Tuning Structural and Optical Properties of WO₃ NPs Thin Films by the Fluency of Laser Pulses

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ABSTRACT
In this paper, tungsten oxide thin films were synthesized successfully by the laser pulse deposition (PLD) method using a pulsed laser (ND-YAG) and wavelength (1064 nm) on a glass substrate at different laser fluencies. The effect of increasing laser fluency on the optical and structural properties of WO₃ nanoparticle thin films were investigated by UV-Visible spectrophotometer, X-Ray diffraction (XRD), atomic force microscope (AFM) and Scanning Electron Microscope (SEM). X-Ray measurements for all samples of WO₃ NPs thin films have shown that by increasing the laser fluencies from 5.175 to 6.369 J/cm², the intensity of the (2 0 1) diffraction peak increases due to the film continuing to grow with increased crystallization.

KEYWORDS: WO₃; Thin films; pulsed laser deposition; vacuum; nanoparticles.

INTRODUCTION
One of the semiconductor metal oxides is tungsten oxide WO₃, which has an energy gap ranging from 2.6–3.0 eV, due to its unique features, including electrochromism, photochromism, gas sensing, thermoelectric, and catalytic capabilities; it has been widely applications [1–7]. Smart windows, electronic information displays, electrochromic devices, gas sensors and photocatalysts, photovoltaic devices, and photo-electrochemical devices are all possible uses. [8–12]. Tungsten oxide has lately been used as an efficient hole (for WO₃) and electron (for WO₃ X) injection/transport layer in hybrid organic–inorganic optoelectronic devices due to its high work function of roughly 6.2 eV and great transparency in the visible region [13, 14]. Sintering the W₁₈O₄₄ nanorod film yielded WO₃ nanorods, which were used as photoelectrodes in dye-sensitized solar cells [15]. Ramgir et al., have revealed that modifying WO₃ films with CuO improves their H₂S sensing characteristics. [16]. Because of numerous configurations, such as triclinic [17], orthorhombic [18], monoclinic [19], and oxygen deficient tungsten oxide structural changes, tungsten oxide is a difficult material in terms of crystal structure and thermal stability [20]. The typical WO₃ crystal structure is a cubic ReO₃ structure with an octahedral alignment of oxygen atoms enclosing the action, and the polymorphs of WO₃ are aberrations from the cubic structure [21]. As a result, the WO₃ structure is comprised of a three-dimensional lattice of WO₆ octahedral corner sharing. For various applications, unique compositions and structures of WO₃ coatings are commonly preferred. Amorphous WO₃ films with high coloring efficiency and quick coloration/bleaching kinetics are commonly employed in monitors and color memory chips, but polycrystalline WO₃ films exhibiting strong gas sensors sensitivities can be used as ambient gas sensors. Zhang et al. developed a WO₃ reactive film-based gas sensor with a monoclinic phase structure that demonstrated a greater sensitivity and much more selective identification of NO₂ at ambient temperature when illuminated by visible light. [22]. Diverse deposition processes, like as chemical vapor deposition, have already been established thus far to create WO₃ films with distinct properties, crystallinity and structure [23, 24], preparation by laser, spray coating, electro-synthesis, spin deposition, sol–gel techniques, flashing, heat deposition and degradation of WO₃ layers [25-37]. Within these techniques, pulse laser
deposition has indeed been largely regarded for the expansion of handset films, and it is encouraging in depositing WO$_3$ layers over traditional coating methods number of advantages, such as low preparation temperature, better wet to the substrate, reversibility and predictability of stoichiometry and crystal composition, and the simple synthesis of composite materials and mixtures of materials with various vapor pressures. As a result, the PLD manufacturing method is well suited for electrochromism technologies based on the synthesized WO$_3$ electrochromic layer. The synthesizing processes and deposition circumstances, such as substrate temperature and fluence density, have a significant impact on the microstructure, constitution, shape, and physical characteristics of WO$_3$ thin films by laser pulses. The current research focuses on the depositing of WO$_3$ layers on glass substrates using laser pulses, as well as a comprehensive examination of the impact of various laser energies on the structural, topological, and spectroscopy aspects of the formed WO$_3$ layers.

EXPERIMENTAL PROCEDURE
In this work, WO$_3$ thin films were fabricated under different conditions using powder with purity of 99.99%. The powder was pressed as pellet with 1.5 and 0.3 cm diameter and thickness, respectively. At a pressure of 7 ton, the hydraulic position was employed for 15 minutes. The tungsten oxide layer was deposited on glass substrates (1.5×1.5 cm). These glass substrates were cleaned with distilled water to eliminate any leftover dust and filth from their surfaces. After that, an ultrasonic device was used to wash the glass substrates in alcohol for 5 minutes to remove certain oxides and grease. The air from shoveling was utilized to dry the glass substrates in this technique. Lastly, light paper has been used to wash the plates before using a Nd:Yag laser to prepare films at room temperature using the laser pulses technique with wavelengths of 1064 nm and fluences of 5.175, 5.573, 5.97, and 6.369 J/cm$^2$. The repetition rate was 5Hz, and it took place at a 45o angle on the pellet surface. Under low pressure (1×10$^{-3}$ mbar) and oxygen (1mbar), the spacing between substrate and WO$_3$ pellet is 1.5 cm [38], as seen in Figure 1.

RESULTS AND DISCUSSION
Structural studies
The effect of increased laser fluencies on crystal structure and orientation of all the WO$_3$ NPs thin films through X-ray examinations can be observed. Since this increase has an effect that 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), as shown in Figure 2.

Figure 1. The pulsed laser deposition process is depicted schematically [38].

Figure 2. X-ray diffraction of WO$_3$ NPs thin films at different laser fluencies 5.175, 5.573, 5.97 and 6.369 J/cm$^2$.

WO$_3$ NPs thin films have been showing that the sharp peak at $2\theta = 26.827$ correspond to (201) plane and exhibited preferential orientation along (001) plane of all the samples, as shown in Figure 3.
The increase and decrease in the broadness of $(201)$ diffraction peak by increasing the laser fluencies from $5.175$ to $5.573 \text{ J/cm}^2$ are due to the decrease in the crystal size from $85.09$ to $64.7$ nm and from $5.97$ to $6.369 \text{ J/cm}^2$ due to the increase in the crystal size from $95.7$ to $97.2$ nm, respectively. By increasing the laser fluencies from $5.175$ to $5.573 \text{ J/cm}^2$ the intensity of $(201)$ diffraction peak increases due to the film continuing to grow with increased crystallization [39].

As the laser fluencies continue to increase from $5.573$ to $6.369 \text{ J/cm}^2$, we notice a decrease in the intensity of the $(201)$ diffraction peak due to the decreases in the thickness of $\text{WO}_3$ NPs thin films and decrease in the adsorbed atoms on the substrate surface [40].

SEM images show a clear effect of increasing the laser fluencies in the range $5.175$, $5.573$, $5.97$ and $6.369 \text{ J/cm}^2$ on the prepared films through the interspaces between the nanoparticles, as shown in Figure 4. The increased laser fluencies provide sufficient heat for the particles to cause them to coalesce and aggregate, thus reducing the interfacial distances between them [41].

It is also evident from the SEM images that the particle size of $\text{WO}_3$ NPs decreased and increased as $37.96$, $34.5$, $67.26$, and $87.9$ nm with the increase in the laser fluency of $5.175$, $5.573$, $5.97$, and $6.369$, respectively, as shown in Figure 4, a; b; c; and d.

EDX measurements of the $\text{WO}_3$ NPs were accomplished to monitor the increase in the concentration of the ratio O/W, shown with the SEM images in the Figure 4.

As laser fluency increases, the ratio of O/W also increases as a result of oxidation processes.

Whereas the increase in the percentage of oxygen indicates the atom's tendency to gain an electron to reach a stable state, as shown in Figure 5.

The three-dimensional AFM micrograph and granularity of the $\text{WO}_3$ NPs thin films as deposition. By investigating AFM, we note that the deposited thin films are in the form of small connected crystal granules distributed regularly without cracks, as shown in the Figure 6, a; b; c and d. As the laser fluencies were increased from $5.175$ to $6.369 \text{ J/cm}^2$, the roughness and RMS of $\text{WO}_3$NPs thin films increased, as shown in Table 1.

Figure 3. X-ray diffraction in the $(201)$ plane of $\text{WO}_3$ NPs thin films at different laser fluencies $5.175$, $5.573$, $5.97$ and $6.369 \text{ J/cm}^2$.

Figure 4. SEM and EDS images with particle size of $\text{WO}_3$ NPs: a, b, c and d at the fluencies $5.175$, $5.573$, $5.97$ and $6.369 \text{ J/cm}^2$, respectively.
This is because the removal of atoms from the target increases as the fluencies of laser energy increase, resulting in more melting and fusing [42]. In addition, the fluencies of high laser energies improve the coalescence process of neighboring atoms in the crystal [41].

**Optical studies**

The absorbance intensities of WO₃ NPs thin films were recorded by spectrophotometer within the wavelength ranges 300-900 nm. The absorbance spectra of WO₃ NPs exhibit increased behavior with increasing all laser fluencies for the wavelengths above 400 nm, as shown in the Figure 7.

For the absorbance spectra in the range less than 400 nm, different behavior can be observed where all the absorbance values increase with increasing laser fluencies to reach the maximum values at wavelength 305 nm except for laser fluency 6.369 J/cm² which is at wavelength 315 nm to give the red shift, as shown in the Figure 8.

This behavior is probably ascribed to the increase of particle sizes and surface roughness with increasing laser fluencies [43].
For incident photon energy greater than the band gap and above the exponential, the optical absorption follows a power law [44]:

\[ (a\nu) = \beta (\nu - E_g)^n \]  

(1)

Where \( \nu \) 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.

Figure 9 depicts the direct optical energy gap of WO3 NPs for various laser fluencies. When the laser fluencies were increased from 5.175 to 5.57 J/cm², the energy gap was raised because of increased local levels within the energy band gap due to enhanced recrystallization of the thin film and a change in the crystal phase that reduced crystallite size [45].

Continuously increasing the fluency of the laser from 5.57 to 6.36 J/cm² decreases the energy bandgap due to local reduction within the energy bandgap due to improved crystallization as well as increased crystal size [46], as shown in Figure 9.

Figure 9. Energy gap (\( E_g \)) of WO3 NPs thin films at the fluencies 5.175, 5.573, 5.97 and 6.369 J/cm².

CONCLUSIONS

In this study, the mechanism of increasing the laser fluency made prepare thin films of WO3 NPs with high crystalline at 5.573 J/cm² of the diffraction peak (201). This increase also leads to the stability of the prepared films as a result of oxidation processes by increasing the ratio O/W. As the laser fluencies were increased from 5.175 to 6.369 J/cm², the roughness and RMS of WO3NPs thin films increased. This increases the possibility of employing the prepared films in the field of manufacturing gas sensors.

The increase of laser fluencies from 5.175 to 5.97 J/cm² led to reaching the values of absorbance maxima at wavelengths of 305 nm except for laser fluency 6.369 J/cm² which is at wavelength 315 nm to give the red-shift. The absence of a shift in the maximum values of the absorbance at the fluencies from 5.175 to 5.573 J/cm² enables us to use the prepared films in the applications of photodetectors. Increasing the fluency of laser from 5.175 to 5.573 J/cm² lead to an increase in the optical energy bandgap this leads to blue shift. Otherwise increasing from 5.573 to 6.369 J/cm² gave the red shift.

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REFERENCES


https://doi.org/10.1016/j.apsusc.2019.144063


https://doi.org/10.1016/j.snb.2021.130135


https://doi.org/10.1021/acssensors.0c00113


https://doi.org/10.3390/s20123473


https://doi.org/10.1016/j.matlet.2019.06.037


https://doi.org/10.1016/j.jallcom.2019.153194


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