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Influence of Mo\(^{+2}\) ion concentration on crystallization, microstructure, crystal imperfection and morphology of WO\(_3\) sprayed thin films

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Abstract

Compositional dependence of microstructure and morphological properties of Mo\(_x\)W\(_{1-x}\)O\(_3\) (0.2 ≥ x ≥ 0.0 at. %) thin films was studied. MoWO\(_3\) films were deposited by chemical spray pyrolysis technique on pre-heated glass substrates at 400 °C and the sedimentation rate was kept constant at 70 ml min\(^{-1}\) with the deposition time fixed at 10 min to keep the film thickness constant at about 650 ± 5 nm. The prepared thin films were studied using x-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and energy dispersive x-ray analysis (EDAX) techniques. The nature of the as-deposited films displayed by XRD showed beyond a reasonable doubt that they are amorphous. After thermal annealing at 500 °C for 2 h, all samples will be transferred to a polycrystalline having a triclinic structure. The microstructural parameters of the pure and doped samples were measured, using different methods and a comparison between them to determine the accuracy percentage of the measurement of these methods. The results also showed that the average crystallite size of the films decreased from 24 to 12 nm, on the contrary the internal microstrain increased from 23 × 10\(^{-3}\) to 30 × 10\(^{-3}\) with the addition of Mo element in WO\(_3\). Field emission scanning electron microscopy (FE-SEM) analysis also revealed that Mo dopant caused significant changes in the surface morphology of the films as well as an increase in particle size with increasing molybdenum concentration. The EDX results exhibited that the percentages of the isotropic elements Mo\(_x\)W\(_{1-x}\)O\(_3\) agree well with those determined by atomic weight. In general, the results obtained in this study confirm that Mo\(_x\)W\(_{1-x}\)O\(_3\) with these properties, is suitable for photovoltaic and optoelectronic applications.

1. Introduction

In the last three decades, the preparation and characterization of nanomaterials have acquired a lot of attention, this is due to the fact that there is a close relationship between the properties and structure of interconnected materials. Transition metal oxides as semiconductors (TiO\(_2\), V\(_2\)O\(_5\), α-Fe\(_2\)O\(_3\), NiO, Ir\(_2\)O\(_3\) and WO\(_3\)) have attracted great interest due to its huge and multiple advantages [1–7]. WO\(_3\) is a very important metal oxide because it has a wide bandgap at room temperature, is inexpensive and is used in optoelectronic devices [8, 9]. The physical properties of nanomaterials are affected by changes in microstructure and surface morphology. Therefore, intensive efforts have been made in the field of morphology and microstructure of nanomaterials.
Various states of WO$_3$ nanoparticles, nanowires, nanosheets, nanorods, nanotubes, hollow spheres, nanoflowers and hierarchical nanostructures have been widely synthesized and studied extensively [10–17], while in this work we focus on a detailed microstructure study of WO$_3$ nanocrystals. Wherein, nanocrystalline tungsten oxide is prepared using a variety of methods, including chemical vapor deposition, spraying, hydrothermal, electrospinning, and spray pyrolysis [18–20]. However, the above-mentioned methods for producing nanoparticles at mass scales are relatively expensive. Spray pyrolysis is a cheap, simple, common, and useful method for producing nanoparticles. Moreover, research into the optical and structural properties of Mo-doped WO$_3$ nanoparticles prepared by spray pyrolysis is still limited. As a result, we focus on a detailed study of this very important research. In this work different atomic ratios (0 wt%, 2 wt%, 5% wt%, 10 wt and 20 wt%) of Mo-doped WO$_3$ nanoparticles were synthesized by spray pyrolysis technique. In addition, the effects of doping on imperfections in the microstructure, morphology and crystallinity of the synthesized nanoparticles were examined.

2. Experimental

2.1. Thin film deposition technique

The chemical spray pyrolysis method was used to prepare tungsten oxide films. The chemicals used for the synthesis of Mo$_x$W$_{1−x}$O$_3$ thin films were of analytical reagent grade and were utilized as received. Mainly, ammonium paratungstate \( [(\text{NH}_4)_6\text{W}_{12}\text{O}_{41}·5\text{H}_2\text{O}] \) (99%, Sigma Aldrich), and ammonium metamolybdate \( [(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}] \) (98%, Thomas Baker) was used as cationic precursors for Mo$^{4+}$ and doped with WO$_3$ by atomic percentage 2%, 5%, 10% and 20% and all samples were homogeneous uniform films. The precursor solution was prepared by solving ammonium paratungstate and ammonium metamolybdate of solution molarity (0.005) in 100 ml hot distilled water at 60 °C. In order to obtain uniform thin films, suitable preparation conditions were carefully chosen which produced high quality films that have a surface morphology without pin holes and high adhesion to the surface of the glass substrate as well as good surface roughness. The starting solution was prepared just before the spraying began. This solution was run through a pneumatic system atomizer with a nozzle of 0.7 mm in diameter. The time period between sprays was around 3 min. This period is long enough to prevent the glass substrates from overheating. Hydrochloric acid was used to keep the pH of the solution constant at 2.35. The spray rate utilized was 70 ml hr$^{-1}$ using a pre-adjusted peristaltic pump. The nitrogen flow rate was kept constant at 80 ml h$^{-1}$ by a regulator connected to the nitrogen container. The usual Radio Corporation of America (RCA) cleaning process was used to ultrasonic glass substrates using alcohol for 10 min followed by 5 min in an ultrasonic bath with deionized water. In addition, the substrates were dipped in 1% hydrofluoric acid for 1 min before being loaded into the heater holder for spray pyrolysis. Samples were prepared on a glass substrate preheated at 400 °C and the solution concentration was at 0.005 mol and the thickness of a thin film was at 650 nm. Through thermocouples, the temperature controller measured the growing temperature and controlled the resistance heater. The prepared samples were subsequently annealed in air at 500 °C for 2 h.

2.2. Film thickness and characterization

The produced samples’ film thickness remained constant at 500 nm during all precipitation procedures and it was measured that using a Fizeau multi-beam fringes upon reflection using either white light or monochromatic light. The colored interference fringes allowed us to determine the order of magnitude of the fringe shift, whereas the monochromatic edges shift when a portion of the arrangement separation is measured with an ocular micrometer. Effect of preparative conditions on energy gap, absorption coefficient, electrical conductivity and activation energy were studied, to get optimum preparative conditions for electrochromic applications. In order to achieve the Mo$_x$W$_{1−x}$O$_3$ thin film structure, a JEOL x-ray diffractometer (model JSDX-60PA) operating at 40 kV and 35 mA using Cu–K$\alpha$ radiation with wavelength 1.54 Å and energy 8.06 kV was used to obtain the patterns of diffraction. Continued scanning was used with an extremely slow scanning speed (1°/min) and a detector time constant of 1 s. A range of 2θ was scanned from 5° to 90° in order to detect all probable diffraction peaks. A high-crystalline silicon powder free from polycrystalline defects was utilized for instrumental correction. The current samples’ composite chemical analysis was investigated utilizing energy dispersal analysis in x-ray spectroscopy, abbreviated as EDX (Oxford Model Instruments, England).

3. Results and discussion

3.1. X-Ray diffraction analysis

Figure 1 displays the XRD pattern of Mo$_x$W$_{1−x}$O$_3$ deposited on a glass substrate preheated at 400 °C by spray pyrolysis. All diffraction patterns with different concentrations of Mo$^{4+}$ ions were amorphous structures. While
after thermal annealing at 500 °C for 2 h as shown in figure 2, all the x-ray diffraction patterns convert to the crystalline form, as indicated by the appearance of the characteristic lines of tungsten oxide showed strong diffraction peaks at Bragg’s angles (2θ) of 11.60°, 20.60°, 24.20°, 28.30°, 33.00°, 49.90°, 52.30°, 58.40° which correspond to the planes (001), (111), (200), (112), (022), (400), (024) and (332). These peaks are indexed to Triclinic (Anorthic) structure with SPGR: P-1(2); Lattice parameters a = 7.312 Å, b = 7.525 Å and c = 7.689 Å; α = 88.85°, β = 90.91° and γ = 90.94° matching to card number 01-083-0947.

Moreover; at a higher concentration of Mo^{1+2} ions; some strong diffraction peaks of MoO\textsubscript{3} appear at 2θ namely; 12.80, 25.70, and 39.00°, which correspond to the (020), (040) and (060) planes, respectively. The peaks were correlated with an orthorhombic crystal structure (α-MoO\textsubscript{3}) and lattice constants of: a = 3.962 Å, b = 13.858 Å, c = 3.697 Å (JCPDS Card No. 005-0508). This reveals that long α-MoO\textsubscript{3} rectangles develop with a significant preference for orientation.
The peaks are matched to the literature, which indicated the presence of orthorhombic MoO$_3$ structures and $\alpha$-phase. The extreme intensities of the reflection peaks of $(0k0)$ with $k = 2, 4$ and $6$ prove the presence of structure of lamellar [21, 22].

3.2. Relative intensity and texture coefficient, TC

The diffraction intensity of the major lines generated during deposition improved after thermal annealing of the crystallized precipitate of tungsten oxide doped with molybdenum ion, as shown in figure 3(A) and Table 1. Even with an increase in the molybdenum ion concentration, it demonstrates a considerable rise in the strength of the principal diffraction lines, and it remains the dominant component at different concentrations, especially at higher concentrations. This is evidence of an improvement in the crystallization process of tungsten oxide with the addition of molybdenum ion. On the other hand, the variation of relative intensity of the diffraction pattern of the identified binary phase (WO$_3$) also changes.

The ratio between the peak intensities of $(001)$, $(111)$, $(112)$ and $(022)$ with that of $(200)$ peak with Mo$^{+2}$ ions concentration is shown in figure 3(B) & table 1. The intensity of this peak is highest in the case of higher concentration of Mo ions. It is clear that, the variation with relative intensity indicates that the preferred

![Figure 3](image-url)

**Figure 3.** (A) Variation of x-ray intensity of five major lines (001), (111), (200), (112) and (022) as a function of Mo doping percent (B) Variation the relative intensity of x-ray diffraction of four planes (001), (111), (112), (022) with respect to (200) plane as a function of Mo doping percent.
| x   | XRD intensity | Relative intensity | Texture coefficient |
|-----|---------------|--------------------|---------------------|
|     | (001) | (111) | (200) | (112) | (022) | I_{(001)}/I_{(200)} | I_{(111)}/I_{(200)} | I_{(112)}/I_{(200)} | I_{(022)}/I_{(200)} | (001) | (111) | (200) | (112) | (022) |
| 0.00 | 33.4 | 28.1 | 36.5 | 32.4 | 22.6 | 0.0334 | 0.0281 | 0.0324 | 0.0226 | 1.615 | 1.359 | 0.159 | 1.439 | 0.426 |
| 0.02 | 36.8 | 19.3 | 19.4 | 22.4 | 16.2 | 0.0368 | 0.0193 | 0.0224 | 0.0162 | 2.172 | 1.658 | 0.194 | 1.214 | 0.372 |
| 0.05 | 45.8 | 25.3 | 24.4 | 27.4 | 19.2 | 0.0458 | 0.0253 | 0.0274 | 0.0192 | 2.162 | 1.194 | 0.104 | 1.188 | 0.353 |
| 0.10 | 56.8 | 32.3 | 30.4 | 35.4 | 26.2 | 0.0568 | 0.0323 | 0.0354 | 0.0262 | 2.149 | 1.222 | 0.103 | 1.230 | 0.386 |
| 0.20 | 55.8 | 36.3 | 35.4 | 37.4 | 29.2 | 0.0558 | 0.0363 | 0.0374 | 0.0292 | 1.978 | 1.287 | 0.113 | 1.218 | 0.403 |
orientation along (200) directions with the concentration of Mo$^{12+}$ ions. One can conclude that the change in the intensities of all planes is very pronounced in the Mo ion concentration with a maximum at $x = 0.20$.

The most suitable direction in the texture of materials is called the preferred orientation of crystallization, which usually arises in the material as a result of a significant tendency for crystallization to occur in a certain direction. If the texture coefficient value, $TC_{(hkl)}$, is equal to one, then the crystallization will take place in the sample in a random way. But if the sample has $(TC_{(hkl)} > 1)$, the sample will crystallize in a specific (hkl) direction [23–26]. The orientated crystals number increases periodically with the increase in the texture coefficient value, TC and the texture coefficient value, TC is estimated using the following formula [23, 27–29]:

$$\text{TC} = \frac{\left(\frac{I_{(hkl)}}{I_{o(hkl)}}\right)}{1/N\sum_{i}^{N}\left(\frac{I_{(hkl)}}{I_{o(hkl)}}\right)}$$

where $I_{(hkl)}$ is the experimentally determined intensity for a certain line and $I_{o(hkl)}$ is the standard intensity acquired from JCPDS cards and corresponds to the same lines (hkl). $N$ represents the total number of reflections, whereas $N$ represents the number of diffraction peaks [23, 29]. Table 1 and figure 4(A) show the computed values for this coefficient for the five principal diffraction lines. Among all the existing lines of the acquired Mo$_x$W$_{1-x}$O$_3$ samples, the diffraction line (001) with the greatest intensity (I) had the highest TC value. This implies that the diffraction line (001) of Mo$_x$W$_{1-x}$O$_3$ thin films is the most suitable line (in the studied range of Mo content) for small crystal growth, since it has the lowest surface energy. However, the TC value reduced with increasing Mo$^{12+}$ ion concentration, from 1.615 to 2.172, indicating that this line may be the most advantageous if the concentration of Mo$^{12+}$ ions is more than 5.0%. It was also discovered that line (111) had the lowest intensity and TC value. Similar findings have been discovered by other researchers in previous literatures [26, 30].

3.3. Evaluation of the index of crystallinity

The physical characteristics of thin films are influenced by the crystallization index and the growth direction during the deposition process. Usually, these two parameters vary depending on the preparation process and preparative circumstances such as substrate type and temperature, film thickness, deposition rate, distance between the source and the substrate, solution concentration, and so on. Also, the crystallization process in the thin films increases due to the effect of kinetic and thermal energies within the deposition process. As a result, residual internal stresses, lattice strains, and internal forces rise, preventing the particles from irregularly arranging to create the specific crystal structure and stacking process in the crystal form. Therefore, the index of crystallization in thin films relies mostly on the materials’ preparation conditions. Therefore, the crystalline structure of the thin films is often a combination of the crystalline and amorphous phases. Thus, the x-ray diffractogram of the obtained Mo$_x$W$_{1-x}$O$_3$ thin films seem polycrystalline, and the presence of the Mo$^{12+}$ ion promotes crystallization. Where the peaks of the main Bragg’s diffraction lines appear more intense with the increase of the Mo$^{12+}$ ion content, which is the crystalline phase of the current tungsten oxide. The degree of crystallization of thin films may be determined using x-ray diffraction data, which is especially useful for partly crystallized or polycrystalline films [31, 32]. This approach was successful in integrating all of the diffraction peaks corresponding to the observed diffraction lines, namely (001), (111), (200), (112), (022), (400) and (024) and (332), where the intensity of the x-ray diffraction peaks is being shown in figure 2. The regions beneath the diffraction lines are then integrated into a single intensity indicating the integral of the crystal portion. A two-stage approach was used for the ensuing examination, which is often used to amorphous thin films that participate in the investigated spectrum and appear as large diffraction bands. This contribution is estimated by the background curve that distinguishes the amorphous and crystalline parts. Then, for each sample, the index of crystallization may be calculated as the ratio of the area under the crystal peaks to the total area under the diffraction curve. As illustrated in figure 2, a standard fitting approach was used to separate the crystal peaks from the amorphous halo of the Mo$_x$W$_{1-x}$O$_3$ thin films. Using the Hermans Weidinger approach [33], EVA software separated the crystalline material from the non-crystalline component. The index of crystallinity, $X_{\text{Cryst}}$, of each sample was calculated using the following simple formula [33–36]:

$$X_{\text{Cryst}} = \frac{A_{\text{Cryst}} / (A_{\text{Cryst}} + A_{\text{Amorph}})}{\times 100}$$

$$\text{Crystallinity index (CI)} = \frac{\text{Area of all the crystalline peaks}}{\text{Area of all the crystalline and amorphous peaks}}$$

As a result, the crystallinity index was calculated and summarized in table 2 and figures 4(B) & (C). As can be seen, the index of crystallinity and total area under the curves grow progressively as Mo concentration increases. This demonstrates that the film crystallinity has improved and the x-ray diffraction intensities have increased.
Figure 4. (A) The texture coefficient, TC of five major planes as a function of Mo doping percent in WO$_3$ thin films (B) & (C): The crystallinity and amorphousity degree as a function of Mo doping percent.

Table 2. The index of amorphousity and index of crystallinity of Mo$_x$W$_{1-x}$O$_3$ thin films.

| Sample | Area under XRD of as-deposited | Area under XRD of after annealing | Index of crystallinity $= \left(\frac{A_{cr}}{A_{cr} + A_{am}}\right) \times 100$ | Index of amorphousity $= \left(\frac{A_{am}}{A_{cr} + A_{am}}\right) \times 100$ |
|--------|-------------------------------|----------------------------------|----------------------------------|----------------------------------|
| X = 0.00 | 406.28                        | 436.65                           | 6.96                             | 93.04                            |
| X = 0.02 | 412.55                        | 503.04                           | 17.98                            | 82.02                            |
| X = 0.05 | 417.62                        | 524.59                           | 20.39                            | 79.61                            |
| X = 0.10 | 426.89                        | 549.31                           | 22.29                            | 77.71                            |
| X = 0.20 | 428.28                        | 571.54                           | 25.07                            | 74.93                            |
This causes the amorphous ratio of the MoₓW₁₋ₓO₃ thin films to drop. As the Mo⁺² content grows from 0.0 to 0.2, the crystalline percentage, XCrystal of MoₓW₁₋ₓO₃ increases from 6.96 to 25.07 percent. This indicates that the improved crystallization with Mo-ratios has resulted in an increase in the degree of crystallinity of MoₓW₁₋ₓO₃ films. As a result, it is possible to conclude that increasing the concentration of Mo has an obvious and effective influence on the crystallization index of MoₓW₁₋ₓO₃ films [7, 37].

3.4. Estimation of microstructure parameters in imperfect crystals

The broadening of the diffraction peaks of the imperfect crystal depends on the three factors, namely ‘crystallite size’, ‘microstrain’ and ‘fault’.

The ‘crystallite size’ part is due to the finite size from the material crystallization which is obtained by using x-ray line profile analysis method. The crystallite size measured is called the domain size. Where is defined as the length of a region perpendicular to the plane being viewed, in the material that incoherently diffracts (or diffracts independently) with respect to all other regions.

An incoherent diffraction occurs when the phase difference between the diffraction from one domain to any other has an equal probability of being between 0 and 2π. The broadening of crystallite size occurs because the coherent region being finite, thus there is no scattering beam canceled all scattering beams around the Bragg angle [38].

The ‘strain’ part may be divided into the variations of the interplanar spacing within a grain (is often called the microstrain) and variations in the lattice spacing in different grains is often called the macro-strains (or interplanar strains), which are concerned with the movement of the diffraction peaks. The two cannot be separated easily, and the former is often treated exclusively as its effect is believed to be the greater in most situations [39].

The ‘fault’ part is consisting of the planers, stacking and twin’s faults of the crystal structure; which is effect in the layers of atoms. Moreover, these effects, the instrument is not ideal which is contributes to the shape and breadth of peaks.

The convolution of these parts by measured broadening of line profile (B) [40], or similarity product of the Fourier coefficients (A):

\[ B_{obs} = B_{cry} * B_{str} * B_{fau} * B_{inc} \]  

\[ \ln(A_n^{obs}) = \ln(A_n^{cry}) + \ln(A_n^{str}) + \ln(A_n^{fau}) + \ln(A_n^{ins}) \]

The integral breadth, \( \beta_{hkli} \), of a peak is the area under a diffraction peak, excluding the background divided by the peak’s height.

3.4.1. Sherrer’s method

The factors that cause broadening of the x-ray diffraction peaks in materials are divided into two parts physical broadening: the crystal defects of the material (crystallite size and internal strains) and the broadening caused by the instrumental used [41–44]. The following relationship can be used to correct this instrumental broadening:

\[ \beta_{correct} = \sqrt{\beta_{obs}^2 - \beta_{inst}^2} \]

Where \( \beta_{obs} \) represents the measured broadening, \( \beta_{inst} \) denotes the instrumental broadening and \( \beta_{correct} \) denotes the corrected broadening. For position calibration and instrumental broadening measurement, crystalline silicon was employed as a standard reference material. The sample’s instrumental and physical broadening were determined as integral breadth (area beneath the peak/maximum intensity of peak).

One of the most significant methodologies for diffraction peak profile analysis (DPPA) processes is the Scherrer approach. Scherrer established that if the broadening is due to crystallite size alone, the integral width of the peak at a given angle is proportional to the inverse of crystallite size. The relationship can be derived from the kinetic theory of diffraction [45]. This effective expansion can be corrected by using the following relationship,

\[ <D_{hkli}>_V = \frac{K \lambda}{\beta_{hkli}(2\theta) \cos \theta_{hkli}} = \frac{K}{\beta_{hkli}(g)} \]

Where, \( g \) is the reciprocal of the interplanar spacing at the Bragg’s angle (\( g = 1/d \)), \( \beta_{hkli}(g) \) and \( \beta_{hkli}(2\theta) \) is the integral breadth (area under the peak/maximum intensities) of the broadened peak without instrumental broadening on a scale of 2θhkli and g, respectively, measured diffraction angle both \( \beta_{hkli}(2\theta) \) and \( \theta_{hkli} \) are in radians, The Scherrer constant K is ~0.94, and the incident beam’s x-ray wavelength is λ, and V the size-weighted crystallite size perpendicular to a given plane.
To convert between the values on the two scales, $\theta_{hkl}$ in radians and $g$, the following equation is used:

$$\Delta \theta = \frac{\Delta d_{hkl}}{d_{hkl}} \tan \theta_{hkl} = \frac{\Delta g}{g} \tan \theta_{hkl} = \frac{\Delta g}{2 \cos \theta_{hkl}}$$

(8)

Only the Scherrer equation is expected to be significant for determining the size of crystallite below 100 nm [41, 44]. It is often thought of as a qualitative description and is rarely used [45–48]. A problem with the method is that it ignores the distribution in crystallite sizes and shape. The average crystal size may be determined from the slope of the graph by the correlation between $\beta_{hkl}$ versus $1/\cos \theta_{hkl}$ for $\text{Mo}_x\text{W}_{1-x}\text{O}_3$ nanoparticles (Figure 5), which ranges from 12.51 to 22.28 nm with increasing $\text{Mo}^{2+}$-ion. The internal strains were also estimated according to equation (10), and they ranged from $15.86 \times 10^{-3}$ to $20.61 \times 10^{-3}$ with an increase of $\text{Mo}^{2+}$-ion as recorded in Table 3.

### 3.4.2. Williamson-Hall method

In developing the Scherrer equation, only the influence of crystallite size on the broadening of the x-ray diffraction peak was considered, with no regard for lattice microstructures (strain effect). In nanocrystals, internal strain occurs owing to point defects, grain boundaries, triple junctions, and stacking faults [49, 50]. Many approaches, including as the Williamson Hall method, the Warren-Averbach method, and others, take into consideration the strain effect generated by the broadening of the XRD peak and may be used to determine the intrinsic strain as well as the particle size. Among all these methods, the Williamson-Hall (W-H) method is the simplest and most straightforward [51, 52]. As a result of the exact crystallite size and microstrain of the nanocrystals, the physical line broadening of the x-ray diffraction peak occurs, and the whole broadening may be expressed as,

$$\beta_{\text{total}} = \beta_{\text{cryst}} + \beta_{\text{strain}}$$

(9)
This intrinsic strain does have an effect on the physical broadening of the XRD profile, and the strain-induced peak broadening may be described as follows:

\[
\beta_{\text{strain}} = 4 \varepsilon \tan \theta_{hkl}
\]

Therefore, the overall strain-induced broadening and crystallite size at a particular peak having an hkl value can be expressed as,

\[
\beta_{hkl} = \beta_{\text{crystal}} + \beta_{\text{strain}}
\]

Where, \(\beta_{hkl}\) is the integral breadth for different diffraction planes.

\[
\beta_{hkl} = \frac{k\lambda}{D_{hkl}} \cdot \frac{1}{\cos \theta_{hkl}} + 4 \varepsilon \tan \theta_{hkl}
\]

\[
\beta_{hkl} \cdot \cos \theta_{hkl} = \frac{k\lambda}{D_{hkl}} + 4 \varepsilon \sin \theta_{hkl}
\]

where \(\beta_{hkl}\) is the sample’s estimated pure broadening, the diffraction angle is denoted by \(\theta_{hkl}\). The shape factor, \(k\), is equal to 0.94, wavelength \(\lambda = 0.154184\) nm, The average crystallite size is \(D_{hkl}\), and the average microstrain is \(<\varepsilon>\).

The Uniform Deformation Model (UDM) equation, represented by equation No. 13, takes into account the isotropic nature of crystal characteristics and represents a first-order linear relationship. Figure 6 illustrates the plot of this correlation, with the terms \((4 \cdot \sin \theta_{hkl})\) along the X-axis and \((\beta_{hkl} \cdot \cos \theta_{hkl})\) along the Y-axis corresponding to each \(\text{Mo}_xW_{1-x}O_3\) nanoparticle diffraction peak. The slope of this straight line produces the value of average microstrain, \(<\varepsilon>\), whereas the intersection yields the average crystallite size of the \(\text{Mo}_xW_{1-x}O_3\) nanocrystals, \(D_{hkl}\). This straight line plotted is a good fit line, matching to all values, since the value of correlation coefficient of \(R^2\) is 0.8816. Table 3 summarizes the results of the average crystallite size and average microstrain calculations. The average crystallite size ranged from 9.64 to 18.03 nm as the Mo\(^{+2}\) ion concentration increased from 0% to 20%. It is obvious that the obtained values of crystallite size, \(D_{hkl}\), increased with increasing percentages of Mo\(^{+2}\) ions in WO\(_3\). This is due to the Mo\(^{1+2}\) insertion into the WO\(_3\) unit cell. This produces a strong attractive force between W and O, which activates atom diffusion. The formation of the lattice strain is mostly due to the extension or shrinkage of the lattice in nanocrystals as a result of size retention. Thus, the presence of more Mo\(^{1+2}\) leads to enhanced fusion of neighboring particles [44, 51]. Thereby, the atoms will form larger structural agglomerations, which will lead to increased crystallite size values. Again, a positive UDM pattern slope was found, indicating lattice stretching [53] and thus producing an intrinsic strain in the nanocrystals. The internal strain was found that it increases from \(8.07 \times 10^{-3}\) to \(9.11 \times 10^{-3}\) with the concentration of molybdenum ion as in table 3. These data are compatible with previous studies [47, 54, 55].
3.4.3. Size-strain plot (SSP) method

In fact, the Williamson-Hall approach is based on the combined influence of crystallite size and lattice strain on peak broadening as a function of diffraction angle ($2\theta$). But there are models that treat peak profile analysis as a mixture of Gaussian and Lorentz distributions, as the size-strain plot (SSP) method. Considering that the Lorentz function is defined as the broadened size XRD profile and the Gaussian function is the name given to the expanded strain profile \[50\].

Therefore, the overall broadening of the SSP might be stated as follows;

$$\beta_{hkl} = \beta_L + \beta_G$$

(14)

where $\beta_L$ and $\beta_G$ are the Lorentz and Gaussian function peak broadenings, respectively. Moreover, the SSP technique always produces better isotropic broadening results, because it prioritizes low-angle reflections, which have more accuracy and precision than the one at higher angles.

It is because the XRD data is of poorer quality at higher angles and at large diffraction angles, the peaks overlap extensively greatly. Therefore, the SSP is calculated using equation [33], as

$$\left(\frac{d_{hkl}(\beta_{hkl} \cos \theta_{hkl})}{D_{hkl}}\right)^2 = \frac{k\lambda}{d_{hkl}^2} \left(\frac{\beta_{hkl} \cos \theta_{hkl}}{\beta_{hkl}} + \frac{\langle \varepsilon^2 \rangle}{4}\right)$$

(15)

where $d_{hkl}$ is the lattice distance between the planes (hkl) in the cubic system

$$d_{hkl} = \frac{a^2}{h^2 + k^2 + l^2}$$

(16)

Using equation (15), figure 7 shows a graphic with $(d_{hkl}^2 \beta_{hkl} \cos \theta_{hkl})$ term along X-axis and $(d_{hkl} \beta_{hkl} \cos \theta_{hkl})^2$ along Y-axis corresponding to each diffraction peak. As described in table 3, the slope of the straight line indicates the average crystallite size, while the intercept shows the microstrain of the Mo$_x$W$_{1-x}$O$_3$ nanocrystals.

3.4.4. Halder-wagner method

Whereas, the pure broadening using the SSP method, is due to the assumption that the size broadening of the XRD peak profile is expanded as a Lorentzian function, while the strain broadening is due to the Gaussian function. However, the XRD peak is not a Lorentz function nor a Gaussian function, and its tail falls extremely rapidly with miss matching. On the other hand, the profile tails completely fit into the Lorentz function, but this failed to match the XRD peak region [56, 57]. To solve this complex problem, the Halder-Wagner technique is utilized, which is predicated on the assumption that the peak broadening is a symmetric Voigt function [50, 58], since it is a combining of the Lorentzian and Gaussian functions [59]. As a result, the full width at half maximum of the physical profile for the Voigt function may be expressed using the Halder-Wagner approach [58]

$$\beta_{hkl} = \beta_L \beta_{hkl} + \beta_G^2$$

(17)
Where, $\beta_L$ and $\beta_G$ are the Lorentzian and Gaussian function’s full width at half maximum. This approach has the benefit of giving more weight to peaks in the low and intermediate angle ranges, where diffraction peaks overlap considerably less.

The Halder-Wagner technique is now used to determine the relation between crystallite size and lattice strain.

$$\left( \frac{\beta_{hkl}}{d_{hkl}} \right)^2 = \frac{1}{d_{hkl}^2} \left( \frac{\beta_{hkl}}{\lambda} \cos \theta \right) + \left( \frac{\varepsilon^2}{4} \right)$$

(18)

In which $\beta_{hkl} = \beta_{hkl} \cos \theta / \lambda$ and $d_{hkl}^* = (2d_{hkl} \sin \theta / \lambda)$. Figure 8 depicts a plot of equation (18), with $\left( \frac{\beta_{hkl}}{d_{hkl}} \right)$ term along X-axis and $\left( \frac{\beta_{hkl}}{d_{hkl}^*} \right)^2$ term along the Y-axis for each XRD peak. The average crystallite size is determined by the slope of the straight line, whereas the intersection represents the internal strain of the Mo$_x$W$_{1-x}$O$_3$ nanocrystals. With an increase in Mo-ion addition ratio from 0.0 to 0.2, the average crystal size ranged from 10.97 to 21.92 nm, which is consistent with the SSP method. The estimated value of lattice strain from the Halder-Wagner diagram ranged from $13.57 \times 10^{-3}$ to $50.15 \times 10^{-3}$, which is approximately five times the amount achieved using the other techniques outlined above. This rise in the calculated lattice strain value is attributable to the contribution of the low and mid-angle XRD data. Moreover, the greater value of the lattice strain determined using the Halder-Wagner technique is referred to as the lattice dislocation [58], which has a significant impact on broadening peaks at smaller angles. Table 3 illustrates the estimated values for average crystallite size and intrinsic lattice strain. The average crystallite size computed by Scherrer and Williamson-Hall (W-H), Size-Strain plot (SSP), and Halder-Wagner (H-W) is clearly comparable in this table. The Williamson-Hall (W-H) approach is clearly the best for predicting crystallite size and internal lattice stresses, provided that the broadening is estimated using a Gaussian distribution. This is because, unlike the Scherrer technique, this approach relies on a large number of x-ray diffraction lines rather than a single diffraction line.

4. Crystal lattice defects

4.1. Crystallite size and average microstrain

The inverse relationship between the average values of the crystallite size ($D$) and those of the microstrain, $\varepsilon$ for the current Mo$_x$W$_{1-x}$O$_3$ thin films were obtained directly from different methods as shown in figures 9(A) & (B) and table 3 lists their specific values.

As demonstrated, the values obtained from the microstrain were increased when the size of the crystallite was increased. This logical result can be related to the increase in the size occupied by the atoms arranged in a featured crystal agglomeration. Therefore, the total area of the sample is found to decrease. As a result, changing the surface area causes the plane’s location to shift, resulting in an increase in the precise microstrain. It is noteworthy that, as shown by the XRD results, the Mo doping of WO$_3$ helps to improve the crystallization
process and leads to more agglomeration and to smaller crystallite sizes or the coalescence of neighboring particles, so the free sizes in the grain boundaries will also be increased \[50, 60\]. As a result, there is an increase in crystallite and a microstrain value, which will increase the defects of the samples \[61, 62\].

4.2. Internal stress
Total internal stresses in thin films result from several factors, including temperature changes, phase transitions, deformations, and substrate materials. The intrinsic stress is caused by the cumulative effect of crystallographic imperfections formed throughout the film’s creation. X-ray diffraction an important tool for determining internal stresses in natural or manufactured materials \[63\]. To determine the internal stress using x-ray diffraction, the average microstrain within the crystal lattice must first be calculated. For highly melting materials such as Mo\(_x\)W\(_{1-x}\)O\(_3\) in deposition thin films, the total internal stress was found to be about 5% up to 500 °C. Therefore, it is believed that residual internal stress accumulates and tends to control thermal stress. As a result, the internal stress (\(\sigma\)) may be derived from the average microstrain of the values using this easy known equation:

\[
(E(hkl)) = \frac{\text{Internal stress}}{\text{average microstrain}} = \frac{\sigma}{<\varepsilon>} \quad \text{Hence,} \quad \sigma = <\varepsilon> E(hkl)
\]

where \(E(hkl)\) the elastic modulus of WO\(_3\) is about 13.6 GPa \[64\]. Table 4 and figure 10(a) show the computed values of internal stress using the best approach for accurate estimation of fine stress (Williamson-Hall method). It has been noted that internal stress values increase as Mo content increases. This result may be attributed to the free volumes, which may exist between the grain boundaries. The shrinkage process occurs as a result of crystal aggregation and fusion of the structural unit. Whereas, an increase in molybdenum causes an increase in crystallite agglomeration. At the same time, when Mo increased, the unit cell size dropped, and therefore the vacancies reduced. As a result, the surface area of the crystal volume increases. Hence, the internal pressure values decreased \[65\]. It should be noted that increasing the Mo concentration enhances the crystallization nature of the samples and minimizes crystal imperfections.

4.3. Number of crystallites per unit area
The number of crystallites per unit area (\(N\)) for Mo\(_x\)W\(_{1-x}\)O\(_3\) thin films is derived using the following relationship from the expected crystallite size (\(D\)) \[66, 67\]:

\[
N = \frac{1}{D^2}
\]
where t is the thickness of the film. The calculated values of N as a function of Mo concentration are recorded in table 4 and shown in figure 10(B). As can be observed, a rise in Mo ions resulted in a reduction in the number of crystallites/m². This is because the crystal size of MoₓW₁₋ₓO₃ films has increased for all Mo concentrations. The obtained values for the number of crystallites/m² are consistent with previous data [66, 68, 69].

4.4. Dislocation density

Dislocations are formed on the basis of the material’s internal stresses, and the density of the dislocation plays an important role in the material’s rigidity, stiffness, and ductility. This form of defect is also influenced by the material’s morphologically, crystallite size, and composition. Dislocations can be estimated on the best form for the sizes of crystallites and and may be described as the dislocation line length per unit volume of crystals [70]. Using the fundamental Williamson-Smallman formula, the XRD Line Profile Analysis (LPA) approach may simply determine the dislocation intensity, which is written as [23, 70, 71]:

\[
N = \frac{t}{D^3}
\]  

Here D denotes the approximate crystallite size. Table 4 summarizes the observed dislocation intensity values presented in figure 10(c). It is evident that when the Mo concentration in WO3 thin films increased, the distortion density dropped. The decreasing value of the dissociation intensity may be related to the samples’ crystallization process which is improved by adding more Mo. As addition of Mo decreases the free volumes and vacancies which in turn decrease dissociation intensity [70, 71]. This obtained result confirms the refinement of the synthesized MoₓW₁₋ₓO₃, where the value of dislocation density denotes the empty spaces between crystal agglomerates, i.e. it the average area between grain boundaries has been reduced. Depending on the previous results, one can conclude that addition of more Mo enhances the crystallization nature of the samples and eliminates crystal imperfections.

5. EDS and compositional elements

Energy dispersive x-ray spectroscopy (EDS) is a good technique for analyzing the constituent elements of chemical compounds, especially the ratios of weak elements present in a chemical compound.
It also contains a software and compares the percentage of the elements present with the standard data of all elements starting with an atomic weight equal to 3 and determining the percentage of the components of the elements in the compound. EDS spectra were measured on doped and undoped Mo<sub>x</sub>W<sub>1-x</sub>O<sub>3</sub> to determine the ionization of homogeneously distributed Mo, W and O elements and clearly indicate the presence of Mo in the WO<sub>3</sub> host lattice. Moreover, EDS analysis was carried out to assign the overall compositional elements of the samples to selected parts of the sample surface while they were examined by electron microscopy at room temperature at different regions of the sample and the average values were considered. Figures 11(a)–(e) shows the EDS spectra of the constituent elements of the samples for pure WO<sub>3</sub> and Mo-doped WO<sub>3</sub>. We notice that the lines characteristic of elements W, O and Mo appear in the samples with characteristic peak of varying intensity. As the electron beam scans an area from 80 mm<sup>2</sup> to 150 mm<sup>2</sup>, it also penetrates deep into the sample from 0.5 μm to 3 μm. Thus, the concentration of the elements is measured on the basis of the area under the characteristic peak of the resulting x-ray fluorescence of the elements, which depends on the percentage of the element in the sample in addition to the atomic weight of this element and compared to the standard values of the element recorded in the instrument’s software.

It can be observed that the percentages of detected elements (Mo, W and O) agree well with those that have been selected in experimental. The obtained results which are tabulated in table 5, it can be fully confirmed that the uncapped and Mo<sub>x</sub>W<sub>1-x</sub>O<sub>3</sub> samples are monophasic samples and no impurities are inferred. It is noteworthy that there is a slight increase in the proportions of oxygen in their atomic ratios. This minor excess of...
oxygen in samples may be present due to slight oxygen uptake from the ambient air while the sample is cooled at room temperature [72]. Referring to what was previously published for similar samples, the same behavior was found, and it was found that a stoichiometric measurement of oxygen can be produced [73]. In general, analysis of the compositional elements using EDX spectrometer gives a good evaluation of the examined sample with an accuracy of about 0.1%. In general, there is good consistency between the proportions obtained experimentally and those calculated theoretically.

6. Surface morphology study

The field-emission scanning electron microscope (FE-SEM) technology has been highly popular in recent years and is used to investigate the structural and morphological characteristics, particularly of nano-dimensional materials. Many researchers favor FE-SEM over scanning electron microscopy (SEM) in studying material morphology because it produces a crisper image with higher resolution and magnification that reveals every detail. In addition, it is possible to successfully survey and study the surface nature of the tested samples, regardless of whether their surface is smooth, rough, crystalline or granular [74–76]. Besides, the description of
the obtained FE-SEM images can give good details and information about the surface of the studied sample, the use of low accelerating voltages to operate the field emission scanning electron microscope can give good images with more resolution, the lower accelerating voltages is better and is more suitable for microscopic examination of sensitive samples. It can also be noticed that if the sample’s crystalline sizes or grains have a regular and homogenous shape, it will have a smooth surface. In this case, the material with a smooth and homogeneous surface has high transmittance and low reflection, as well as low absorption and high conductivity. But if the surface of the sample is rough and heterogeneous, then that sample usually has physical properties that are not at the required level, and its transmittance and conductivity is low, while its absorption and reflection of light are high, which is considered a defect that must be avoided [74, 75]. To investigate the influence of adding Mo-ions on the surface morphology of samples prepared from WO3, it was found that the surface morphology comprising of the pure WO3 film is island-like and consists of tiny grains as shown in figures 12(A)–(E). The film has a cross-linked, nest-like shape at 2% Mo doping. The morphology transforms to a root-like structure when doping is increased to 5%. The film has a dense, nest-like crosslinked morphology after further optimization to 10% Mo doping. With the increase in the proportion of molybdenum to 20%, the density of the islands increases. The increased crosslinked channels in the 5 percent Mo-doped film provide ample pathways for ions to easily diffuse into the film network, as well as accelerated kinetics that improve the electrical performance of the films [77].

### 7. Conclusion

Microstructure and morphological properties of MoₓW₁₋ₓO₃ (0.2 ≥ x ≥ 0.0 at. %) thin films were studied. MoWO₃ thin films were deposited using chemical spray technique onto glass substrates at 400 °C. XRD revealed that, the as-deposited films have an amorphous structure while after thermal annealing at 500 °C for 2 h, all samples transfer to the polycrystalline as triclinic structure. The microstructural parameters (crystallite size and microstrain) of the prepared samples, both pure and doped, were measured using different methods and a comparison of the accuracy of these methods was made. The Williamson–Hall (W–H) approach was indeed the best for assessing crystallite size and internal lattice stresses, with the broadening estimated using the Gaussian distribution. Because it depends on many x-rays diffraction lines and not a single diffraction line as in the Scherrer method. According to FE-SEM image analysis, the 5 at% Mo-doped film has the largest image surface area. The compositional elements using an EDX spectrometer give a good evaluation of the examined sample with an accuracy of about 0.1%. In general, there is good consistency between the proportions obtained experimentally and those calculated theoretically. It is clear that the results of this mixture are distinguished in opto-electronic devices and electrochromic applications.

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### Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
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