Structural, morphological and optical characterization of nanocrystalline WO_3 thin films

M. H. Saeed[a], M. H. Al-Timimi[b,*], O. A. A. Hussein[c]
[a]*Al-Mustansiriyah University, College of Basic Education, Science Department, Iraq*
[b]*University of Diyala, College of Science, Physics Department, Iraq*
[c]*Al-Rafidain University College, Department of Radiology, Iraq*

WO_3 Nanocrystalline thin films were prepared by Electron Beam Evaporation on cleaned glass substrates. The effect of annealing temperature on the structural, morphological, and optical properties of WO_3 thin films has been studied. The single-phase monoclinic structure of the WO_3 3 films has been confirmed by x-ray diffraction analysis, all films have homogenous morphology surfaces. The transmission of prepared films was measured in the wavelength range 300-900 nm. WO_3 thin films show the indirect band gap ware decreased from about (3.193 eV) before annealing to about (3.061 eV) and (2.952 eV) after annealing.

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Keywords: WO_3 thin films, X-ray diffraction, Energy band gap, Annealing effect.

1. Introduction

Tungsten oxide (WO_3) is a semiconducting material that has unique electronic properties, has an energy gap of 31-2.65 eV, the energy gap is dependent on the structures phase and the degree of distortion from the ideal cubic phase and accompanied by a change in energy gap[1],as the occupied levels of the W 5d states change [2]. It is an n-type semiconductor, with the valence band is a 2p orbital of oxygen (O) and the conduction band is empty tungsten (W) 5d orbitals and has several important applications such as used in smart windows, solar energy storage cells [3,4] , photocatalysis [5], gas sensors[6] and batteries [7]. The three crystalline structures that WO_3 includes triclinic, monoclinic, orthorhombic, tetragonal, hexagonal, and cubic. the crystals structure of WO_3 are triclinic, monoclinic, orthorhombic, and tetragonal phases[8], The crystalline phase of the WO_3 depends to an important on the annealing process and the transition from one phase to another due to heat and cooling [9] , it is important to elucidate the physical properties of the films needed to obtain good optical characteristics. Structural and optical properties of WO_3 films depend on the preparation conditions [10]. WO_3 thin films have been prepared by various different processes techniques such as: pulsed laser [11], spray pyrolysis [12] , sputtering [13] , thermal evaporation [14] ,Spin Coating [15],chemical vapour deposition [16],co-precipitating method [17] , and Sol-gel [18] .

In the present study, we have tried to make a complete study of WO_3 thin films on glass substrates by the electron beam evaporated technique and studied the effect of annealing temperatures at 350 °C and 550 °C respectively in an oxygen environment along with changes in the structural properties, absorbance and energy band gap of the WO_3 thin films . The physical properties of the films were investigated using different techniques such as XRD, SEM, AFM and UV-vis spectrophotometry.

[*] Corresponding author: muhammadtimimi@yahoo.com

2. Experimental part

Tungsten oxide thin film were synthesized by utilization of evaporation of electron beam, WO_3 powder (99.9%) was employed in this experiment as a starting material on a glass substrates along with using tungsten crucible, pressure was set to less than 10^{-5} mbar before deposition under oxygen into the chamber of evaporation . on the other hand, substrate temperature was set to 200 °C with a distance of 30 cm between source and substrate, while rotated at 25 RPM during deposition to obtain homogeneous films, the thickness of the film was about (250 ± 25 nm). These films were annealed at temperature of 350°C and 550 °C for two hours. Transmittance and Absorbance measurements were carried out using double bean UV/VIS spectrophotometer (shimadzu Japan) in the wavelength range (300-900) nm, and using (Shimadzu, Japan) XRD-6000 powder diffractometer with Cu Kα radiation to determine the types of crystalline structures of resultant thin films of WO_3.

3. Results and discussion

3.1. X-ray diffraction

By using (Shimadzu, Japan) XRD-6000 powder diffractometer with Cu Kα radiation, determined the crystalline structures types of WO_3 Thin films samples. The Figure (1) shows x-ray spectra for WO_3 Thin films before and after annealing , observed there are several peaks the strong peak at 24.221° (-202), 26.413° (-121), 28.781° (111), 41.353° (220) , 49.722° (-141) and 53.32° (024) as prepared and after annealed at 550 °C observed several peaks 23.421° (020), 26.413° (-121), 33.981° (200), 41.753° (-224) , 49.722° (-141) and 53.303° (024) . the strong peak at which indicate to formation WO_3 phase as a monoclinic crystal system and the space group is P21 /c, and space group number 14 with lattice parameters: a= 7.3000 Å , b = 7,5400 °A, c = 10,5245 °A and Alfa(α) =90° A, Beta(β) = 133.1420°A and Gama (γ)= 90 ° A,at reference code : (04-002-3163) . This result also is supported by similar obtained from other researchers studied the WO_3 thin films [19 ,20,21] .

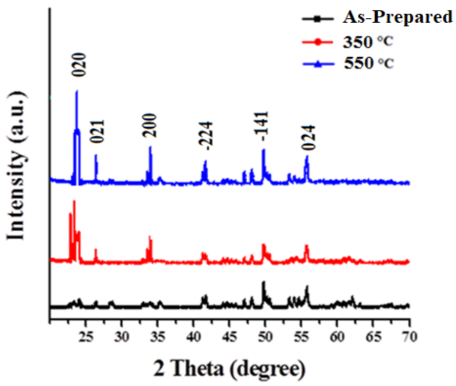

Fig. 1. XRD patterns of WO_3 *thin films; as-Prepared , annealed at 350 °C and 550 ºC.*

3.1. Scanning Electron Microscopy (SEM) and Energy Dispersion X-Ray Analysis (EdXA)

Fig. 2 Show (EDXA) the Energy Dispersion X-ray Analysis performed of WO_3 thin films shows the presence of only the W and O. As shown in Table 1 the W: O atomic ratio calculated based on this EDXA result is equal to 0.33: 1.

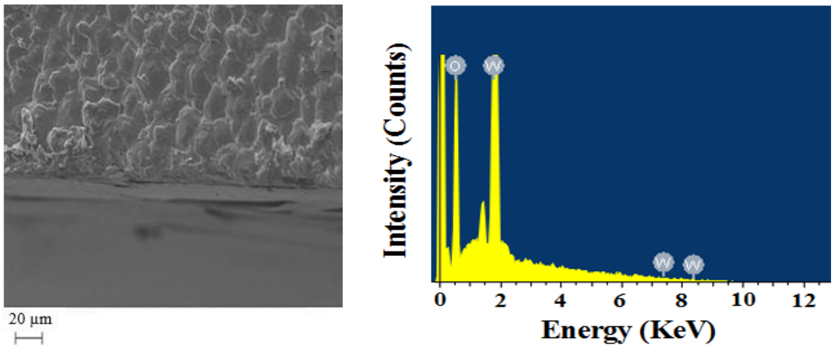

Fig. 2. EDX spectra of WO_3 thin films As deposited.

Table 1. Show the elements ratios of WO_3 from EDXA As deposited.

Element	Weight (%)	Atomic (%)
O	20.60	74.88
W	79.40	25.12
Total	100	100

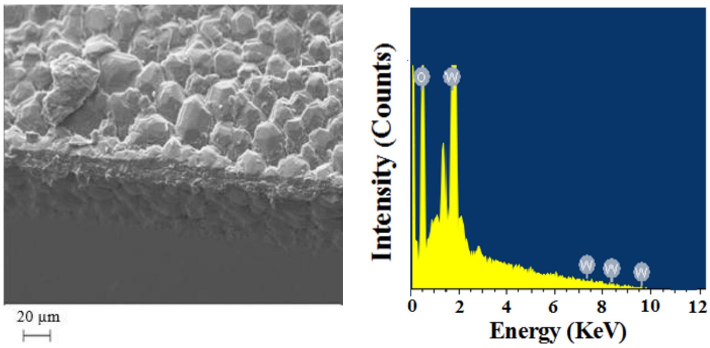

Fig. 3. EDX spectra of WO_3 thin films Annealed at 600^oC.

Fig. 3 Show (EDXA) the Energy Dispersion X-ray Analysis performed of WO_3 thin films shows the presence of only the W and O. As shown in Table 2 the W: O atomic ratio calculated based on this EDXA result is equal to 0.33: 1.

Table 2. Show the elements ratios of WO_3 from EDXA Annealed at 550 ^oC.

Element	Weight (%)	Atomic (%)
O	20.93	74.25
W	79.07	24.75
Total	100	100

3.2. The Surface Morphology of The WO_3 Films By AFM:

The AFM images of the as-deposited and annealed WO_3 thin films are shown in Fig. 4. It is seen that the surface of the films are smooth and consist of 37-58nm sized grains. The grain boundaries are not clear for as deposited films and became more visible after annealing. The particle sizes of the films are increased with increasing annealing temperature. RMS value was found to be varied and surface was continuous. There was a very small increase in surface roughness with annealing. The structure became discrete relatively and some deep valleys were developed.

All the grain size and RMS values were determined via Image Plus program. The surfaces of as-synthesized and annealed at 350 and 550 ^{o}C films are smooth and consist of nano-sized grains. The roughness and average grain size of as synthesized and annealed film were shown in Table 3. From the Fig. 5 it was seen that the grain size of the films was increased with increasing annealing temperatures. The grains at high temperatures were increased and became clearer. The continuous structure of the surface became discrete. Moreover, changing in colors of the films was observed with changing the annealing temperature. In our experiments, the as-prepared films have a blue color, while annealed films at 350 ^{o}C have light violet color, and annealed films at 550 ^{o}C have yellow-green color.

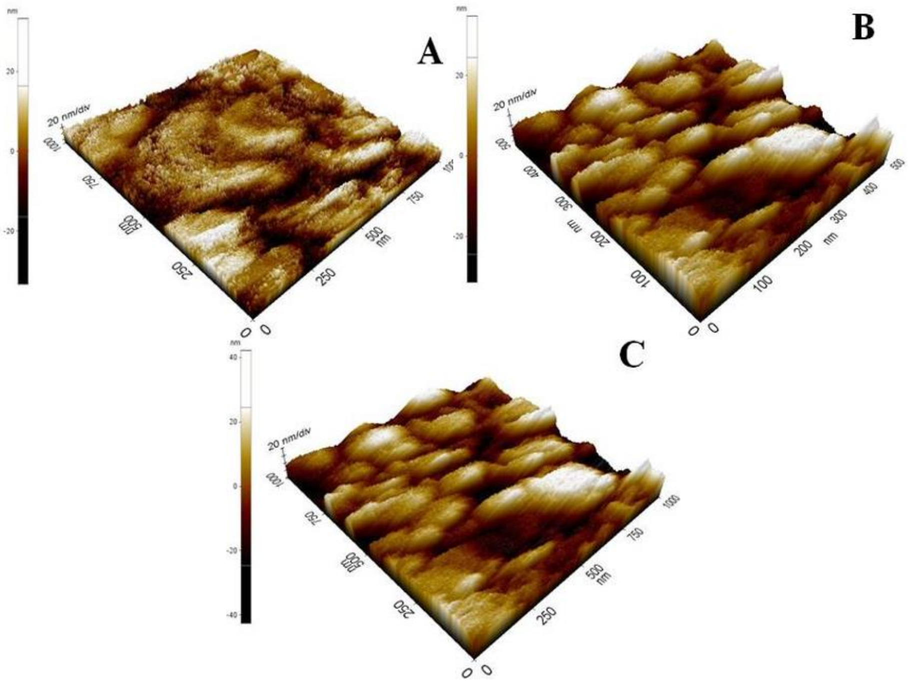

Fig. 4. AFM images of WO_3 thin films; (A) as-Prepared , (B) annealed at 350 °C and (C) 550 ºC.

Table 3. Show the roughness and average grain size thin films of WO_3; (A) As prepared sample, (B) when annealed at two temp. 350 °C, (C) 550 ºC.

Sample	Annealing Temperature (^{o}C)	Average Roughness (nm)	Average Grain Size (nm)
1	As prepared	2.58	43
2	350	2.93	52
3	550	4.58	58

3.3. Optical properties

The optical transmittance spectra were recorded for the prepared thin films in the wavelength range of 300-900 nm. The effect of annealing temperatures 350 and 550 °C on the transmittance, reflectance, and energy band gap (Eg) are studied.

Fig. 5 shows the transmission and reflectance for prepared WO_3 thin films at room temperature and annealing effect with two temperatures at 350 and 550 ° C on glass substrates. the increased transparency and the transmittance of the WO_3 films in the range of 70% and 50% after annealing temperature effect [22].The reason for this, is attributed to the that photons have sufficient energy to excite the electrons from the valence band to the conduction band while the photons are absorbed through the film to reduce the transmittance [23].

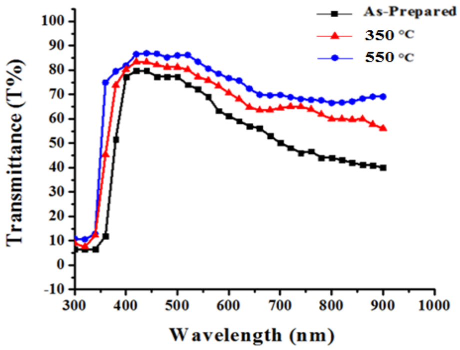

Fig. 5. Transmittance vs. wavelength of WO_3 films with different annealing temperatures.

Fig. 6 shows the reflectance for prepared and annealed WO_3 films. the value of reflectance decreases with the increased of annealing temperature.

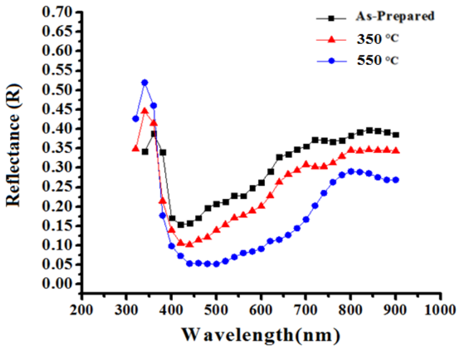

Fig. 6. Reflectance vs. wavelength of WO_3 thin with different annealing temperatures.

Fig. 7 had shown that the energy gap of thin films of WO_3 as-deposited was 3.193 eV. However, while annealed at 350 °C and 550 °C it was found 3.061 eV and 2.952 eV respectively. From deposited to higher annealing temperatures, energy gaps are increasing due to the over formation of oxygen-ion vacancies in the films during post heat treatment in a vacuum [24]. X-ray diffraction studies revealed increasing the crystallite size as temperature increases. Nevertheless, the grain's boundary density within the thin film was found to be reduced, thereafter, decreasing the scattering transporter at the grain boundary in the resultant thin films [25,26].

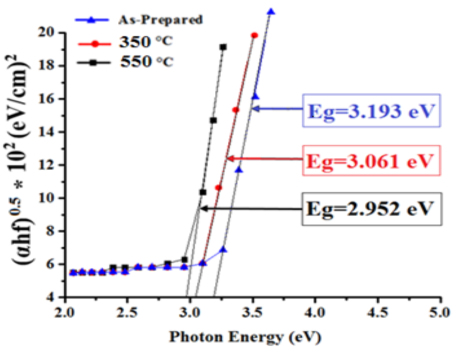

Fig. 7. Energy band gap for thin films of WO_3 with different annealing temperatures.

4. Conclusions

WO_3 films with a thickness of 250 nm were deposited on glass substrates by using electron beam evaporation deposition. It is shown that the Amorphous WO_3 films and obtained crystalline films after the annealing temperature, and all prepared films have surfaces with homogenous morphology without any crack on the surface of films before and after annealing. The growth of orientation nanocrystalline thin films enhances by the annealing temperature. The Energy band gap before annealing is (3.193 eV) and after annealing (3.061 eV) and (2.952 eV). WO_3 thin films show high transparency and make them suitable as a layer of window for solar cell applications.

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