Effect of x-rays and ɣ radiation on the optical and structural properties of vanadium oxide thin film

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Abstract— In this study, the aim is determination of the changes that occurred in the structural and optical properties of vanadium pentoxide (V2O5) thin films which deposited with spray pyrolysis coating method, as a result of exposure to ionizing radiation. Firstly, the films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), wavelength dispersive X-ray fluorescence (WDXRF) and UV-vis spectrophotometries. In order to irradiate the thin films, x- rays and 59.54 keV gamma-rays emitted from 100 mCi, 5 Ci Am241 radioactive sources were used. After irradiation; the XRD, SEM, AFM WDXRF and UV-vis measurements were taken again and the obtained results were compared. Radiation damage induced by the x- rays and gamma-rays emitted from 100 mCi, 5 Ci Am241 has led to several differences of the structural properties of V2O5 films. Although the structural changes have occurred as a result of V2O5 film on the glass substrates with the absorbed dose, it has been observed that vanadium oxide thin films are resistant to radiation with different doses of radioactive sources. This absolute result is lead to play key roles in devices performance and efficiency.

Index Terms— Vanadium oxide, irradiation, structral and optical properties, spray pyrolysis method

1 Introduction

Within a period of a few decades, the field of materials science and engineering has emerged as a focal point for developments in virtually all areas of engineering and applied science. The study of thin film materials has been one of the unifying themes in the development of the field during this period. The area encompasses films bonded to relatively thick substrates, multilayer materials, patterned films on substrates and free-standing films. Significant advances in methods for synthesizing and processing these materials for ever more specific purposes, as well as in instrumentation for characterizing materials at ever diminishing size scales, have been key to modern engineering progress [1].

Metal oxide films are widely used in optical and microelectronic applications [2-5]. Vanadium oxide thin films and the thin-film components, depending on a variety of industrial applications in the antireflective structures, optical waveguides, capacitors are used in automotive electronics, mobile phones, paging devices, electronic circuits, reflective coatings on solar cells, are widely used [6, 7]. Vanadium oxides thin films depending on the film deposition or coating methods are used in many applications have different optical characteristics and high-refractive material. Because of the high refractive index of vanadium oxides and wide variety of stable oxidation states such as VO, V2O3, V5O9 and V2O5, the most intensive usage is still going on with the glass manufacturing at the photo lenses.

X- and gamma rays are form of electromagnetic radiation. X-rays have energies in the range 100 eV to 100 keV. Gamma rays have energies in the range 100 keV to 10 MeV. X- and gamma-rays are used radiographic testing or industrial radiography and are nondestructive testing method of rocks, minerals, sediments, semiconductor and fluids. Developing the properties of the material by exposure to radiation can be applied in various industrial fields. The applied radiation can significantly change the physical and chemical properties of thin films [8].

In this work, it is investigated the effects of x- and gamma-rays irradiation on the V2O5 thin films. The samples were irradiated with x-rays, 59.54 keV gamma rays emitted from 100 mCi and 5 Ci Am241 radioactive sources. The results of structural and optical studies on these films are compared with before and after x- and gamma-rays irradiation.

2 Experimental

Vanadium oxide thin films were deposited on glass substrates using spray pyrolysis method at room temperature. The glass substrates were cleaned ultrasonically for 10 min, first in acetone, second in a 1:1 ethanol: water solution and then by rinse in de-ionized water of 18 MΩ. The substrate temperature was set at 400 °C and the nozzle to substrate distance was optimized to be 20 cm. The precursor solution was prepared as 0.05 M by mixing 0.393 gr of vanadium trichloride (VCl3) in 50 mL of de-ionized water. The solutions were mixed together in appropriate volumes to obtain the vanadium oxide and then sprayed through a nozzle on to the preheated glass substrates. The deposition parameters were 5 mL in 1 minute solution flow rate, 90° position of spray nozzle towards the substrate. Atmospheric air was used as carrier gas with 2.5 mbar pressure. After the XRD, SEM, AFM, WDXRF

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and UV-vis measurements of fabricated thin films were performed, these films were irradiated. Later, the XRD, SEM, AFM, WDXRF and UV-vis measurements were repeated and the results were compared. For structural studies, a Rigaku 2200D/ Max, X-Ray Diffractometer using Cu Kα (λ=1,5405 Angstrom) radiation with 2θ of 20-60° was used. Surface morphologies were studied using the Zeiss Supra 50 VP model SEM, AFM which was produced by Nanomagnetics-Instrument and WDXRF which was produced Rigaku ZSX100e model. The absorption measurements were carried out using a Perkin-Elmer UV/VS Lambda 2S Spectrometer with a wavelength resolution better than ±0,3 nm at room temperature.

3 Results and discussions

X-ray diffraction (XRD) measurements were employed to investigate the phase and structure of the synthesized samples. XRD pattern of un-radiated and radiated with x and gamma-rays V2O5 are given in Fig. 1. X-ray analysis of the samples was obtained in the range of 2θ between 10° and 80°. From the results obtained on V2O5 thin film, diffraction peaks were observed for (200), (110), (002), (021), and (303) planes. The peak pattern for un-radiated and radiated thin films, matches with the Joint Committee on Power Diffraction Standards (JCPDS) no. 00-009-0387 data for orthorhombic phase V2O5. On the other hand, on radiated samples it is evident from Fig. 1 that the relative intensity of peaks were decreased, this decrease in the relative intensity of each peak refers to the formation of V2O5 thin film that are affected by the process of radiation [9].

The crystallite sizes or grain sizes of the thin film samples were calculated using Debye- Scherrer's equation [10],

$$D=0,9\lambda/\beta\cos\theta \quad (1)$$

where D is the grain size, λ is the x-ray wavelength used, β is the angular line width at half-maximum intensity in radians and θ is Bragg's angle. We calculated the grain size, dislocation density and strain of the films using the FWHM of the dominant peak in all the films obtained through the Scherrer's method. The average crystallite size was calculated by resolving the highest intensity peak. As listed in Table 1 and Table 2, the crystallite size of the films became smaller with x and gamma radiation indicating that the film crystallinity deteriorated and no major change in preferred orientations of crystal planes. Additionally, to have more information on the amount of defects in the films, the dislocation density (δ) was evaluated by the formula [10],

$$\delta=1/D^2 \quad (2)$$

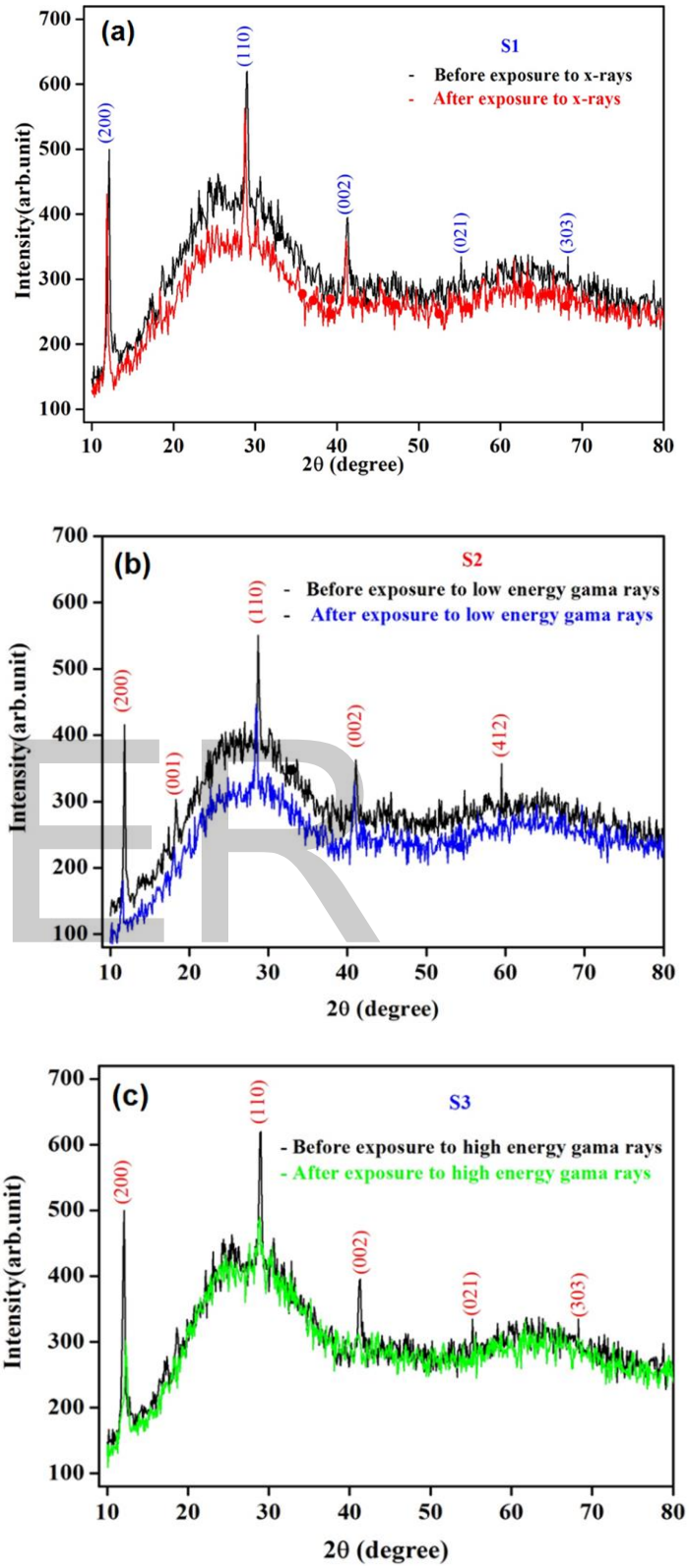


Fig. 1. XRD patterns of vanadium oxide thin films before and after irradiation a) x rays, b) gamma-rays emitted from 100 mCi and c) gamma-rays emitted from 5 Ci sources.

Table 1. The Grain Size (D), Dislocation Density (Δ), Strain (ε) And Full Width At Half Maximum (FWHM) Values Of Vanadium Oxide Thin Films Before Irradiation.

V_2O_5	FWHM	D (nm)	$\delta x10^{-3}$ (nm^{-2})	$\varepsilon x10^{-2}$ ($line^{-2}m^{-4}$)
S1	0.3401	5.097	0.0343	0.0845
S2	0.2318	6.510	0.0276	0.0576
S3	0.3210	4.341	0.0531	0.0798

Table 2. The grain size (D), dislocation density (δ), strain (ε) and full width at half maximum (FWHM) values of vanadium oxide thin films after irradiation, a) x rays, b) gamma-rays emitted from 100 mCi and c) gamma-rays emitted from 5 Ci sources.

V_2O_5	FWHM	D (nm)	$\delta x10^{-3}$ (nm^{-2})	$\varepsilon x10^{-2}$ ($line^{-2}m^{-4}$)
S1a	0.2583	4.393	0.0595	0.0642
S2b	0.4921	4.831	0.1247	0.1224
S3c	0.6002	2.323	0.1853	0.1492

The strain values were calculated from the following relation [10],

$$\varepsilon=\beta\cos\theta/4 \quad (3)$$

From Table 1, the dislocation density of un-radiated V2O5 thin film was measured at less than radiated V2O5 thin film. The radiated samples have increased the amount of defects on the thin films and modified the surface structures which lead to the increasing in the concentration of lattice imperfections [11]. It can be seen that the diffraction angles move to larger angles and the mean grain sizes decrease for all samples after radiation. It may be because that some vacancies occur after radiation, the lattice constant becomes smaller and the crystalline quality becomes bad. Meanwhile, the distribution uniformity of the large nanoparticles of V2O5 films decreases after radiation.

We observed that the intensities and full width at half maximum (FWHM) values of these peaks changed with x- and gamma-rays irradiation. Radiation has led to changes in the physical and chemical properties of the film structure, due to the excitation of free carriers and the formation of new pairs of electron cavities. These changes may be attributed to the no deteriorate of crystallinity of the films, rearrangement atoms and cause of the defects with changing irradiation [12].

The surface morphology of irradiated V2O5 thin films was determined by using SEM technique and it was shown that the changes occurring by increasing the absorbed dose depend on grain structure. It can be seen that the mean grain sizes decrease for all samples after radiation, which are supported by SEM results. The reason that some vacancies come to the films exposed to radiation can be expressed as the decrease of the the lattice constant becomes smaller and the crystalline quality becomes bad [13]. As can be seen in Fig. 2, the appears on the surface of films at different doses. The surface properties clearly began to change in the highly exposed film. Along with the dose increase, the grain sizes are becoming smaller but forming cluster. The amount of droplet that is absorbed is an important key parameter depending on the irradiated color centers and the changes in grain size. The appropriate particle size can be selected together with the change in absorbed dose depending on the application procedure. The collection of small particles of irradiated films can be explained by the change of the valance states of pure atomic ions and the formation of new electronic arrangements of defect centers.

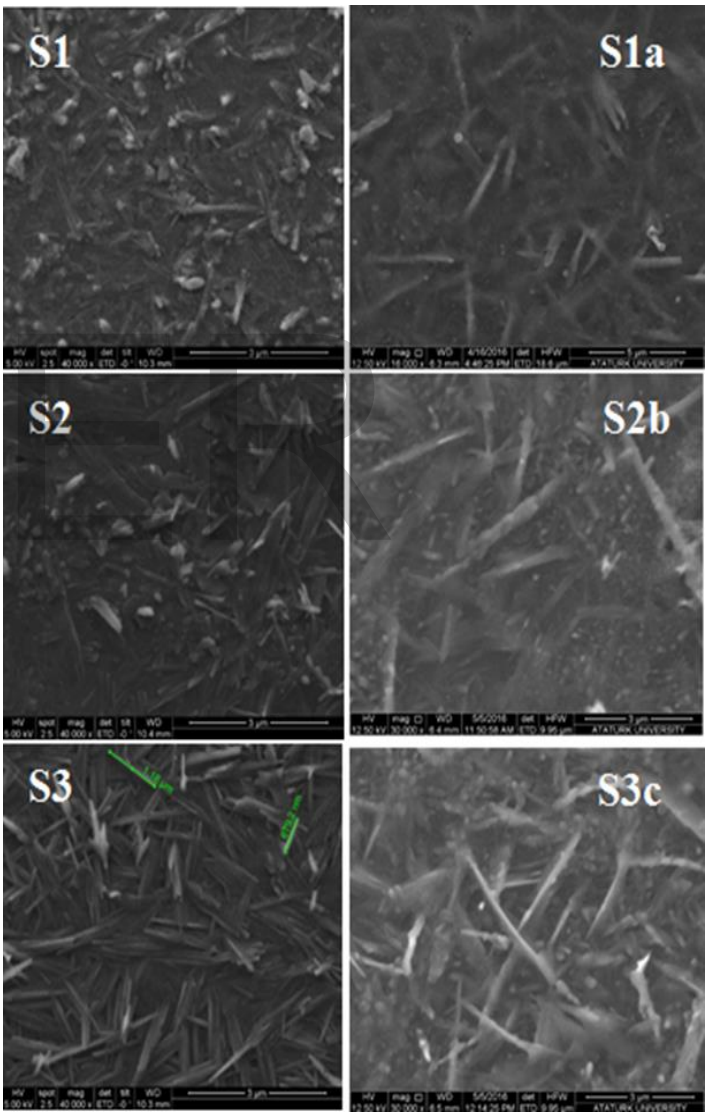


Fig. 2. SEM images of the vanadium oxide thin films before and after irradiation a) x rays, b) gamma-rays emitted from 100 mCi and c) gamma-rays emitted from 5 Ci sources.

The images confirm that the irradiation with x rays have little impact on the microstructural characteristics of the films. These films could not be obtained since the films were ex-

tremely adherent and could not be removed without excessive mechanical damage. After irradiation at x rays, there was a reduction in crystalline size for the orthorhombic phases. In contrast, irradiation with gama rays at low dose provoked a slight increase in size of the orthorhombic phases. Since irradiation using gama rays at high dose should result in enhanced displacement damage relative to x ray irradiation, and it is for this film that we are starting to observe a slight increase in crystalline size for the orthorhombic phase, one could conclude that the present materials are rather sensitive to whether irradiation is conducted in the electronic or nuclear energy loss regime [14].

To observe and characterize the topography of the V2O5 thin films, atomic force microscopy (AFM) was applied at room temperature as shown in Fig. 3. Analysis of V2O5 thin films by AFM reveals that radiated samples had smoother surface areas compared with un-radiated because of decreased crystallite sizes. The absorbed dose caused in the grains of metal oxides thin film started to occur together and pile up at various spots on the surface of the film. The decrease in roughness data occurred in parallel with the decrease in crystallite size or grain size in the XRD data [15].

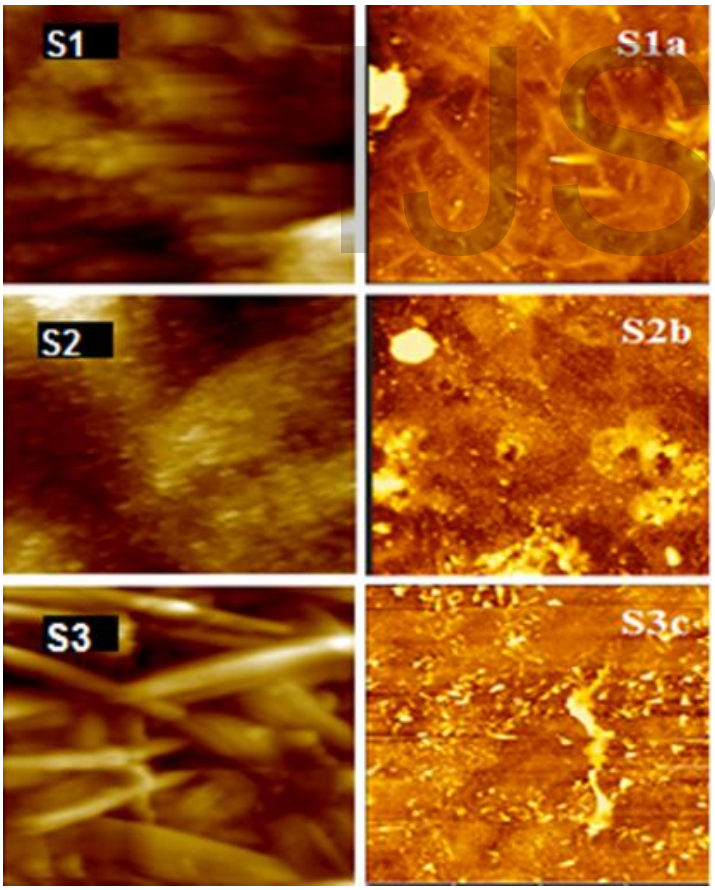


Fig. 3. The AFM surface images of vanadium oxide thin films before and after irradiation a) x rays, b) gamma-rays emitted from 100 mCi and c) gamma-rays emitted from 5 Ci sources.

We investigated how destructive x- and gamma-rays on the expected elements of V2O5 thin films. The films were analyzed by WDXRF system before and after irradiation with x- and gamma-rays. WDRXF results for V Kα x-ray peak are given in Table 3. Also, V2O5 concentrations were accurately identified by using the semi-quantitative calibration (SQX) in WDXRF spectrometer and are given in Table 3. As seen from Table 3 that there are not the shifts at peak centroits after x- and gamma-ray irradiation. But, the intensities of V Kα x-ray peak and the concentrations of V2O5 decrease after x- and gamma-ray irradiation. These results show that the thickness or composition of V2O5 thin films irradiated with x- and gamma-rays can be destroyed.

Table 3. WDXRF results for V Kα x-ray peak before and after irradiation with x- and gamma-rays.

	S1		S2		S3	
	Before	**After**	**Before**	**After**	**Before**	**After**
Peak centroid (nm)	0.2508	0.2508	0.2508	0.2508	0.2507	0.2508
V conc. (%)	1.7656	1.4386	0.7400	0.4749	0.6337	0.6257
V2O5 conc. (%)	1.5149	1.2298	0.6937	0.5635	0.6289	0.5888

The absorption measurements of V2O5 thin film were carried out at room temperature before and after x-and gamma-ray irradiation. The decline of absorbance of the V2O5 films in Figure 4 may be related to the decrease of crystalline quality. It is because that the radiation at the V2O5 film was higher which cause a decrease of the stability of V2O5 film decreases, its crystalline structure is easier to worsen when exposed to radiation, so the absorbance decline is much more pronounced with radiation doses [16].

The optical band gap (E_g) of the samples has been estimated from the well-known expression [17] for direct transition, by fitting experimental absorption data with the equation:

$$\alpha=(A/h\nu)(h\nu-E_g)^n \quad (4)$$

where A is a constant and n assumes values of 1/2, 2, 3/2 and 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively.

Plots of $(\alpha h\nu)^2$ versus hν and $(\alpha h\nu)^{1/2}$ versus hν were analysed and better linearity was observed for the optical band gap as shown in Figure 5. For this study, n value is determined as 1/2 for $(\alpha h\nu)^{1/n}$. From the plot, the band gap energy was determined by extrapolating the linear portion of the graph to hν = 0. It is determined that there is an allowed direct transition as $(\alpha h\nu)^2$ for V2O5 film. The optical bandgap of V2O5 thin films were 2.44, 2.43 and 2.42 eV. It can be seen that the bandgaps increase after radiation in Fig 5. It may be because that the grain sizes decrease after radiation, the grain boundary defects increased in the films, thus resulting in the changing of the optical bandgaps [18].

Table 4. The bandgap (Eg), refractive index (n), optical static dielectric constant (ε_0) and optical high frequency dielectric constant (ε_∞) values of vanadium oxide thin films before irradiation.

			Moss relation		Herve and Vandamme	
V2O5	Eg (eV)	ε_0	n	ε_∞	n	ε_∞
S1	2.44	11.005	2.57	6.605	2.53	6.401
S2	2.41	11.066	2.58	6.656	2.54	6.452
S3	2.43	10.173	2.51	6.300	2.44	5.954

Table 5. The bandgap (Eg), refractive index (n), optical static dielectric constant (ε_0) and optical high frequency dielectric constant (ε_∞) values of vanadium oxide thin films after irradiation.

			Moss relation		Herve and Vandamme	
V2O5	Eg (eV)	ε_0	n	ε_∞	n	ε_∞
S1a	2,52	11.035	2.58	6.656	2.53	6.401
S2b	2,71	10.758	2.55	6.503	2.50	6.250
S3c	2,87	09.680	2.47	6.101	2.38	6.664

The refractive index (n) and dielectric constant (ε) of semiconducting materials is very important in determining the optical and electrical properties of the crystals. The refractive index of the films was calculated using Moss relation [19] that is directly related to the fundamental energy bandgap (E_g),

$$E_g n^4 = k \quad (5)$$

where k is a constant with a value of 108 eV. This relation is preferred to other relations because it is found to give better agreement with the known data for n in II-VI semiconductors. A different relation between the refractive index and bangap energy is presented by Herve and Vandamme in the following for [19],

$$n = (1+(A/(E_g+B)^2)^{1/2} \quad (6)$$

where A and B are numerical constants with values of 13,6 and 3,4 eV, respectively.

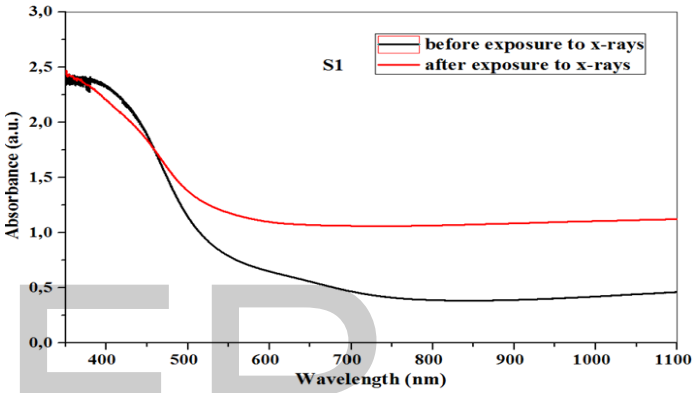
The dielectric behaviours of solids are important for several electrondevice properties. Both static and high frequency dielectric constants were evaluated for all the films. The values of the high frequency dielectric constant (ε_∞) were calculated from the following relation [20],

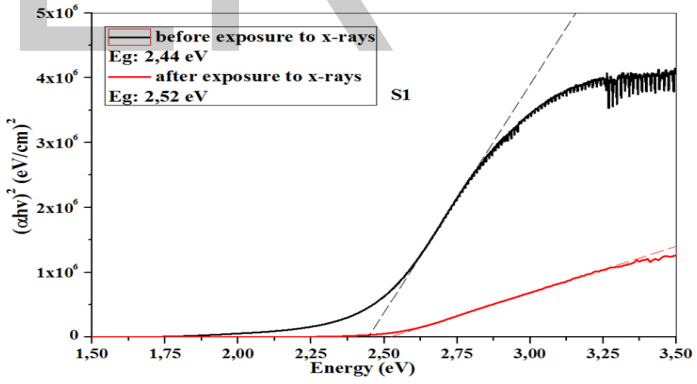
$$\varepsilon_\infty = n^2 \quad (7)$$

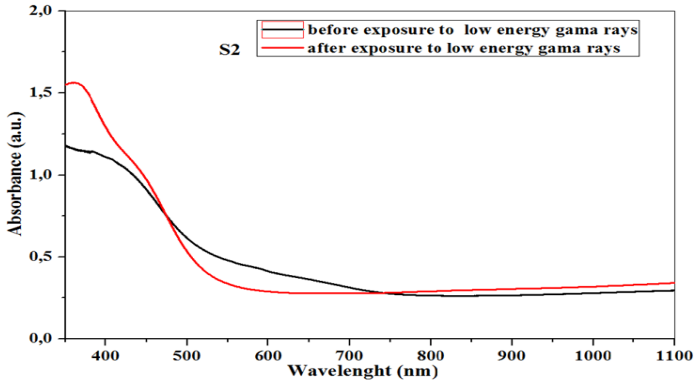
where n is refractive index. The values of the static dielectric constant (ε_0) of the films were calculated using a relation expressing the energy bandgap dependence of ε_0 for semiconductors compounds in the following form [20],

$$\varepsilon_0 = 18{,}52 - 3{,}08 E_g \quad (8)$$

The optical constants of V2O5 thin films were affected by the x and gamma irradiations. It was possible to determine the changes in optical constants such as the refractive index, extinction coefficient and absorption coefficient with the change of the grain size in this study. The change of the optical constants of the irradiated films was related with the gathering of the grains at the surface of the film with the controlling of the absorbed dose according to the SEM images.







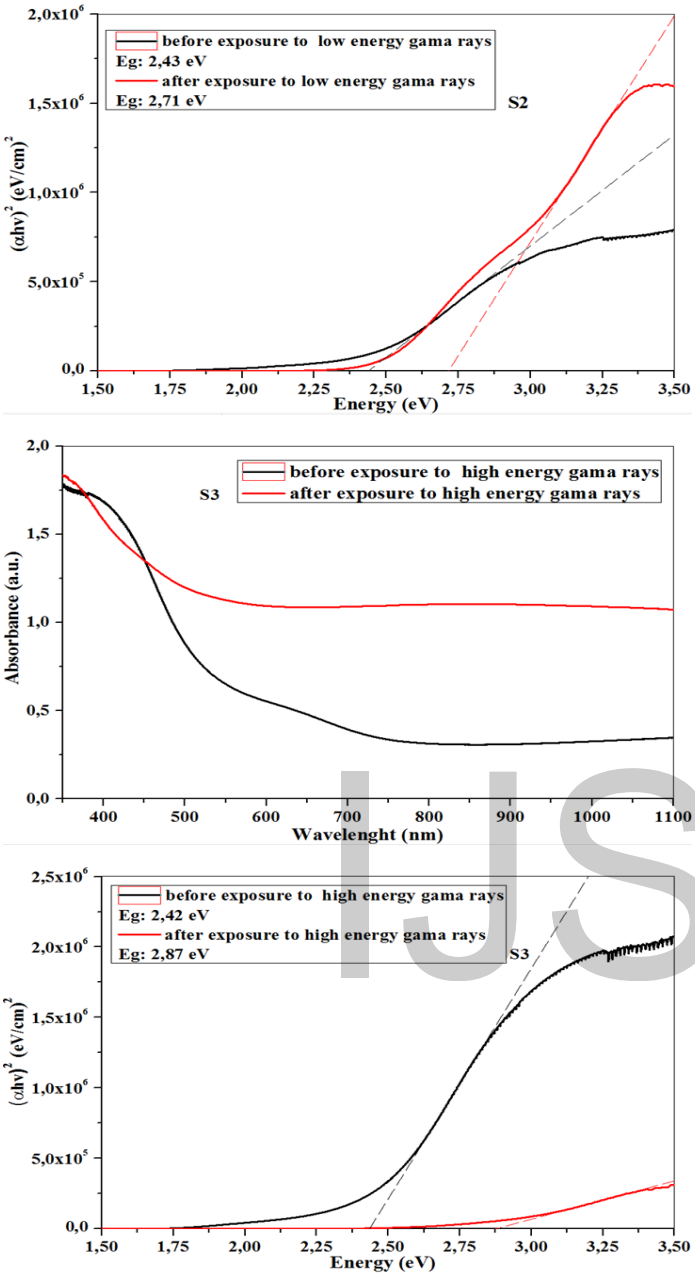


Fig. 4. Plots of absorbance versus wavelenght and $(\alpha h\nu)^2$ versus hν for vanadium oxide thin films before and after irradiation,respectively.

It is clear that the stable radiation damage formed at a certain temperature not only relies on the radiation conditions but also on the starting material and subsequent processing details. This implies that the radiation performance can be optimized or improved by a smart choice of starting material. Not only doping type, but also the doping atom can play a role. Besides the type of dopant and its concentration, oxygen and carbon play a decisive role in the radiation performance. When oxygen diffused material exhibits a better radiation performance. Furthermore, oxygen-doping by diffusion in the range of a few times 1017 cm^{-3} clearly improves depletion voltage compared with standard undoped material. It is speculated that this behavior is closely related to the reduced introduction of V2O5 centers upon irradiation, which are thought responsible for the carrier removal by introducing a compensation acceptor level near midgap. It has been found that the addition of small of impurities during deposition V2O5 (Cl, F and etc.) can have beneficial effect on the radiation response. It turns out that for most additives, an optimum concentration exists, which implies that the deposition conditions need to be well-controlled. It is believed that the presence of F or Cl at the interface changes the local bond strain distribution. A possible mechanism leading to the reduce strain is the interaction of F atom a non-bridging oxygen bond, resulting in local strain relaxation [12].

4 Conclusion

Effects of the x and various gamma irradiations on V2O5 thin films on glass substrates grown by spray pyrolysis method at room temperature have been investigated with structural and optical parameters. It has been showed that the V2O5 thin films irradiated x rays with little effect and the increase of the irradiation doses with gama rays would lead to change of the quality of V2O5 thin films. Based on these results, there is a possibility for controlling the structural and optical properties of V2O5 thin films by adjusting the radiation dose. Hence, the industrial and environmental applications of V2O5 thin films could be expanded and this absolute result is lead to play key roles in devices performance and efficiency.

References

[1] L. B. Freund, S. Suresh, Thin Film Materials, (2003) Division of Engineering Brown University.

[2] A. Baltakesmez, A. Yenisoy, S. Tüzemen, E. Gür, "Effects of gold nanoparticles on the growth of ZnO thin films and p-Si/ZnO heterostructures", *Materials Science in Semiconductor Processing* 74, 249-254, 2018.

[3] S. Akin, E. Erol, S. Sonmezoglu, "Enhancing the electron transfer and band potential tuning with long-term stability of ZnO based dye-sensitized solar cells by gallium and tellurium as dual-doping", Electrochimica Acta Volume 225 243-254 2017)

[4] A. Kösemen, Z. A. Kösemen, B. Canimkubey, M. Erkovan, F. Başarır, S. E. San. Osman Örnek, A.V.Tunç, "Fe doped TiO2 thin film as electron selective layer for inverted solar cells", Solar Energy 132 (2016) 511-517

[5] G. Turgut, E. Sönmez, "Synthesis and characterization of Mo doped SnO2 thin films with spray pyrolysis", Superlattices and Microstructures, 69 (2014) 175-186.

[6] F. N. Dultsev, L. L.Vasilieva, S. M. MAroshina, L. D. Pokrovsky, "Structural and optical properties of vanadium pentoxide sol–gel films", Thin Solid Films, 510 (2006) 255-259.

[7] H. Hirashima, I. Michihisa and T.Yoshida, "Memory switching of V2O5-TeO2 glasses", Journal of Non-Crystal Solids, 86 (1986) 327-225

[8] Vladimir G. Baryshevsky, Alexander P. Ulyanenkov, Ilya D. Feranchuk, "Parametric X-ray Radiation in Crystals", (2005) Springer Tracts in Modern Physics.

[9] A. A. Darwish, Shams A. M. Issa, Taymour A. Hamdalla, M. M. El-Nahass, "Effect of X-ray irradiation on the optical properties of nanostructured thin films TCVA based on structural analysis", Optic Quantum Electron 49: 398 (2017) 1-12.

[10] M. Ali Yıldırım, Sümeyra Tuna Yıldırım, Aytunç Ates¸ "Cadmium con-

centration effect on structural, optical and electrical properties of nanostructured CdxZn1-xO thin films", Journal of Alloys and Compounds 701 (2017) 37-42.

[11] A. Reyhani, A. Gholizadeh, V. Vahedi, M. R. Khanlary, "Effect of gamma radiation on the optical and structural properties of ZnO nanowires with various diameters", Optical Materials 75 (2018) 236-242.

[12] C. Claeys and E. Simoen, "Radiation Effects in Advanced Semiconductor Materials and Devices", (2002) Springer-Verlag Berlin Heidelberg, NewYork.

[13] E. Ö. Zayim, N. D. Baydogan, "Irradiation effect in WO3 thin films, Solar Energy Materials and Solar Cells", 90 (2006) 402-413

[14] Ayelen M. Manzini, Martin A. Alurralde, Gustavo Gimenez, Vittorio Luca, "The radiation response of mesoporous nanocrystalline zirconia thin films", Journal of Nuclear Materials 482 (2016) 175-186

[15] N.Baydogan, "Evaluation of optical properties of the amorphous carbon film on fused silica, Materials Science and Engineering", 107 (2004) 70-77.

[16]K. E. Sickafus, E. A. Kotomin, B. P. Uberuaga, "Radiation Effects in Solids (2004)", Proceedings of the NATO Advanced Study Institute on Radiation Effects in Solids Erice, Italy.

[17] S. Sarangi, "Controllable growth of ZnO nanorods via electrodeposition technique: towards UV photo-detection", Journal Physics D: Applied Physic 49 (2016) 355-341.

[18] X.Wang, Y. Zhang, "The effects of UV radiation on the structure and properties of AZO thin films deposited on quartz glass by magnetron sputtering", Materials Letters 188 (2017) 257-259.

[19] M. A. Yıldırım, The effect of copper concentration on structural, optical and dielectric properties of CuxZn1−xS thin films, Optic Communication 285 (2012) 1215-1220.

[20] B. Güzeldir and M. Sağlam, "Using different chemical methods for deposition of copper selenide thin films and comparison of their characterization", Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 150 (2015) 111-119.