image of 8 hrs gamma irradiated TiO_2 thin films (c): SEM image of 16 hrs gamma irradiated TiO_2 thin films. (d): SEM image of 24 hrs gamma irradiated TiO_2 thin films.

3.2 Optical properties

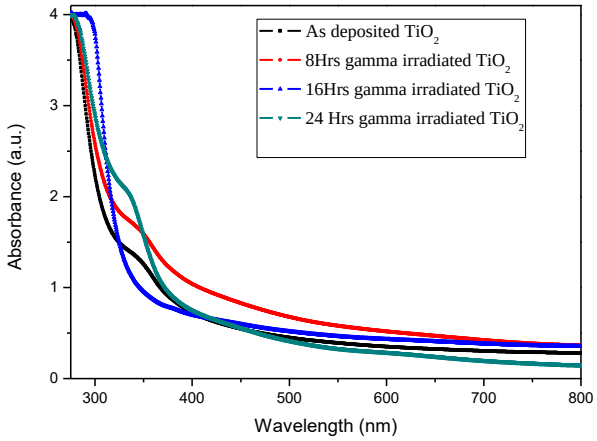


Fig 3. Absorption spectra of as deposited and gamma irradiation TiO_2 thin films.

The optical properties were investigated using UV-Visible spectroscopy. Absorption spectra of As deposited and gamma irradiation TiO_2 thin films were studied in the wavelength range of 200-800 nm as presented in fig 3. It has been observed that the absorption decreases with increase in wavelength and absorption peak is found to be around 310 nm. With the increase in gamma irradiation exposure, the absorption peak first shifted to higher wavelength and then at 24 hours exposure, it goes back to original position. Such behavior is also observed in the case of grain size. The grain size first decreases with increasing radiation exposure and at 24 hours exposure, size become same compared to the original As deposited sample. This variation in structure might be responsible for the similar absorption trend in the samples.

Optical band gap is an important property of materials and governs an important role in many scientific and engineering applications. Optical band gap is directly related to absorption coefficient (α) and can be expressed with the following tauc relationship [29-31],

$$(\alpha h\nu) = B\,(h\nu - E_g)^n \qquad (2)$$

Where h represents plank constant, E_g and ν are the band gap and the frequency of incident photon respectively, B and n are constants. n determine the type of optical transition. In one electron approximation "n" have values of ½ for allowed direct transition , n= 3/2 for forbidden direct transition, n= 2 for allowed indirect transition and n= 3 for forbidden indirect transition. In the allowed direct transitions, conduction electron transfer from the top of valence bands to the bottom of conduction bands. In case of absorption the value of energy band gap for allowed direct transition (n= ½) is determined by intercepting the straight line obtained by plotting the $(\alpha h\nu)^2$ versus (hν) which follows the following Tauc equation [32];

$$(\alpha h\nu)^2 = B\,(h\nu - E_g) \qquad (3)$$

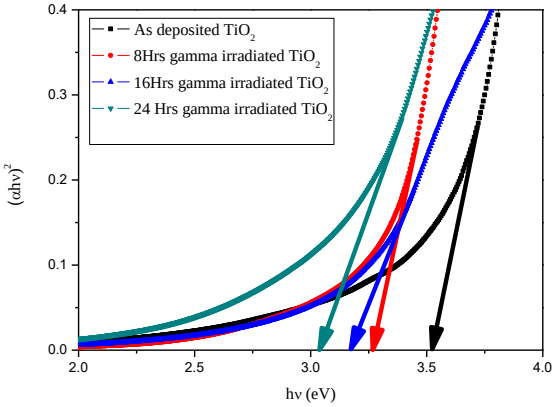


Fig. 4. Tauc plot for calculation of band gap of As deposited and gamma irradiation TiO_2 thin films.

The optical band gap was estimated by intercepting and extending the linear part of the curves which is obtained from fig 4 using equation 3. It is shown that the optical band gap decreases with increasing exposure of gamma irradiation. The elaboration of the Fig 4 is given in Table.2 and decline effects can be observed clearly with gamma energy. Similar results are abtained by M.M. El-Nahass et al [33] in InSe with increasing gamma dose.

Table 2. Optical band gap with and without gamma irradiation.

Sample treatment	**E_g (eV)**
As deposited	3.5289
8hrs gamma Exposure	3.27076
16hrs gamma Exposure	3.178200
24hrs gamma Exposure	3.0432

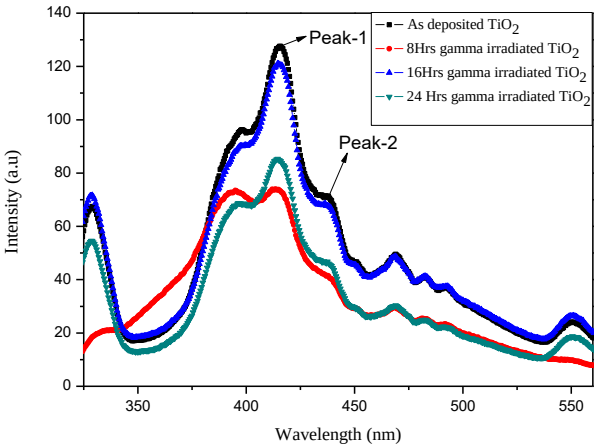


Fig. 5. Photoluminescence spectra of as deposited and gamma irradiation TiO_2 thin films.

Fig. 5 demonstrates the photoluminescence spectra of the sample before and after gamma irradiation at 8, 16, 24 hours under room temperature condition. It is shown that the intensity of photoluminescence peak is highest for As deposited sample and with the gamma radiation exposure, the intensity of the peaks decreases irregularly.

Fig. 5 also reveals that there is a shift in wavelength in both peaks (1&2). The shift is also irregular like the change in peak intensity. Variation in intensities and the shift in wavelengths of these peaks with gamma radiation exposure time are given in table 3.

Table 3. Variation in intensity and wavelength shift in Photoluminescence peak with and without gamma irradiation.

Sample treatment	**Peak-1**		**Peak-2**	
	Wavelength	**Intensity**	**Wavelength**	**Intensity**
As Deposited	415.7693	127.7	438.23	71.42
8 hours Exposure	413.78	74.06	438.89	40.83
16 hours Exposure	415.10	121.29	437.57	67.66
24 hours Exposure	414.44	85.33	438.23	46.19

4. Conclusion

The effect of gamma rays on nanostructured TiO_2 thin film is presented in this paper. XRD patterns show that crystalline structure changes with gamma irradiation. The change is not linear. At 8 and 16 hrs exposures, grain size decreases but with further exposure it increases. Same pattern was observed in SEM micrographs as well. Optical band gap decreases linearly with increasing gamma exposure. The obtained results give an understanding of the TiO_2 thin films based electronic instruments behavior which are being used in nuclear installation with heavy gamma dose.

Acknowledgments

This project is supported by King Saud University, Deanship of Scientific Research, College of Science, Research Center.

References

[1] M. Hussain, Salah. U. D. Khan,W. A .Syed, 20th International Conference on Nuclear Engineering (ICONE20), Anaheium, California, USA. July 30th, 2012.
[2] J. P. McCaffery, H. Shen, B. Downtown, Mainegra-Hing, Medi. Phys. **34**(2), 530 (2007).
[3] M. Hussain, Salah. U. D. Khan,W. A. Syed, Shahab. U. D. Khan, Science and Technology of Nuclear Installation, Volume 2014, Article ID 874134, http://dx.doi.org/10.1155/2014/874134.
[4] S. C. Kim, K. R. Dong, W. K. Chung, Ann. Nuclear Energ, **471** (2012)
[5] D. R. McAlister, http://www.eichrom.com/PDF/ gamma-ray-attenuation-white-paper-by-d.m.-rev-4.pdf
[6] M. Jalali, S. Dauterstedt, A. Michaud, R. Wuthrich, Compos. Part B-Eng. **42**, 1420 (2011).
[7] M. R. Baig, W. A. Farooq, S. M. Ali, T. M. Alrashidi, M. ATIF, S. S. AL-Ghamdi, M. S. Algarawi, J. Optoelectron. Adv. M. **16**, 712 (2014).
[8] A. Hiroki, H. T.Tran, N. Nagasawa, T. Yagi, M. Tamada, Radiation Physics and Chemistry **78**(12), 1076 (2009).
[9] S. Jipa, T. Zaharescu, R. Setnescu, E. S. Dragan, M. V. Dinu, Materials Chemistry and Physics **112**(2), 616 (2008).
[10] T. Li, H.G Park, S. H. Choi, Materials Chemistry and Physics **105**, 325 (2007).
[11] R.L. Clough, Nuclear Instruments and Methods in Physics Research Section B—Beam Interactions with Materials and Atoms **185**, 8 (2001).
[12] N. Salah, Habib, S.S.Khan, S. Al-Hamedi, F. Djouider, Radiation Physics and Chemistry **78** (11), 910 (2009).
[13] J. Akhavan, E. Kronfli, S.C. Waring, Polymer **45**(7), 2119 (2004).
[14] S. Machi, Radiation Physics and Chemistry **47**(3), 333 (1996).
[15] S.Y. Ye , Y.C. Fang, X. l. Song, S. C. Luo, L. M.Ye, Chemical Engineering Journal **225,** 499 (2013).
[16] R. Kaur, S. Singh, O. P. Pandey., Journal of Molecular Structure **1049,** 409 (2013).
[17] F. H. Batal., Indian j Pure & Appl. Phys. **47**, (2009).
[18] M. S. Roy, A. K. Gautam, M. Kumar, N. Prasad, Y. Janu, Y. S. Deol, R. K. Mishra, G. R. Choudhary, A. K. Sadh, AIP Conference Proceedings **1004**, 23 (2008).
[19] J. C. G. Juárez, J .J .Becerril, J. C. Álvarez, J. Mex. Chem. Soc. **54**(3), 157 (2010).
[20] N. Ghoneim, M. Marzouk, T. Daoud, F. Ezzeldin, Indian J Phys **87,** 39 (2013).
[21] M.Todica, L. Udrescu, G. Damian, S. Astilean., Journal of Molecular Structure **1044,** 328 (2013).
[22] R. Kralchevska, M. Milanova, M. Tsvetkov, D. Dimitrov, D. Todorovsky., J Mater Sci **47**, 4936 (2012).
[23] M.Todica,T. Stefan, D. Trandafir, S. Simon., Cent. Eur. J. Phys. **11**(7), 928 2013.
[24] M. R. Baig, W. A. Farooq, Syed Mansoor Ali, Talal Mohammed Alrashidi, M. Atif, S. S. AL-Ghamdi, M. S. Algarawi, J. Optoelectron. Adv. M. **16**(5-6), 712 (2014).
[25] J. R. DiMaio, URL: https://www.sbir.gov/sbirsearch/detail/303339
[26] M. Saiyad, N. M. Devashrayee, R. K. Mewada, Compos Part B **57**, 71 (2014).
[27] B. Buyuk, A. B. Tugrul, Radiat. Phys. Chem. **97,** 354 (2014).
[28] W. A. Farooq, S. M. Ali, Walid Tawfik, Amanullah Fatehmulla, M. Aslam, A. S. Al-Dwayyan, M. S. AlSalhi, Russian Journal of Chemistry A, **88**(13), 2446 (2014).
[29] A. Kitai, Principles of Solar Cells, LEDs and Diodes: The role of the PN junction,John Wiley & Sons, p.144, (2011).
[30] W. Aslam Farooq, M. Atif, Syed Mansoor Ali, Amanullah Fatehmulla, M. Aslam Optics and Spectroscopy, **117**(3), 386 (2014).
[31] W. A. Farooq, M. R. Baig, A. Fatehmulla, M. S. Al-Salhi , S. S. Al-Ghamd, F. Yakuphanoglu, Acta Phys. Pol. A, **123,** 106 (2013).
[32] M. Hashim Jabbar, S. Hussam Al-Selman, Variation of band edge, optical constant and dispersion parameters of CdS thin films due to disorder induced by fast neutron irradintion, J.Thi-Qar Sci, **2**(1), 152 (2010).
[33] M. M. El-Nahass, A.A.A. Darwish, E.F.M. El-Zaidia, A.E. Bekheet, Journal of Non-Crystalline Solids **382,** 74 (2013).

*Corresponding author: drskhan@ksu.edu.sa
wafarooq@hotmail.com