The Improvement of Structural and Optical Properties of WO₃ Nanoparticles by Regulation Substrate-Target Distance in Pulsed Laser Deposition Technique

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ABSTRACT
Pulsed laser deposition technique has been employed to prepare thin films of WO₃ nanoparticles on a glass substrate at 400K under vacuum (1 mbar) by the increasing of the substrate-target distance in the range of about (0.5, 1.5, 2.5 and 3.5 cm). X-Ray diffraction (XRD), Scanning electron microscopy (SEM), Atomic force microscopy (AFM) and UV-Visible investigations have been observed the effect of substrate-target distance on the structural and optical properties of WO₃ nanoparticles thin films. Calculations of the transmittance data for all films were given when increasing the distance between the target and substrate in the range (0.5, 1.5, 2.5, and 3.5 cm), respectively.

KEYWORDS: Pulsed laser deposition; optical properties; tungsten oxide; absorbance; gas sensor.

INTRODUCTION
Tungsten oxide (WO₃) is a semiconductor metallic oxide with a bandgap of (2.6–3.0 eV), which has been extensively studied because of various distinctive properties, such as electrochromism, photochromism, gas sensing, thermoelectric and catalytic properties [1,2]. It has potential applications in smart windows, electronic information displays, electrochromic devices, gas sensors and photocatalysts, photovoltaic devices, and photoelectrochemical devices [3]. With a very high work function of about 6.2 eV and high transparency in the visible region. Tungsten oxide has been recently applied in hybrid organic–inorganic optoelectronic devices as efficient hole (for WO₃) and electron (for WO₃-X) injection/transport layer [4, 5]. So far, various deposition techniques have been developed to prepare WO₃ films with different morphologies, crystallinity and structure, such as chemical vapor deposition [6,7], pulsed laser deposition [8], spray pyrolysis [9], electrodeposition [10], spin coating [11], sol-gel methods [12], sputtering [13], and the evaporation technique [14]. Among those methods, the pulse laser deposition technique has been considered largely for the growth of device quality films, and is promising in preparing WO₃ films over the classical deposition methods due to its several advantages, including low deposition temperature, good adhesion to the substrate, reproducibility and controllability of stoichiometry and crystal structure, and the easy deposition of alloys and compounds of materials with different vapor pressures. The microstructure, composition, morphology and physical properties of the several material films deposited by PLD strongly depending on the synthesis process and the
deposition conditions, e.g., substrate temperature and power density [15, 16]. Precisely stoichiometric tungsten oxide thin films have been synthesized utilizing pulsed laser deposition in a few published papers [17, 18]. However, there are few reports on plasma behavior in various substrate positions. In the present study will be focusing on the influence of substrate-target distance \( D_{st} \) on the structural and optical properties of the WO\(_3\)NPs thin films prepared by the pulsed laser deposition technique.

**EXPERIMENTAL PART**

The ceramic WO\(_3\) target used is a pellet with dimensions (2*0.3 cm), density (3.66 g/cm\(^3\)), and purity (99.99%). It is produced by pressing squeeze at (13 ton) and sintering WO\(_3\) powder under vacuum at 400K for 3hrs. It is a suitable target for PLD since it is dense and flat, enabling uniform energy transfer to its surface and the absence of voids keeps large particles being ejected from the surface. WO\(_3\) NPs films were prepared by pulsed laser deposition system of WO\(_3\) pellet fixed to a target holder located at different locations and parallel to the substrate surface. The PLD was carried out by using a Q- switched ND: YAG laser with wavelength (1064 nm), number shots of laser (1000), the substrate-target distances \( D_{st} \) are (0.5, 1.5, 2.5, 3.5 cm), laser flounce (5.57 J/cm\(^2\)) and spot diameter (d=3mm) at an angle of (45\(^o\)). The repetition rate of the laser beam was (5 Hz). The target and substrate were rotated at (10 and 6 rpm) respectively, by using a DC motor to avoid the drilling effect. The chamber of substrate and target holder evacuated to 1*10\(^{-3}\) mbar and to 1 mbar by exposing oxygen gas [19], as shown in Figure 1.

**RESULTS AND DISCUSSION**

**Structural studies**

The effect of distance between substrate- target on crystal structure and orientation of all the WO\(_3\)NPs thin film by XRD patterns are investigated. In the Figure 2 at different \( D_{st} \), it can be indexed to the polycrystalline structure compared to JCPDS card no. 00.32.1395 monoclinic (\( a=7.309, b=7.522, c=7.678 \)). The increase in the \( D_{st} \) in the range (0.5, 1.5, 2.5 and 3.5 cm) lead to preferential orientation ((\( \bar{1}12 \)), (\( \bar{2}02 \)), (\( \bar{1}22 \)), (002), (200), (220), (122), (311)), (021), (201), (1\( \bar{1}2 \)), (022), (202), (1\( \bar{2}2 \)), (222) and (121)) diffraction peaks, respectively, as shown in Figure 2.

**Figure 1.** The schematic of the pulsed laser deposition technique [19].

**Figure 2.** X-ray diffraction of WO\(_3\) NPs thin films at the \( D_{st} \) (0.5, 1.5, 2.5 and 3.5 cm).

**Figure 3.** X-ray diffraction dominate peak of WO\(_3\) NPs at the \( D_{st} \) (0.5, 1.5, 2.5 and 3.5 cm).
The intensity of (1̅21) diffraction peak decreases with increases of D_{s-t} by 0.5, 1.5, 2.5 and 3.5 cm giving rise up decrease in the crystallite size of about 85.95, 78.63, 39.76 and 30.94 nm, respectively, due to the decrease in the thickness of WO₃ NPs thin films. Agglomerations decrease in the form of nanoparticles were observed by SEM and average particle size distribution (D) images when the distance between the target and the substrate was increased in the range (0.5, 1.5, 2.5 and 3.5 cm) to be (163, 119, 112 and 83 nm), as shown in Figure 4: a, b, c and d, respectively.

Moreover, the particle flux density also increases due to the plume expansion. These high-density laser-ablated particles fast showered onto the substrate. Further, the re-sputtering of deposited material from the film surface on the shot to the shot basis of the laser beam is increased at a large target–substrate distance due to the increases in kinetic energy of the WO₃ atom [20].

The AFM images have been focused on the effect of D_{s-t} on the surface roughness of WO₃ NPs thin films, as shown in Figure 5. When the distances between the target and the substrate are increased, the surface roughness (Sa) and RMS (Sq) of WO₃ NPs thin films definitely increase, as shown in the Table 1. The increase of D_{s-t} leads to the increase of hemispherical expansion of the laser-induced plasma which in turn leads to an increase in the surface roughness when the substrate area at a large distance is exposed to a uniform plasma plume.

Optical studies

The dependence of the optical properties of WO₃ NPs thin films on the D_{s-t} was investigated by transmittance values. The fall of the light beam on the films causes an increase or decrease scattering of photons, thus affecting the values of the transmittance and absorbance of the prepared films, as shown in Figure 6. Demonstrates the optical transmission spectra of WO₃ thin films prepared at different distances between the substrate and target that the increasing of these distances from (0.5 - 3.5 cm) lead to an increase in the transmittance and reach a maximum of 78% at the distance 3.5 cm, which shows the uniform of the prepared films and these indicate to the reduction in surface roughness is due to plume expansion [21]. The optical absorption coefficient of these films was evaluated using the relation, [22]:

\[ \alpha = \frac{1}{t} \ln \left( \frac{T}{(1 - R)^2} \right) \]  

![Figure 4: SEM and size distribution (D) images of WO₃ NPs: a), b), c) and d) at the D_{s-t} (0.5, 1.5, 2.5 and 3.5 cm), respectively.](image)

![Figure 5: AFM images of WO₃ NPs thin films at the D_{s-t}: a) 0.5, b) 1.5, c) 2.5 and d) 3.5 cm.](image)

Table 1. The roughness (Sa) and RMS (Sq) of WO₃ NPs thin films at D_{s-t} (0.5, 1.5, 2.5 and 3.5 cm).

<table>
<thead>
<tr>
<th>Distance(cm)</th>
<th>Roughness(sa) nm</th>
<th>RMS (sq) nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>7.45</td>
<td>9.19</td>
</tr>
<tr>
<td>1.5</td>
<td>13.4</td>
<td>17.1</td>
</tr>
<tr>
<td>2.5</td>
<td>29.4</td>
<td>38.1</td>
</tr>
<tr>
<td>3.5</td>
<td>69.2</td>
<td>88.9</td>
</tr>
</tbody>
</table>

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Where $T$ is the transmittance, $R$ is the reflectance and $t$ is the film thicknesses which are (153, 140, 113 and 103 nm) at the $D_{s-t}$ (0.5, 1.5, 2.5 and 3.5 cm), respectively.

Figure 6. The transmittances of WO$_3$ NPs thin films at the distances (0.5, 1.5, 2.5 and 3.5 cm).

The optical absorption coefficient of WO$_3$ NPs thin films at the fundamental absorption edge was found to be exponentially dependent on the photon energy such that the increase of distances leads to a decrease in the values of the absorption coefficient as shown in Figure 7. The exponential dependence of the optical absorption coefficient may arise from the electronic transitions between localized states, which have tailed off in the band gap.

Figure 7. The absorption coefficient of WO$_3$ NPs films at the distance at (0.5, 1.5, 2.5 and 3.5 cm).

For incident photon energy greater than the band gap and above the exponential, the optical absorption follows a power law [23, 24]:

$$(ah\nu) = \beta(h\nu - E_g)^n$$  \hspace{1cm} (2)

Where $h\nu$ is the incident photon energy, $\beta$ is the edge with parameter and $n$ is an exponent, $E_g$ is the optical bandgap, and $\alpha$ is the absorption coefficient. The exponent $n$ determines the type of electronic transitions causing the absorption and takes the values 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively [25,26]. The maximum values of absorbance spectra in Figure 8 at wavelengths shorter than 400 nm decrease when the distances between the substrate and target increases, as a result of the reduction of surface roughness.

Figure 8. The absorbance spectra of WO$_3$NPs thin films at the distances (0.5, 1.5, 2.5 and 3.5 cm).

Thus, the optical band gap of WO$_3$ NPs thin films deposited at different distances determined by plotting $(ah\nu)^{1/2}$ versus the incident photon energy $(h\nu)$, as shown in Figure 9.

Figure 9. Energy gap ($E_g$) of WO$_3$ NPs thin films at the distances (1.5, 2.5 and 3.5 cm).

The increases in the values of energy bandgap in Figure 9 explain the effect of the increase in the substrate-target distance and which leads to a decrease in the grain size of WO$_3$ NPs thin films according to the quantum confinement effect. Decreasing the particle size of the prepared WO$_3$ thin films leads to an increase in the surface reaction of the films [27].
CONCLUSIONS
The regulation of substrate-target distance gives several indications when to prepare WO$_3$ NPs thin films. The optimum substrate-target distance is 2.5 cm such that the absorbance at the maximum value in the UV region gives the possibilities to use films as window device applications. At the distances of 0.5 and 1.5 cm all the UV-Visible spectrum absorbed in this region, so it can be used for solar cell applications. Also, at the distance 3.5 cm, the prepared films of WO$_3$ NPs can be employed in the field of gas sensors, due to the high surface roughness.

ACKNOWLEDGMENT
This work was done with the possibilities available in the thin film laboratory of the Physics Department at the Faculty of Science, Mustansiriya University, Baghdad, Iraq.

REFERENCES