Enhancing electrical and thermoelectrical properties of WO$_3$ thin films by spray pyrolysis technique

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Abstract. Tungsten trioxide WO$_3$ thin films have been deposited on glass substrates by spray pyrolysis technique with three different rates $R_1 = 1$ ml/min (sample A$_1$), $R_2 = 3$ ml/min (sample A$_2$) and $R_3 = 7$ ml/min (sample A$_3$). We have then annealed all samples for 2 h at 500 °C in air. Structural, morphological, optical and electrical properties of WO$_3$ thin films are investigated in detail. According to the FESEM images, all layers are formed in various circular strings with different diameters. The diameter of each strain decreases when the deposition rate increases. The XRD structural analysis indicates that before annealing, except the lowest deposition rate sample $R_1$ with a polycrystalline nature and mixed tetragonal and hexagonal phases, other samples are grown in an amorphous phase. After annealing, sample A$_2$ (with rate $R_2 = 3$ ml/min) remains in an amorphous phase, while samples A$_1$ and A$_3$ (with the corresponding rates $R_1 = 1$ ml/min and $R_3 = 7$ ml/min respectively) are polycrystalline. Moreover, from UV-Vis. spectra analysis we found that by increasing spray rate the band gap of the layers monotonically decreases. This phenomenon is the result of attenuation of the quantum confined effect. The thermoelectric properties confirm being $n$-type conductivity of the layers, also variation in the current-voltage characteristic is in accordance with the oxygen vacancies sites. We found that the sample A$_3$ with the highest rate has lowest resistivity.

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1. Introduction

Semiconductor characterization is a key enabler in the development of semiconducting technology. Among the intermediate metals oxide, tungsten trioxide WO$_3$ as a $n$-type semiconductor with large indirect band gap ($\approx 2.4 - 3.7$ eV) is extensively studied due to its optoelectronic properties in possible applications such as smart windows [1–6], front contacts in photovoltaic solar cells [7–9], variable-reflectance mirrors, and etc. [10,11].
Due to excellent electrochemical stability, thin films of the material WO$_3$ have been widely used as photo-anodes in photo-electrochemical cells. Moreover, the intrinsic reaction mechanism of WO$_3$/electrolyte interfaces in various electrolytes has been reported in previous studies [12–15]. Heretofore, WO$_3$ thin films have been grown by different techniques such as physical vapor deposition (PVD), chemical vapor deposition (CVD) [16], evaporation [17–19], electrodeposition [20], sputtering [21,22], sol-gel deposition [19,23] and spray pyrolysis technique [24–27]. The latter technique presents many advantages such as: (i) short time deposition, (ii) simple technology, (iii) low-cost, (iv) lake of need to vacuum, and (v) large scale area of thin film production.

Many researchers have devoted themselves to study WO$_3$ thin films prepared under different spray rates [20] and the effect of annealing temperature on the structural, surface morphological and optical properties of WO$_3$ films [17,21,23,28,29]. This article presents the influence of the deposition rate and annealing process on various physical properties of WO$_3$ thin films grown by spray pyrolysis method.

2. Experimental Setup

WO$_3$ thin films were deposited on glass substrate by spray pyrolysis method. The precursor solution was 50 ml ammonium tungstate [(NH$_4$)$_2$WO$_4$] made of pure WO$_3$ powder (99.9%, Merck) in ammonia and distilled water which are deposited with three different spray rates $R_1 = 1$ mil/min, $R_2 = 3$ mil/min and $R_3 = 7$ mil/min, respectively. Other deposition parameters such as spray solution volume, nozzle to substrate distance and substrate temperature were maintained at, respectively, 50 ml, 30 cm and 400 $^\circ$C. Before deposition, all substrates were washed with soap and water, then were placed in a container including acetone and distilled water then set in an ultrasonic machine for 16 minutes. Ultimately, all three samples were washed with twice ionized water, and were dried with nitrogen gas.

The preparation of transparent WO$_3$ thin films was carried out in two steps. At the first step we sprayed a solution of ammonium tungstate [(NH$_4$)$_2$WO$_4$] on glass substrate. The coating solution was sprayed on preheated substrates (400 $^\circ$C) by using air (as a gas conveyor). The experimental setup used for the preparation of spray-deposited films has already been described in Ref. [15]. The obtained films are completely transparent, amorphous, homogeneous and well-adhere to the substrate. At the second step annealing of the sprayed films in free air was carried out. In order to obtain WO$_3$ films with a proper crystallinity, the annealing temperature was fixed at 500 $^\circ$C and the annealing time at 2 h. The obtained films are transparent with a slightly yellowish color. We expect the WO$_3$ thin layer deposition follows the chemical reactions according to Eqs. (1) [30]:

\[
\begin{align*}
\text{WO}_3 + 2\text{NH}_3 + \text{H}_2\text{O} &\rightarrow (\text{NH}_4)_2\text{WO}_4, \\
(\text{NH}_4)_2\text{WO}_4 &\rightarrow \text{WO}_3 + \text{H}_2\text{O} + 2\text{NH}_3.
\end{align*}
\]

In the present work, the morphologies of the samples are investigated using field emission scanning electron microscope (FESEM S.4160 model). The structural characterizations of films are carried out by X-ray diffraction with CuK$_\alpha$ radiation, wavelength 1.54 Å, with 2$\theta$ angle range of 10 – 70 degree (XRD; Bruker AXS). In order to study of optical properties, photoluminescence (PL) spectra of samples are measured at room temperature by the fluorescence spectrophotometer (Cary Eclipse fluorescence spectrophotometer model), which contains xenon lamp arc with exciting
wavelength of 253 nm. In order to measure the transmittance spectra of the studied samples we used UV–Vis. spectrophotometer (Shimadzu UV–Vis. 1800) within the wavelength range of 300 – 1100 nm. For thickness measurement the Taylor/Hobson profile meter with accuracy of +20 nm was applied.

3. Results and discussions

3.1. Non-annealed characterization of the WO$_3$ layers

3.1.1. Surface morphology: Field Effect Scanning electron microscopy (FESEM) analysis Figure 1 shows the FESEM images of the grown samples A$_1$, A$_2$ and A$_3$ with the corresponding rates R$_1$, R$_2$ and R$_3$ on two scales 20 µm and 5 µm. It is clear from this figure that all layers indicate the presence of tungsten filaments formed in various circular strings with different diameters. Their diameters decrease as the deposition rate increases.

3.1.2. Structural properties The XRD patterns of the studied layers are shown in Fig. 2. By inspecting this figure one can see that the lowest deposition rate sample R$_1$ has a polycrystalline nature, as well as, has both of the tetragonal (with lattice parameters $a = b = 23.33$ Å and $c = 3.79$ Å) and hexagonal phases (with lattice parameters $a = b = 7.29$ Å and $c = 3.89$ Å (JCPDS 05-0392)). Other samples (R$_2$ and R$_3$) are grown in amorphous phase.

Using the theoretical analysis associated to the crystalline structure one can deduce the distance between the adjacent planes and the crystallite size in the grown samples. The distance between crystal planes $d(hkl)$ can be obtained using Bragg’s
Enhancing electrical and thermoelectrical properties of WO₃

Figure 2. The XRD spectra of studied WO₃ thin layers. The sample A₁ possessing the lowest deposition rate R₁ has been grown with a polycrystalline nature in a mixed tetragonal and hexagonal phases. Other samples were grown in amorphous phase.

Formula
\[ d_{(hkl)} = \frac{\lambda}{2 \sin \theta}. \]  

Accordingly, the crystallite size corresponding to a given Bragg angle \( \theta \), could be found using Scherer's equation
\[ D = 0.9 \frac{\lambda}{\beta \cos \theta}, \]

where \( \lambda \) is the X-ray wavelength and \( \beta \) is the full width at half maximum (FWHM) of the given peak. By using equation (3), for \((3 1 0)\) peak positioned at the Bragg angle of \( \theta \approx 12^\circ \) the crystallite size of sample A₁ is around 16 nm. Also, dislocation density \( \delta \) of the sample can be given by \( \delta = 1/D^2 \) [31] (for more information see table 1).

3.1.3. Electric and thermoelectric properties Figure 3 shows the current–voltage curves of pure and Li-doped samples. As it is evident from this figure, all samples have an ohmic behavior, and the resistivity of the layers is reduced upon increasing the spray rate. The sheet resistance can be defined by the ratio \( R_{sh} = \frac{V}{I} \) and resistivity of the layers is given by the relation \( \rho = R_{sh}t \) where \( t \) is the thickness of the layer. Here, we have measured these quantities in \( 1 \times 1 \) cm² of samples. The resistivity variations of these layers are illustrated in Fig. 4(a). Regarding the results plotted in this figure, the resistivity of the films sharply decrease from 71.3 Ω·cm in R₁ to approximately 18.8 Ω·cm in R₃ which is the highest spray rate. These changes in

Table 1. Crystallite size, distance between the crystal planes, strain and the density of dislocation of planes in the studied sample A₁.

| Sample | D(nm) | \( d_{hkl}(\text{nm}) \) | \( \varepsilon \times 10^{-3} \) | \( \delta \times 10^{-3} \)(nm)^{-2} |
|--------|-------|-----------------|-----------------|-----------------|
| A₁     | 15.93 | 0.733           | 2.17            | 3.9             |
enhancing electrical and thermoelectrical properties of WO$_3$

Figure 3. $I - V$ curves of the three studied samples. Ohmic behavior of the samples are clear in this pattern.

conductivity of layers can be the result of increasing the density of oxygen vacancies in the network-layer when the spray rate increases.

To find out the type of conductivity (n or p) of the samples under consideration, we used Seebeck effect relation $V = S \Delta T$ [32] in which $S$ is the Seebeck coefficient, $V$ is the thermoelectric power and $\Delta T$ is the temperature difference across the sample width. The experimental results for the Seebeck effect (Fig. 4(b)) display that the majority of carriers are electrons through $A_1$ sample so this sample has $n$-type conductivity, while in samples $A_2$ and $A_3$ the majority of carriers are holes revealing the $p$-type conductivity of the samples. These results are derived by reducing the density of donor-like levels (especially oxygen vacancies) and also increasing the density of acceptor-like levels (especially tungsten vacancies) [33,34].

3.1.4. Optical properties Figure 5 shows the UV–Vis. transmittance spectra of the non-annealed samples. As shown in this figure the transmission of the layers in visible region ($\lambda \approx 550$ nm) are approximately 80% in $A_1$, 70% in $A_2$ and 30% in $A_3$. The transmission changes of the films are well-consistent with the improving of crystallinity of layers and their thickness (here $\lambda \approx 200 \pm 20$ nm, $235 \pm 20$ nm and $290 \pm 20$ nm for the corresponding rates $R_1$, $R_2$ and $R_3$, respectively). According to the analysis carried out by M. Regragui et al. [24], the transmittance behavior can be affected by annihilating of the photon scattering. This impressionability is due to better crystallinity arrangement of layers. Thus we witness promotion of the light transmitting in the layers.

Figure 6 depicts the absorption coefficient spectra of the samples as a function of wavelength $\lambda$ using Lambert equation

$$\alpha = -\frac{\ln T}{t}$$

It can be understood from this figure that all three samples have relatively high ($\approx 104$ cm$^{-1}$) absorption coefficients in the ultraviolet region ($\lambda < 400$ nm). As a result, the sample $A_1$ with the corresponding rate $R_1$ has a very sharp absorption
edge at 320 nm. With increase of the spray rate the absorption edge shifts to towards shorter wavelengths. By using these data we could find the optical band gap $E_g$ of the studied films through following formula [35]

$$ (\alpha h\nu)^m = A(h\nu - E_g) , $$

(5)

where $A$ is constant, $h\nu$ is the incident photon energy, and $m$ depends on the nature of band transition ($m = 2$ for direct transitions and $m = 1/2$ for indirect ones). Both of the direct and indirect band gaps could be determined by extrapolating the straight portion to the energy axis, namely $(\alpha h\nu)^m = 0$. The details of our analysis for the indirect band gaps are plotted in Fig. 7 (a), and the final results are shown in Fig. 7 (b). We realized that $E_g$ increases from 3.11 to 3.51 eV when the spray rate decreases. These variations could be explained by the width of the defect state (mainly oxygen vacancies) distribution levels close to either conduction or valence band edges.
3.2. Annealed WO₃ layers characterization

3.2.1. Structural properties  WO₃ thin films have been deposited on glass substrates by spray pyrolysis technique at three different rates R₁ = 1 ml/min, R₂ = 3 ml/min and R₃ = 7 ml/min, then were annealed for 2 h at 500° C in air. The XRD structural analysis indicate that the sample A₂ with the corresponding rate R₂ = 3 ml/min has an amorphous nature, while samples A₁ and A₃ with rates, respectively, R₁ = 1 ml/min and R₃ = 7 ml/min are polycrystalline.

Figure 8 displays the crystalline structure of thin films after annealing. It is noteworthy that before annealing two samples with rates R₂ and R₃ had an amorphous
Enhancing electrical and thermoelectrical properties of WO₃

Figure 7. The details of the band gap determination: (a) indirect band gaps (b) the final calculated results and variations of $E_g$.

nature, while the sample A₁ with rate $R₁$ had polycrystalline monoclinic structure. As shown in Fig. 8 we see that after annealing samples A₁ and A₃ have polycrystalline structure, whereas the sample A₂ remains in the amorphous phase.

Interestingly, the sample A₁ is grown in three phases: monoclinic phase with lattice parameters $a = 14.49\,\text{Å}$, $b = 14.50\,\text{Å}$, $c = 10.92\,\text{Å}$, hexagonal phase with lattice parameters $a = b = 7.28\,\text{Å}$, $c = 3.88\,\text{Å}$ and tetragonal phase with lattice parameters $a = b = 7.56\,\text{Å}$, $c = 3.73\,\text{Å}$. Moreover, A₃ sample is grown in the two aforedescribed phases: monoclinic with lattice parameters $a = 14.49\,\text{Å}$, $b = 14.50\,\text{Å}$, $c = 10.92\,\text{Å}$ and hexagonal with lattice parameters $a = b = 7.29\,\text{Å}$, $c = 3.89\,\text{Å}$ together with two new phases so-called $(5(\text{NH}_4)_2)_{12}\text{WO}_3$ and $(\text{NH}_4)_0.42\text{WO}_3$. The preferential directions for both polycrystalline samples are grown along $(0\,1\,0)$ direction positioned at the Bragg angle of $\theta \approx 12^\circ$ (JCPDS 05-0392). Other researchers have reported the same results for example in Refs. [16, 36]. In order to further investigation of the obtained data, one can calculate crystal size, distance between network planes, strain and density of dislocation $\delta$ by implementing Eqs. (2) and (3).
Figure 8. XRD diagrams of WO$_3$ thin layers prepared at $T_R = 400$°C then annealed at $T_A = 500$°C. (a) A$_1$, (b) A$_2$ and (c) A$_3$. After annealing A$_1$ and A$_3$ have polycrystalline structure and A$_2$ has still an amorphous phase.
Table 2 indicates that, after annealing, by increasing the spray deposition rate the crystal size increases (sample A2 is in an amorphous phase). This phenomenon is in agreement with the obtained results reported in previous works [28, 37, 38]. It is quite surprising that the distance between network planes are very well-matched with each other. Furthermore, when deposition rate increases the strain and the density of dislocation remarkably decrease that is the result of better crystallinity of layers after annealing. This scenario is in an excellent accordance with the density of (0 1 0) peak [28, 37].

3.2.2. Electrical and thermoelectrical properties

In Fig. 9, we display $I - V$ curve of the studied samples after annealing. The amount of sheet resistance $R_{sh}$ of layers decreases from 84 kΩ to 8.3 kΩ. Moreover, we observe a descending behavior of resistivity $\rho$ from 1.9 Ω·cm to 0.26 Ω·cm as shown in Fig. 10 (a). The descending behavior of $R_{sh}$ could be due to two reasons: firstly the increase of mobility of carriers, since it is depends on the dislocation density, secondly increasing carrier density. The later corresponds to the increasing of the acceptor on the oxygen vacancies when spray rate deposition and annealing increase [24, 39–42]. The experimental results for Seebeck effect of the samples after annealing are plotted in Fig. 10 (b). These results indicate that the Seebeck coefficients of the samples are negative, hence $n$-type conductivity in these layers is concluded. In previous researchers the inverse proportion of the Seebeck coefficient to the conductivity of the layer has been reported [42]. This scenario is in an excellent agreement with our obtained values ($I - V$ data) for the

| Sample | D(nm) | $d_{hkl}$(nm) | $\varepsilon(\times 10^{-3})$ | $\delta(\times 10^{-3})(nm)^{-2}$ |
|--------|-------|---------------|-----------------|-------------------|
| A1 | 30.66 | 0.804 | 1.14 | 1.06 |
| A3 | 39.42 | 0.814 | 0.87 | 0.64 |

![Figure 9](image-url) $I - V$ characteristics of the studied samples after annealing. Ohmic behavior of samples are clear in this pattern.
sheet resistance $R_{sh}$ of the samples. It is therefore quite surprising that by comparing analysis of the annealed samples with the obtained results before annealing, one finds that the resistance of samples has been significantly reduced after annealing.

3.2.3. Optical properties The optical properties of the WO$_3$ thin films in terms of three annealed samples were comprehensively investigated. As shown in Figs. 11 (a) and (b), after annealing the transmittance and reflectance of layers around $\lambda = 550$ nm considerably decrease. After annealing, in spite of improving the crystallinity properties, electrical properties of the layers affect on this reduction process.

After annealing the absorption coefficient ($\alpha$) of the samples increases compared with the non-annealed stage. Therefore, one can conclude that studied samples have high absorbance property ($\alpha \approx 105$ cm$^{-1}$) in the ultraviolet wavelength region.
Enhancing electrical and thermoelectrical properties of WO$_3$

Figure 11. (a) Optical transmittance and (b) reflectance spectra of WO$_3$ thin layers deposited on glass substrate for three different deposition rates annealed for 2 h at 500$^\circ$C in air. The transmission and reflection decreases after annealing. (λ ≤ 400 nm). Figure 12 demonstrates the absorption as a function of wavelength λ for annealed samples. Here, one can straightforwardly derive the indirect optical band gap of layers by using absorption coefficient as we have depicted in Figs. 13 (a) and (b). It can be understood from these figures that the band gap of the considered layers reduces from 2.77 eV in A$_1$ to 2.50 eV in A$_3$ when the spray deposition rate increases. Another notable result is that, this reduction is related to increase of the crystal size and attenuation of quantum confinement effect [42].

4. Conclusion

Here we have reported the influence of the deposition rate and annealing on various physical properties of WO$_3$ thin films grown by spray pyrolysis method. The FESEM images displayed the formation of various circular strings with different diameters. The diameters decreased with increasing of the deposition rate. According to XRD patterns we found that the sample A$_1$ has a polycrystalline structure with mixed
hexagonal and tetragonal phases, while the remaining samples A₂ and A₃ have had an amorphous nature. The optical data analysis revealed that the indirect band gap of the layers decreases from 3.51 eV to 3.11 eV due to the change in width of the band tails of oxygen vacancies defect states around band edges. The experimental results for the Seebeck effect confirmed being \( n \)-type conductivity for sample A₁ (in which majority of careers are electrons), as well as, being \( p \)-type conductivity of samples A₂ and A₃ (in which majority of careers are holes). Moreover, after annealing our obtained results showed that prepared samples A₁ and A₃ were crystallized in various structures, while sample A₂ was grown in amorphous phases. In this stage, the deposited films depicted a relatively high absorption coefficient around \( \alpha \approx 105 \text{ cm}^{-1} \) and an indirect transition gap within the 2.50 – 2.77 eV domain for the samples A₁ and A₃. We have also found that, after annealing, these materials had \( n \)-type characteristics. As our future plan, the electrical measurements are in progress in order to reach the optimal resistivity of such thin films.

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Enhancing electrical and thermoelectrical properties of WO₃

Figure 13. (a) Indirect band gaps ($E_g$). Through absorption coefficient we could calculate the indirect optical band gap of layers. (b) Final results for the indirect band gaps $E_g$. The optical band gap of these layers decrease by increasing spray deposition rate.

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