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Oxygen Effect on Structural and Optical Properties of WO3 Films by Pulsed Laser Deposition

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ABSTRACT:

This work includes the deposition of WO_3 as a thin film on glass substrates by pulsed laser deposition method. The influence of Oxygen pressure on the structural and optical properties of tungsten trioxide films was investigated. The X-ray diffraction results show that the structure of the films changes from amorphous to crystalline at an Oxygen pressure higher than 10^{-2} mbar. The color of WO_3 films formed at Oxygen pressure of 10^{-2} mbar is translucent white and it changes to pale blue with increasing the Oxygen pressure. From UV-visible spectroscopy the distinct variations in the transmission spectra and optical energy gap of the thin films were also observed. The optical band gap of the prepared films determined at different Oxygen pressures and it is found to be 3-3.1-3.12 eV at Oxygen pressures of 10^{-2} - 2×10^{-1} -5×10^{-1} mbar respectively.

Keywords: Pulsed Laser Deposition (PLD), WO_3 thin films, Structural properties, Optical properties.

تأثير ضغط الأوكسجين على الخصائص التركيبية والبصرية لأغشية أوكسيد التنكستن بطريقة الترسيب بالليزر النبضي

الخلاصة:

يتضمن هذا العمل ترسيب أغشية أوكسيد التنكستن الرقيقة على قواعد زجاجية بأستخدام طريقة الترسيب بالليزر النبضي. تم مناقشة تأثير ضغط الأوكسجين على الخصائص التركيبية والبصرية لأغشية أوكسيد التنكستن و بينت نتائج حيود الأشعة السينية تغير تركيب الأغشية من عشوائي الى بلوري عند ضغط أوكسجين أعلى من 10^{-2} ملي بار مع تغير اللون من أبيض شفاف الى أزرق باهت. بينت أطياف النفاذية التغيرات الحاصلة لفجوة الطاقة البصرية لأغشية أوكسيد التنكستن والتي كانت قيمتها 3 - 3,1 - 3,12 إلكترون فولت عند ضغط اوكسجين 10^{-2} - 2×10^{-1} - 5×10^{-1} ملي بار على التوالي.

INTRODUCTION

Tungsten trioxide (WO_3) is one of the most interesting materials exhibiting a wide variety of novel properties particularly in thin film form. It exhibits structural transformation and sub-stoichiometric phase transition, which attract the attention to explore their potential scientific and technological applications **[1]**. WO_3 films are n-type semiconductor with wide band gaps from 2.6 to 3.4 eV **[2,3]**. Tungsten oxide (VI), also known as tungsten trioxide or tungstic anhydride, exhibits a cubic perovskite like structure based on the corner sharing of regular octahedra with the oxygen atoms at the corner and the tungsten atoms at the center of each octahedron. The crystal network is the result of alternating disposition of O and WO_2 planes normally to each main crystallographic direction. A schematic view of WO_3 crystal structure is shown in Figure (1).

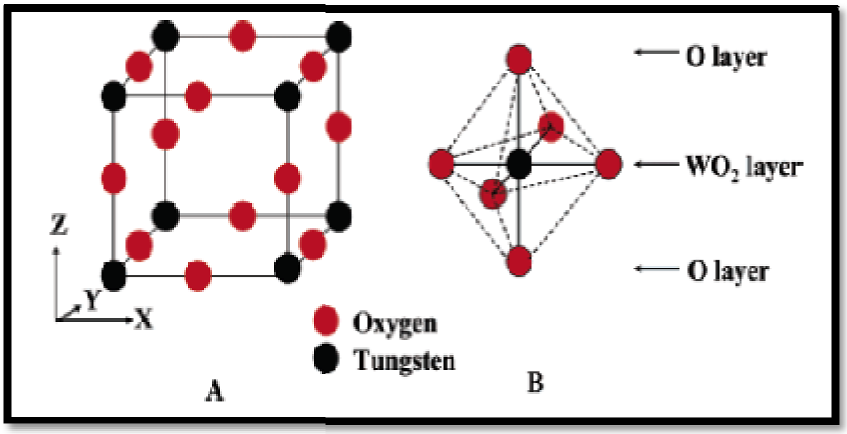

Figure (1):- The crystal structure of WO_3. (A) The ideal cubic structure of WO_3. (B) The WO_6 Octahedra in which WO_2 and O planes are alternating [4].

The symmetry of WO_3 is lowered by two distortions: tilting of WO_6 octahedra and displacement of tungsten from the center of its octahedron. These distortions result in a number of temperature dependent phases of WO_3 since it is tetragonal at temperature above 700°C, orthorhombic from 330 to 740°C, monoclinic from 17 to 330°C, and triclinic from -50 to 17°C **[5]**. Several methods have been developed for synthesis WO_3 thin films such as thermal evaporation, spray pyrolysis, sputtering, pulsed laser deposition, sol-gel and chemical vapour deposition **[6]**. Pulsed laser deposition technique is a versatile method that has been used to deposit a variety of materials under a wide range of deposition conditions such as temperature and background gas pressure. It is anticipated that the synthesis of PLD thin films under various oxygen pressure should be a promising avenue to control the nanostructure of the films and consequently optimize their gas sensing properties **[7]**.

In this study, WO_3 thin films were deposited by PLD on glass substrates at 400C temperature and laser fluence 1.2 J/cm^2.We investigated the oxygen pressure (10^2,$2*10^{-1}$,$5*10^{-1}$)mbar applied during the deposition process on the structural and morphological properties of the films.

Experimental procedure

film preparation

The deposition was carried out using a Q switched Nd:YAG laser with a second harmonic generation (SHG) at wavelength is 532nm with pulse width 7nsec and repetition rate 10Hz. The studied films were prepared from pure WO_3 targets. WO_3 films were grown by pulsed laser deposition on glass substrates at distance of 4cm from the target. During the deposition the chamber was kept at vacuum pressure of 10^{-5} mbar while the substrate temperatures (T_s) were kept at 400 °C and laser fluence at 1.2 J/cm^2.

film characterization

The crystalline structure of the films was determined by X-Ray Diffraction (XRD) measurements (Philips PW 1050, λ=1.54 A^0) using Cu k a . Transmission measurements were performed for a range 300-800 nm using UV-VIS-PV-8800 (Perkin Elemer Company) spectrophotometer. The characterizations included determination of the transmission as a function of incident photon energy and determination the value energy gap.

Result and discussion

- **Figure (2)** shows the XRD measurements results of WO_3 films formed at different Oxygen pressures of 10^{-2}, 2×10^{-1} and 5×10^{-1} mbar on glass substrates at fixed substrate temperature 400 $^\circ$C and laser fluence 1.2 J/cm^2. It can be seen that the film is amorphous at Oxygen pressure of 10^{-2} mbar as shown in Figure (2, a). Figure (2, b) shows dominant peaks on 2θ =23.1°, 2θ =29.3765°, 2θ =33.02°, 2θ =50°, 2θ =53.75° corresponding to the (001), (101), (111), (102), (112) peaks respectively with low intensity. While, Figure (2, c) shows the same dominant peaks on 2θ =23.1° which corresponding to (001) with high intensity and the other peaks on 2θ =29.3765°, 2θ =33.02°, 2θ =50°, 2θ =53.75° corresponding to the (101), (111), (102), (112) peaks respectively with low intensity. The increase in peak intensity indicates an improvement in the crystalline of the films, this leads to decrease in Full Width at Half Maximums (FWHM) of peak and increase in grain size. The color of WO_3 films formed at Oxygen pressure of 10^{-2} mbar is translucent white and it changes to pale blue with increasing the Oxygen pressure. Under Oxygen pressure of 10^{-2} mbar the films became amorphous because the pressure was so high and the plasma that was formed during the deposition was prevented from reaching the surface of the substrates and the kinetic energy was so low that the film of a poor crystallinity was formed. In the case of Oxygen pressure 2×10^{-1} mbar the interaction between the ablated species and Oxygen molecules was very weak in connection which resulted in ablated species with sufficiently high kinetic energy to form the crystalline film. When Oxygen partial pressure increased to 5×10^{-1} mbar the kinetic energy of the ablated species was presumably red**u**ced and resulted in high crystalline film.

Figure (3) shows the optical transmittance of the WO_3 films deposited on glass substrate at Oxygen pressures of 10^{-2}, 2×10^{-1} and 5×10^{-1} mbar and at fixed T_s 400 $^\circ$C and laser fluence of 1.6 J/cm^2 with average thickness 154 nm. It is found that the optical transmission of the WO_3 films at high Oxygen pressure of 5×10^{-1} mbar is higher than that at Oxygen pressures of 10^{-2} and 2×10^{-1}mbar. From all the films analyzed it is observed that the optical transmittance increased with increasing the Oxygen pressures. This behavior can be explained as follows: at lower Oxygen pressure high energy species travel through plasma and large number of tungsten ions reach at the substrate and the heavier mass of tungsten atoms compared with Oxygen molecules leads to low optical transmittance, but at higher Oxygen pressure both the Oxygen and tungsten atoms are effectively react on the substrate surface and form nearly stoichiometric films which leads to high optical transmittance.

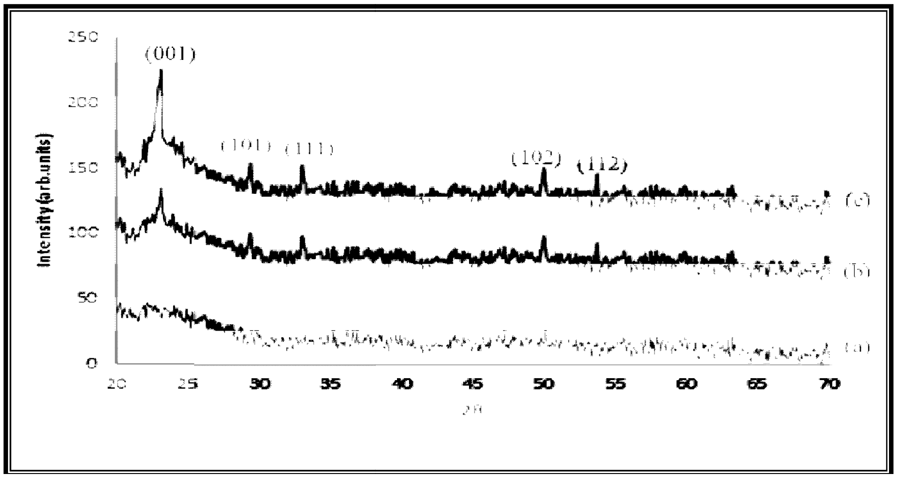

Figure (2):- XRD patterns of WO_3 thin films deposited at various Oxygen pressuresa) 10^{-2} mbar, b) 2×10^{-1} mbar, c) 5×10^{-1} mbar

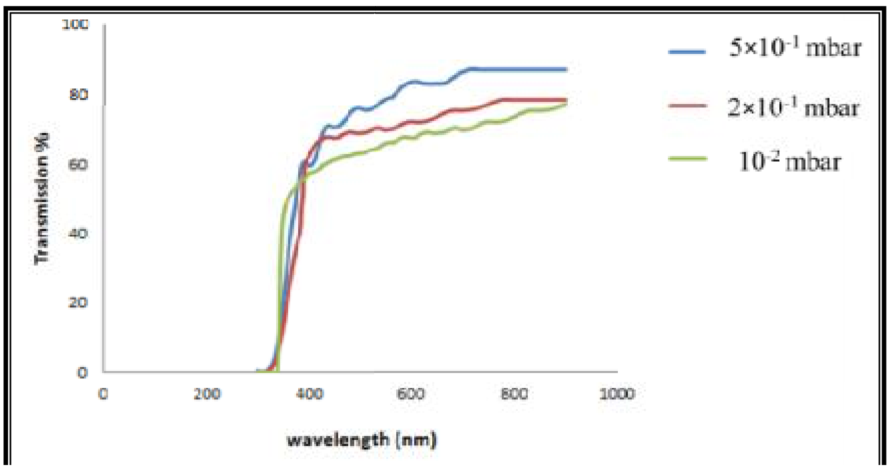

Figure (3):- UV-VIS transmittance spectra of the WO_3/glass films at different O_2 pressure

In order to calculate the band gap energies of WO_3 thin films, the plot of $(\alpha h\nu)^{1\backslash 2}$ as a function of the energy of incident radiation is shown in Figure (4). The energy band gap is obtained from intercept of the extrapolated linear part of the curve with the energy axis. Indirect band gap of the WO_3 films increases from 3 to 3.12 eV as the Oxygen pressure increases from 10^{-2} to 5×10^{-1} mbar at fixed T_s 400 °C and laser fluence 1.6 J/cm^2. This increase can be due to reduction in the Oxygen vacancies by improving the stoichiometry of the films.

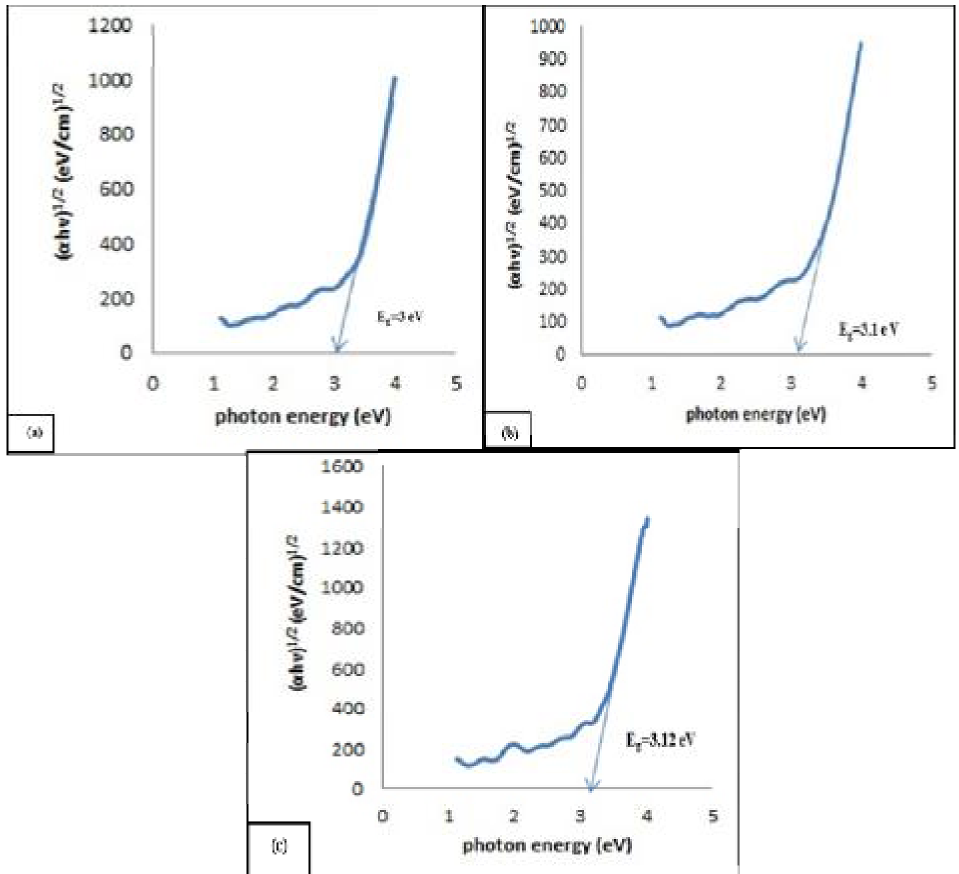

Figure (4):- A plots of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of WO_3 thin films with various oxygen pressurea) 10^{-2} mbar, b) 2×10^{-1} mbar and c) 5×10^{-1} mbar

Conclusion

WO_3 films were deposited on glass substrate by Pulsed Laser Deposition at different oxygen pressure background gas. The structural and optical properties are found to be dependent on the Oxygen pressure. When Oxygen partial pressure increased to 5×10^{-1} mbar the kinetic energy of the ablated species was presumably reduced and resulted in high crystalline film. Bleaching of the films from translucent white to pale blue with increasing Oxygen pressure from 10^{-2} mbar to 2×10^{-1} mbar and 5×10^{-1} mbar corresponds to the changes in the structure and crystalline.

The indirect band gap of the WO_3 films increases from 3 to 3.12 eV as the Oxygen pressure increases from 10^{-2} to 5×10^{-1} mbar due to reduction in the Oxygen vacancies by improving the stoichiometry of the films.

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