Electron Beam Evaporated Nanostructure WO_3 Thin Films

R. Ravi Kumar, P. Jabbar Khan, D. Sampurna Rao, G. Kalpana, A. Sivasankar Reddy*

Department of Physics, Vikrama Simhapuri University College, Nellore-524324, Andhra Pradesh, India

*Corresponding Author: *akepati77@gmail.com*

Abstract: **In this study, nanostructured tungsten trioxide (WO_3) thin films were deposited on glass substrates using electron beam evaporation at room temperature and subsequently annealed at different temperatures. The films were characterized by different analytical techniques such as, X-ray diffraction, scanning electron microscopy, and UV-Vis-NIR spectrophotometry. The films annealed at a higher annealing temperature of 723K, a broad peak cantered at 24.35^o, which can be assigned to the monoclinic plane of WO_3. The microstructure of the WO_3 films changed from nanoflakes to a little lime hydrangea structure upon variation of the annealing temperature. The bandgap of the films reduced from 3.29 eV to 3.15 eV from as deposited to post-annealed films.**

Keywords: ***Thin films, Tungsten oxide, Electron beam evaporation, Nanostructure, gas sensors*.**

I. INTRODUCTION

The development of more accurate and highly sensitive gas sensors is important in various areas of industry for monitoring, and controlling the concentration of gasses. Metal oxides thin films are promising in the gas sensor electronics industry, and the efficiency of the sensors of films is attributed to size, thickness, surface area and stability. Variety of nanostructures of metal oxides, such as ZnO, SnO_2, MoO_3, In_2O_3, and WO_3 have been widely used for gas sensor devices. Among these metal oxides, WO_3 is one of the best semiconductor materials for various applications like gas sensors, electrochromic devices, optical memory, smart windows, and catalysts due to its promising electrical and optical properties [1-2]. WO_3 thin films are prepared using several methods, such as sol-gel [3] electron beam evaporation [4], resistivity heating [5], sparking method [6], sputtering [7] and pulsed laser deposition [8]. In this study, electron beam evaporation was used to prepare a novel type of WO_3 nanostructured films and subsequently annealed at different temperatures, and studied the physical properties of the films.

II. EXPERIMENTAL

WO_3 pellets were used to prepare nanostructured films on glass substrates via electron beam evaporation. Pellets were prepared using high purity (99.99%) of WO_3 powder. The distance between the evaporation source and substrate was 7 cm. The parameters maintained during the deposition of the WO_3films are listed in Table 1. The as deposited WO_3 films were post annealed at 473K, 673K and 723K in air.

Characterization of WO_3 nanostructured films

The structural properties of the films were measured using X-ray diffractometer, and the microstructure was analyzed by scanning electron microscopy (SEM). Energy dispersive spectroscopy (EDS) was used to study the chemical composition of the films. The optical properties were examined by UV-Vis-NIR double beam spectrophotometer. The thickness of all the as deposited films turned to be about 260nm.

TABLE 1:
THE PARAMETERS MAINTAINED DURING THE DEPOSITION OF THE WO_3 FILMS

S. No.	Parameters
1	Accelerating Voltage = 48 kV
2	Accelerating Current = 1.3 mA
3	Base Pressure = 3.8 x 10^{-6} mbar
4	Deposition Pressure =1 x 10^{-3} mbar
5	Deposition Time =10 min
6	Deposition Temperature = Room Temperature

III. RESULT AND DISCUSSIONS

A. Structural analysis

Fig. 1 shows the XRD images of the as deposited and annealed WO_3 films. The as-deposited WO_3 films exhibited an amorphous nature, and the amorphous nature of the WO_3 films did not change even after annealing at 673K. At low temperatures due to the low energy of tungsten oxide ions reaching the surface of the substrate, these low energy ions will prevent the crystallization of the films, consequently, the amorphous phase was obtained [9]. The films annealed at a higher annealing temperature of 723K, a broad peak centered at 24.35°, which can be assigned to the monoclinic plane of WO_3, and showed an improvement of the crystal quality. The surface morphologies of these films are expected to be different. In the literature, Yu et al. [10] observed that the WO_{3-y} films prepared by magnetron sputtering at room temperature are amorphous, no diffraction peaks can be observed. Whereas the annealed WO_{3-y} film apparently shows diffraction peaks at 2θ=23.1°, 24.4° and 34.2° which can be indexed as (002), (200) and (202) monoclinic planes, respectively.

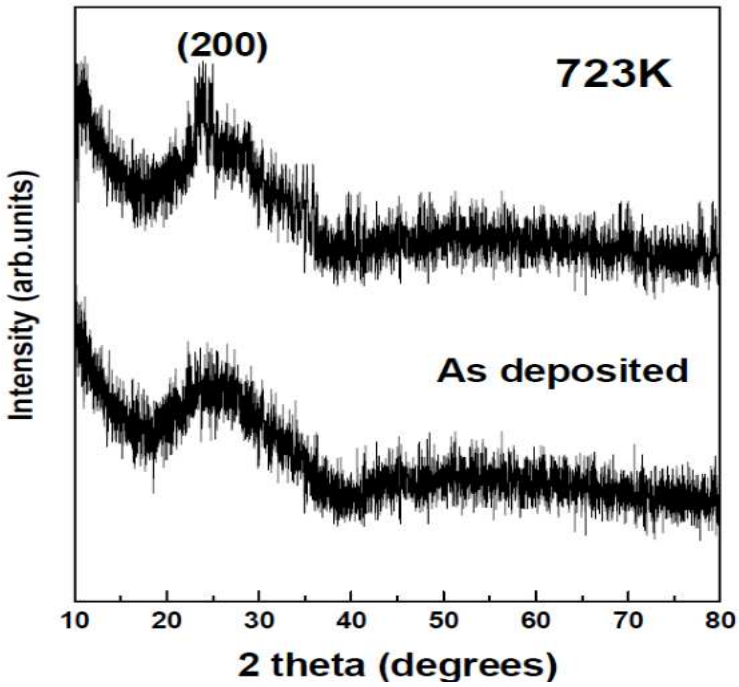

Fig.1. XRD patterns of nanostructure WO_3 films.

B. Morphology and compositional analysis

Figs. 2(a)–(d) show SEM images of the nanostructured as deposited, and annealed WO_3 films. Fig. 2(a) shows that the as deposited WO_3 films exhibited a crack free surface, and smooth and homogenous nanoflakes were uniformly distributed on the substrate. The microstructure of the films changed when the films annealed at 473K, the nanoflakes agglomerated and their size is changed. On further increasing the annealing temperature to 673K, the surface of the films exhibited little lime hydrangea structure. The nanoflakes stacked together to form the little lime hydrangea structure. To the best of our knowledge, this was the first instance of using this technique to obtain this type of nanostructure. The films were annealed at a higher temperature of 723K, the cracks are appeared on the surface of the WO_3 films. Ashok et al. [11] observed that when the films were annealed at 300^{o}C, the cracks appeared on the surface of the film and they were more visible at annealing temperature of 400^oC, which was due to the strain imposed on the layer of film during heat treatment.

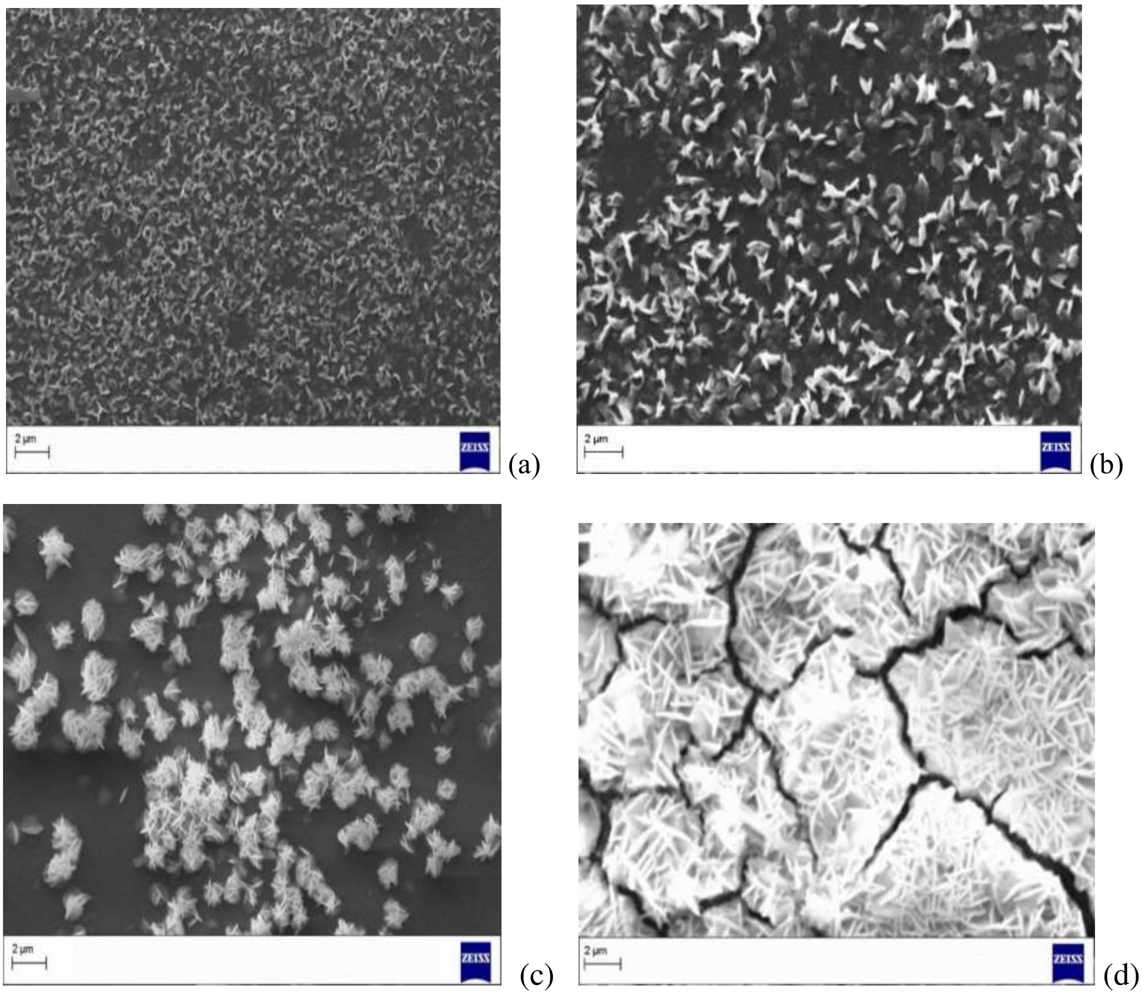

Fig.2. SEM images of nanostructure WO_3 films: (a) as deposited (b) annealed at 423K (c) annealed at 673K and (d) annealed at 723K.

The elemental compositions of the nanostructured WO_3 films are determined using EDS. The nanostructures contained only W and O, and no other impurities were observed. The atomic percentage of tungsten and oxygen of as deposited films and annealed films is listed in Table 2. When the films are annealed, the atomic percentage of tungsten is increased and the oxygen percentage is decreased, consequently, oxygen vacancies are existed.

TABLE 2.
THE ATOMIC PERCENTAGE OF TUNGSTEN AND OXYGEN OF AS DEPOSITED FILMS AND ANNEALED FILMS.

Sample	Atomic percentage of Oxygen (%)	Atomic percentage of Tungsten (%)
As deposited	**89.17**	**10.83**
Annealed at 673K	**85.80**	**14.20**

C. Optical properties

The measured transmittance spectra of as deposited and annealed WO_3 films are shown in Fig.3. The optical properties of the WO_3 thin films were investigated in the wavelength range of 300 -1200 nm. The average transmittance of the films in the visible region is around 83% for the as deposited films, and it decreased to 78% after annealing at 723K. The decrease in transmittance was due to the increase in scattering light caused by the increase of surface roughness of the films, and also the higher annealing temperatures lead to the densification of the films, thus it reduces transmittance [12]. The absorption edge of the films is shifted towards the longer wavelength region as the annealing temperatures increase, as observed in transmittance spectra.

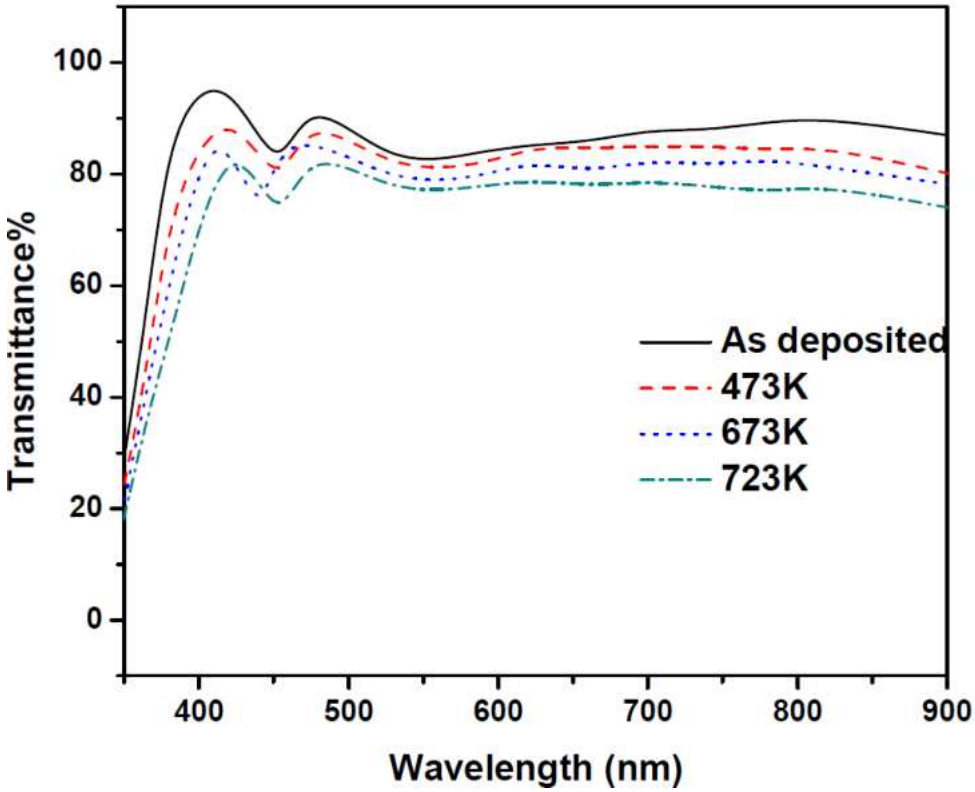

Fig.3. Optical transmittance spectrum of nanostructure WO_3 films.

The optical band gap (E_g) of the films was evaluated from the extrapolation of the linear portion of the plots of $(\alpha h\nu)^{1/2}$ versus ($h\nu$) (α is the absorption coefficient, $h\nu$ is the photon energy). Figure 4 shows the Tauc plot for nanostructure as deposited and annealed WO_3 films. The obtained band gap values are 3.29 eV, 3.24 eV, 3.18 eV and 3.15 eV for as deposited, 473K, 673K, and 723K annealed films, respectively. The larger band gap of the deposited thin films can be attributed to their amorphous nature. The bandgap of the films reduced from 3.29 eV to 3.15 eV from as deposited to post-annealed films. This decrease in the band gap with annealing temperature is due to increase in the crystallinity of films and may be correlated with the formation of oxygen vacancies [13-14]. Similar behaviour was observed by Amar et al. [15] in dc magnetron sputtered WO_3 films, and the band gap values were reduced from 3.2 to 2.7 eV with increasing the annealing temperature from as deposited to 600°C.

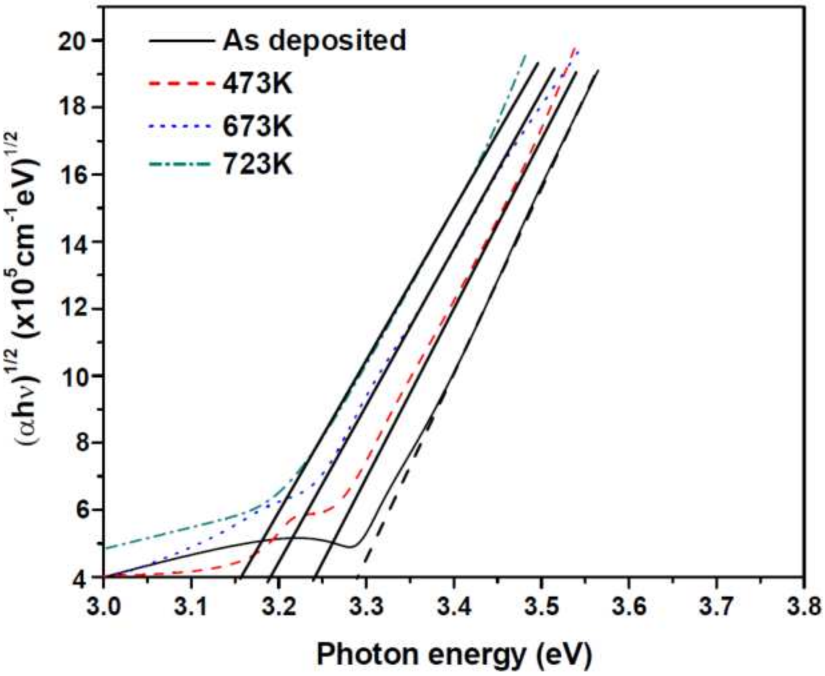

Fig.4. Plot of $(\alpha h\nu)^{1/2}$ vs ($h\nu$) of nanostructure WO_3 films.

IV. CONCLUSIONS

Nanostructured WO_3 films were prepared using the electron beam evaporation method and studied structural, chemical and optical properties of as deposited and annealed films. The as-deposited nanostructured WO_3 films were amorphous in nature. The crystallinity of the films increased after annealing the films at higher temperatures. The microstructure of the WO_3 films was highly influenced by the annealing temperature. The microstructure of the WO_3 films changed from nanoflakes to a little lime hydrangea structure upon variation of the annealing temperature. The average transmittance of the films in the visible region is around 83% for the as deposited films, and it decreased to 78% after annealing at 723K. The present obtained nanostructured WO_3 thin films are cost-effective and very useful for gas sensor applications.

REFERENCES

[1] *Roshini Xavier, Logu Thirumalaisamy, Sridharan Madhanagurusamy, Kalainathan Sivaperuman, Spray deposited pristine and Mo doped WO_3 thin films for acetaldehyde gas sensing at room temperature, Ceramics International 50, 969–976, 2024. https://doi.org/10.1016/j.ceramint.2023.10.187*

[2] *L.G. Teoh, Y.M. Hon, J. Shieh, W.H. Lai, M.H. Hon, Sensitivity properties of a novel NO_2 gas sensor based on mesoporous WO_3 thin film, Sensors and Actuators B 96, 219–225, 2003. https://doi.org/10.1016/S0925-4005(03)00528-8*

[3] *J. Zeng, S.Yan, J.Bai, Y. Zhang, G. Yang, D. Zhang, Z. Liu, X. Liang, Amorphous/ordered porous crystalline stacked WO_3 films fabricated by electrodeposition-assisted sol–gel and its application to electrochromic devices, J. Electroanalytical Chemistry 952, 117969, 2024, https://doi.org/10.1016/j.jelechem.2023.117969.*

[4] *Adilakshmi Griddaluru, Sivasankar Reddy Akepati, Electron beam evaporated gold doped tungsten oxide nanostructured films for sensor applications, Chem Phys Mater 2, 172–179, 2023. https://doi.org/10.1016/j.chphma.2022.09.003*

[5] *Fabien Sanchez, L. Marot, A. Dmitriev, R. Antunes, R. Steiner, E. Meyer, WO_3 work function enhancement induced by filamentous films deposited by resistive heating evaporation technique, J. Alloys and Compounds, 968, 171888, 2023. https://doi.org/10.1016/j.jallcom.2023.171888*

[6] *W. Thongpan,N. Jumrus, P. Tippo, T. Kumpika, N. Jhuntama, A. Panthawan, S. Rucman, E. Kantarak, W. Sroila, P. Singjai, W. Thongsuwan, External magnetic field: Enhancing electrochromic efficiency of magnetic metals composited WO_3 films prepared by sparking method, Materials Science In Semiconductor Processing 170, 107970, 2024. https://doi.org/10.1016/j.mssp.2023.107970*

[7] *Junmeng Zhang, Jianmin Lu , Panzhe Hou, Peipei Lu, Lingna Jia, Zhiyun Yang, Lihu Liu, Huiyuan Sun, Preparation of ordered nanoporous WO_3 thin films and the mechanism of large room-temperature ferromagnetism, J. European Ceramic Society, 43, 7533-7542, 2023. https://doi.org/10.1016/j.jeurceramsoc.2023.08.023*

[8] *Feng Wan, Lequn Li, Chujun Yao, Kai Jiang, Zhigao Hu, Ning Xu, Jian Sun, Jiada Wu, Plasma assisted pulsed laser deposition of WO_3 films for thermochromism, Mater. Chem. Physics, 314,128880, 2024. https://doi.org/10.1016/j.matchemphys.2024.128880*

[9] *Michał Mazura, Damian Wojcieszak, Artur Wiatrowski, Danuta Kaczmarek, Aneta Luba´ nska, Jarosław Domaradzki, Piotr Mazur, Małgorzata Kalisz, Analysis of amorphous tungsten oxide thin films deposited by magnetron sputtering for application in transparent electronics, Applied Surface Science 570, 15115, 2021. https://doi.org/10.1016/j.apsusc.2021.151151*

[10] *Hang Yu, Junji Guo, Cong Wang, Junying Zhang, Jiang Liu, Guobo Dong, Xiaolan Zhong, Xungang Diao, Essential role of oxygen vacancy in electrochromic performance and stability for WO_{3-y} films induced by atmosphere annealing, Electrochimica Acta 332, 135504, 2020. https://doi.org/10.1016/j.electacta.2019.135504*

[11] *Ashok Reddy G V, K. Naveen Kumar, Sheik Abdul Sattar, Hitha D. Shetty, Nunna Guru Prakash, R. Imran Jafri, C. Devaraja, Manjunatha B C, Kaliprasad C S, R. Premkumar, Sabah Ansar, Effect of post annealing on DC magnetron sputtered tungsten oxide (WO_3) thin films for smartwindow applications, Physica B: Condensed Matter 664, 414996, 2023. https://doi.org/10.1016/j.physb.2023.414996*

[12] *X. Sun, H. Cao, Z. Liu, J. Li, Influence of annealing temperature on microstructure and optical properties of sol–gel derived tungsten oxide films, Appl. Surf. Sci. 255, 8629–8633, 2009. https://doi.org/10.1016/j.apsusc.2009.06.042.*

[13] *A. Rougier, F. Portemer, A. Quede, M. AlMarssi, Characterization of pulsed laser deposited WO_3 thin films for electrochromic devices Applied Surface Science 153, 1, 1999. 10.1016/S0169-4332(99)00335-9*

[14] *A.A.Joraid, S.N.Alamri, Effect of annealing on structural and optical properties of WO_3 thin films prepared by electron-beam coating Physica B39, 199–205, 2007. http://dx.doi.org/10.1016/j.physb.2006.09.010*

[15] *Amar Kamal Mohamedkhair, Qasem Ahmed Drmosh, Mohammad Qamar and Zain Hassan Yamani, Tuning Structural Properties of WO_3 Thin Films for Photoelectrocatalytic Water Oxidation, Catalysts 11, 381, 2021. https://doi.org/10.3390/catal11030381*