CHAPTER 3

Nanostructured Tungsten Oxide Thin Films by Reactive Pulsed Laser Deposition Technique
This chapter discusses the synthesis of nanostructured tungsten oxide films by reactive pulsed laser deposition (PLD) technique. Structural, morphological, optical and electrical properties of the as-deposited and the annealed films are investigated using X-ray diffraction (XRD), Scanning electron microscopy (SEM), Atomic force microscopy (AFM) and UV-VIS spectrophotometry techniques. Surface analysis by SEM and AFM depicts a wide range of morphology consisting of compact spherical nanostructures, nano-pores, nanowhiskers and nanorods. The realization of tungsten oxide nanorods and nanowhiskers with comparably high aspect ratio and high degree of crystallinity achieved, foresee their functional exploitation.
3.1 Introduction

The present chapter confers the preparation of WO$_x$ nanostructures on glass substrates starting from metallic tungsten target by reactive pulsed laser ablation method in oxygen ambient. In general, tungsten oxide is a complex material as far as crystal structure and thermal stability are taken into consideration. Tungsten oxide thin films prepared by various techniques exhibit different crystal structures such as monoclinic, triclinic, tetragonal, orthorhombic, cubic and hexagonal. These crystal structures corresponding to stoichiometric and sub-stoichiometric WO$_3$ phases, upon annealing undergoes further changes. Therefore it is important to characterize tungsten oxide films as a function of both the deposition and annealing conditions. Optimization of substrate temperature (T$_s$) and ambient oxygen pressure (pO$_2$) is imperative as the micro-structure, optical and electrical properties of WO$_3$ films are highly sensitive to these parameters.

There are reports detailing the preparation of tungsten oxide thin films starting from metallic tungsten target using techniques like reactive dual magnetron sputtering [1], hot filament chemical vapor deposition (HFCVD) [2], reactive dc magnetron sputtering [3] and resistive heating [4] etc. But, only a very few literatures are available on the fabrication of tungsten oxide thin films from tungsten target using reactive pulsed laser deposition technique [5, 6]. Hence the evolution of micro-structural and morphological features of tungsten oxide thin films as a function of substrate temperature and ambient oxygen pressure using PLD technique is explored in detail. The correlation of the post thermal annealing effects to the crystallographic orientation, optical properties and surface morphology of the films is also investigated. During the annealing process, dislocations and other structural defects will move in the material and adsorption/decomposition will occur on the surface, thereby change the structure and the stoichiometric ratio of the materials. Thermal annealing can also enhance grain growth and recovery of disordered structure.
3.2 Experimental Details

The deposition of the films is done on glass substrates kept at an on-axis distance of 45 mm from the metallic tungsten target (99.95%). During deposition, the tungsten target is ablated with laser pulses having energy 100 mJ for 30 minute duration. Tungsten oxide films are grown under controlled substrate temperatures (300, 523 and 723 K) in different ambient oxygen pressures viz., 0.066, 0.10 and 0.15 mbar. All the deposited films are subsequently annealed in air at 773 K for 1h at the rate of 2 °C/min. Annealing temperature is selected as 773 K as literature suggests tungsten oxide films becomes completely crystallized at this temperature [7, 8]. The micro-structural, optical and electrical properties of the prepared tungsten oxide films are investigated using techniques like XRD, AFM, SEM, UV-Visible spectroscopy and room temperature DC electrical resistivity studies. The experimental details of these measurement techniques are described in Part B of Chapter 1.

3.3 Results and Discussion

3.3(a) XRD Analysis

X-ray diffraction patterns of the WO_x films deposited under various deposition conditions show no XRD peaks [Figures not shown]. The absence of XRD peaks and the presence of only a broad diffuse background between 20 and 40° in the XRD patterns for all the as-prepared films reveal that the films are amorphous or consist of nanocrystallites. Filipescu et al. [6] have recently reported the preparation of WO_x thin films from metallic tungsten target using reactive PLD for different ambient oxygen pressures ranging from 0.01–0.05 mbar, for the substrate temperature range of 320- 873 K. They also observed an amorphous phase for the as-deposited films. On the contrary, Huang et al. have reported crystalline monoclinic WO_3 (001) films by DC reactive sputtering from a metallic tungsten target for T_s = 623 K and 673 K for pO_2 = 0.02 mbar on Si substrates [3].

Figures 3.1(a) -(c) show the XRD patterns of the films post- annealed at 773 K as a function of substrate temperature, deposited under different oxygen pressures. On annealing at 773 K all the films turned into textured and polycrystalline, corresponding to different stoichiometric and sub-stoichiometric crystalline phases of tungsten oxide.
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Thermal annealing at high temperatures enhances the diffusion mechanism, leading to an increase in the film crystallinity owing to the reduction in internal stress and rearrangement of structural atoms [7]. All the annealed films prepared at pO₂ = 0.066 mbar at different substrate temperatures show polycrystalline monoclinic phase of W₁₈O₄₉[9]. The annealed films prepared at pO₂ = 0.1 mbar at Tₛ = 300 and 523 K also exhibit a polycrystalline monoclinic W₁₈O₄₉ structure with preferred orientation of crystal growth along (010) plane whereas a triclinic WO₃ [JCPDS card No. 20-1323] phase is obtained for the films prepared at Tₛ = 723 K.

The annealed films which are deposited at pO₂ = 0.15 mbar at Tₛ = 300 and 723 K show the characteristic X-ray diffraction peaks corresponding to lattice plane reflections of (200) and (001) of the hexagonal phase of WO₃ [10]. Recently Ramana et al. have observed hexagonal phase of WO₃ in PLD deposited tungsten oxide thin films on heated glass substrates (573 K) on post-annealing at 773 K [11]. Mohammed et al. have reported hexagonal phase in thermally evaporated WO₃ films [12]. The film which is deposited at 523 K under the same oxygen pressure, on annealing at 773 K shows a tetragonal WO₃ phase [13]. It is interesting to note that in previous reports, a stoichiometric WO₃ tetragonal phase appears only at higher substrate temperatures (> 900 K). The occurrence of tetragonal WO₃ at comparatively lower substrate temperature (= 523 K) can be due to the combined effect of high laser fluence and higher oxygen partial pressure during the film growth.

The possible planar spacing (d-values) for the tungsten oxide films with tetragonal and hexagonal phase are obtained through the relations 3.1 and 3.2 respectively

\[
\frac{1}{d_{hkl}^2} = \frac{h^2+k^2+l^2}{a^2+c^2} \quad \text{---- 3.1}
\]

\[
\frac{1}{d_{hkl}^2} = \frac{4(h^2 + hk + k^2)}{3\left(\frac{a^2}{a^2}\right)} \cdot \frac{l^2}{c^2} \quad \text{---- 3.2}
\]

The calculated values of the lattice parameters are listed in Table. 3.1.
Figure 3.1(a)-(c): XRD patterns of the films post-annealed at 773 K as a function of substrate temperature prepared at oxygen pressures (a) 0.066 mbar (b) 0.10 mbar (c) 0.15 mbar. Figure 3.1(d) Variation of grain size with substrate temperature for the tungsten oxide films annealed at 773 K which are deposited at different oxygen pressures.

The average grain size of the particles in the annealed films is calculated using the Debye Scherrer’s equation [14]. As seen from figure 3.1(d) a regular or linear sway of substrate temperature on grain size could not be observed. This can be attributed to different growth mechanisms that prevail at the substrate surface at different background oxygen pressures and substrate temperatures. The lattice strain $T$ in the annealed films deposited at 0.15 mbar for different substrate temperatures is estimated using the relationship 2.2 and the estimated values are listed in Table 3.1. The low value of the lattice strain observed for the films indicates good crystalline quality of the films.
3.3(b) AFM Analysis

![AFM images](image)

**Figure 3.2(a) & (b)** AFM [(a) = 2D (b) = 3D] images on a scan area of $5 \times 5 \ \mu m^2$ of annealed films deposited at $pO_2 = 0.10 \ \text{mbar}$ and $T_s = 300 \ \text{K}$

Figures 3.2 (a) & (b) show the 2D and 3D AFM images of annealed tungsten oxide films, which are prepared at an oxygen ambient pressure of 0.10 mbar at $T_s = 300 \ \text{K}$. Surface morphology of this film is intermixed with nanorods of high aspect ratio and spherical nanostructures. The obtained nanorods of crystalline $W_{18}O_{49}$ phase are of high quality with well defined and mono-dispersed diameter of $\approx 100 \ \text{nm}$ and length 2-3 micron. Synthesis of nanorods of crystalline $W_{18}O_{49}$ has been reported by Feng et al. from thermal oxidation of a spiral coil of W metal wire [15].

![AFM images](image)

**Figure 3.3 (a) - (c)** AFM images of as-deposited films at $pO_2 = 0.15 \ \text{mbar}$ and (a) $T_s = 300 \ \text{K}$ (b) $T_s = 523 \ \text{K}$ (c) $T_s = 723 \ \text{K}$

Unique self organization process resulting in the formation of ring shaped nanostructures is apparent from the AFM images of the as-deposited films prepared at 0.15 mbar oxygen pressure. The very early phase of formation of ring structures can be observed in AFM images of film prepared at 300 K (figure 3.3a). Self assembled nano ring having outer diameter 600 nm and wall width less than 100 nm is viewed as a surface feature for film deposited at $T_s = 523 \ \text{K}$, but nano rings with increased wall
width (150 nm) and decreased outer diameter of 400 nm are observed for film deposited at $T_s = 723$ K [figures 3.3(b) & (c)]. The exact mechanism of nano ring formation is not satisfactorily explained so far. Van de Riet et al. [16] have tried to explain the nano ring formation using the model of re-sputtering from the substrate surface at high laser fluence. In our opinion, more than one mechanism plays their role for the formation of nano rings in the films. At higher laser fluence, the ejected particles in the plume collides the substrate surface with higher kinetic energy. Due to inelastic collision, the kinetic energy of the impinged particles can result in local heating and surface boiling. On further impingement of particles, outward pointing forces generates ripples to balance the surface free energy and consequently, the system finds equilibrium in a nano ring structure via material redistribution. The increased wall width for the nano ring observed for films deposited at $T_s = 723$ K can be due to increased diffusion assisted coalescence of the particles constituting the ring wall.

Figure 3.4(a) -- (c) 2D and 3D AFM images of annealed films deposited at $pO_2 = 0.15$ mbar at (a) $T_s = 300$ (b) $T_s = 523$ (c) $T_s = 723$ K (d) enlarged view of layered arrangement observed for the film deposited at $pO_2 = 0.15$ at $T_s = 523$ K
Figures 3.4(a)-(c) show the AFM images of the annealed films deposited at 300, 523 and 673 K at $p_2 = 0.15$ mbar. All these films present a non-uniform morphology. A self assembling of grains to form some ordered structural features is observed for the annealed films deposited at $p_2 = 0.15$ mbar at $T_s = 523$ K. The layered arrangement of grains can be observed from the enlarged view given in Figure 3.4(d). Some agglomerated grain growth is seen for the AFM images of annealed films deposited at $T_s = 673$ K at $p_2 = 0.15$ mbar.

### 3.3(c) SEM Analysis

The SEM images of the annealed films deposited at different substrate temperatures, in an oxygen ambient of 0.066 mbar is presented in Figures 3.5 (a) – (c) and it shows the distribution of nanowhiskers in the films. Cho et al., [17] have reported the formation of sub-stoichiometric tungsten oxide whisker growth on Silicon substrates. A similar anisotropic formation of star/flower shaped morphology oriented in different directions but with more surface coverage can be seen in the film deposited at 723 K. The presence of nanorods formation is also seen in the SEM image of this film.

Figures 3.6(a) - (c) show the SEM images of the annealed films which are deposited at $T_s = 300, 523$ and 723 K respectively for $p_2 = 0.10$ mbar. SEM image of the film deposited at 300 K flaunt a well arranged parallel stacks of nanorods of length $\sim 2$ microns and diameter less than 100 nm. These extended arrangements of rods are repeated in different orientations. SEM image of the annealed film, deposited at $T_s = 723$ K for $p_2 = 0.10$ mbar exhibit a distribution of isolated plate like surface features are discernable through out the film deposited at $p_2 = 0.10$ mbar.
Figure 3.6 (a) - (c) SEM images of annealed tungsten oxide films deposited at $p_{O_2} = 0.10$ mbar at $T_s$ (a) 300 (b) 523 (c) 723 K

Figure 3.7(a) - (c) SEM images of as-deposited tungsten oxide films for $p_{O_2} = 0.15$ mbar at $T_s$ (a) 300 (b) 523 (c) 723 K. Figure 3.7(d) - (f) SEM images of annealed tungsten oxide films deposited at $p_{O_2} = 0.15$ mbar at $T_s$ (a) 300 (b) 523 (c) 723K.

Figures 3.7(a) - (c) show the SEM images of the as-deposited films deposited at $p_{O_2} = 0.15$ mbar at three different substrate temperatures and figure 3.7(d) – (f) show SEM images of the corresponding annealed films. Figures 3.7(a) - (c) indicate the profound influence of deposition temperature on surface morphology. With increase in substrate temperature from 300 to 723 K, the texture of the films changes from a meso-porous network to a relatively smooth granular morphology. The meso-porous surface feature for the films deposited at 300 K can be due to thermodynamically uncontrolled growth kinetics occurring at high deposition rate and thereby slow migration rate of atoms at the cold substrate surface.
Intra-particle porous structure observed in the films deposited at 300 K disappeared with the evolution of disk shaped features along with stacking of nanorods on post-annealing it at 773 K. These disks seem to coalesce to form bigger structures in the annealed film. Instead of fine granular morphology for the as-deposited film prepared at $T_s = 523$ K, the SEM image (figure 3.7e) of the annealed film displays the presence of hazy and lumpy bigger structures dispersed in the matrix of fine grained crystallites. For the film deposited at 723 K also, the SEM image shows a remarkable difference in morphology between as-deposited and annealed films [figure 3.7(e) & 3.7(f)]. A very densely packed granular structure with lack of distinct grain boundaries along with coalesced irregular large plate shaped surface features is perceptible from the SEM images of annealed film. The drastic variation in surface traits between as-deposited and films annealed at 773 K suggests the lowering of surface free energy during post-annealing, ensuing in redistribution of surface characteristics. The non-uniform surface morphology of these films revealed through AFM images is well displayed through their SEM images also.

The assorted surface features obtained for thermally treated tungsten oxide films indeed suggest the lowering of interfacial tension yielding to the thermodynamic stabilization of the system during post-annealing. This lowering of interfacial tension during post annealing can promote the twinning and the preferential growth of nanoparticles or nanorods along their easy axis inducing the formation of a star-shape or flower shaped surface features [18].

3.3(d) UV-Visible Spectra Analysis

Figures 3.8(a) –(c) show the optical transmittance spectra of the as–deposited WO$_x$ films prepared under various ambient oxygen pressures as a function of substrate temperatures. Figures 3.9(a) - (c) exhibit the reflectance spectra of the films deposited at $pO_2 = 0.066$, 0.10 and 0.15 mbar as a function of their substrate temperatures. The films deposited at 300 K exhibits high transmittance compared to those deposited on heated substrates for the oxygen partial pressure of 0.1 and 0.066 mbar, whereas the films deposited at 300 K for $pO_2 = 0.15$ mbar shows lowest transmittance compared to films deposited at higher substrate temperatures. This can be accounted by the high scattering
losses induced by porosity and dissimilar orientation of the grains in this film as unveiled through their AFM and SEM images.

Figures 8(a) – (c) Optical transmittance spectra of tungsten oxide films prepared under different oxygen partial pressures as a function of substrate temperature (a) 0.066 mbar (b) 0.10 mbar (c) 0.15 mbar. The inset shows the corresponding \( (ahv)^{1/2} \) vs \( hv \) plot for each set of films.

Figure 8(d) Dependence of bandgap energy on substrate temperature for as deposited films as a function of oxygen pressure.

From the transmittance spectra, a red shift in absorption edge compared to that of film deposited at \( T_s = 300 \) K is observed for all the as-deposited films prepared at higher substrate temperatures. Similar results have been reported for WO\(_3\) films prepared by HFCVD techniques on silicon substrates [2]. This effect can be attributed to the thermal expansion of the film lattice and the temperature dependence of the electron–phonon interaction [19]. No such shift in absorption band-edge with substrate temperature was observed for tungsten oxide films prepared by RF sputtering in oxygen ambient, on unheated as well as heated glass substrates as reported by Kamal et al [20].
Figure 3.9 (a) - (c) Optical reflectance spectra of the films deposited at $pO_2 = (a)$ 0.066 (b) 0.10 and (c) 0.15 mbar as a function of substrate temperatures.

Figures 3.10(a) - (c) Optical transmittance spectra of annealed tungsten oxide films prepared under different oxygen partial pressures as a function of substrate temperature (a) 0.066 (b) 0.10 and (c) 0.15 mbar. The inset shows the corresponding $(a\nu)^{1/2}$ vs $\nu$ plot for each set of films. Figures 3.10(d) Dependence of bandgap energy on substrate temperature for annealed films as a function of oxygen pressure.
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Figure 3.11 (a) - (c) Optical reflectance spectra of annealed tungsten oxide films deposited at \( pO_2 = 0.066, 0.10 \) and 0.15 mbar as a function of substrate temperatures.

The optical transmittance and reflectance spectra of the annealed tungsten oxide films prepared at different oxygen pressures are shown in figures 3.10(a) – (c) and 3.11(a) – (c) respectively. Quantitative values of bandgap energy \( (E_g) \) are evaluated for both as-deposited and annealed films, using the method discussed in Section 2.3(e) of Chapter 2. The obtained bandgap values for the as-deposited films vary from 3.09 to 3.38 eV depending on the deposition parameters and for annealed tungsten oxide films, the bandgap energy vary from 2.89 – 3.22 eV. The inset of figures 3.8(a) – (c) and 3.10(a) – (c) show the plot of \((ahv)^{1/2}\) vs \(hv\) for bandgap determination at each oxygen pressure under investigation as a function of substrate temperature for as-deposited and annealed films respectively. The estimated bandgap values are found to be in well accordance with reported bandgap values for tungsten oxide films [21]. Figure 3.8(d) and 3.10 (d) show the dependence of optical bandgap energy on the substrate temperature under different oxygen partial pressures for the as-deposited and annealed tungsten oxide films. Corresponding to the red shift in absorption edge with substrate temperature a systematic decrease in bandgap with increase in substrate temperature has been observed for all the as-deposited films prepared at all oxygen partial pressures. The blue shift in bandgap energy with increase in substrate temperature observed for the annealed films can be attributed to increase in oxidation, packing density and microstructure of the annealed films.
Almost all the annealed films show a lesser optical bandgap value than that of the as-deposited films [Figures 3. 8(d) & 3.10(d)]. The XRD data shows that the as-deposited films are amorphous like structures whereas all the annealed films are polycrystalline in nature. Amorphous films consist of very small particles and hence larger number of grain boundaries and imperfections which lead to larger free carrier concentrations and the existence of potential barriers. The electric fields arising from these factors in the disordered state result in the widening of the optical bandgap. Similar results for blue shift in optical bandgap for amorphous thin films have reported for other transition metal oxide films such as V2O5 by Ramana et al., [22]. In the annealed polycrystalline films the band edges are sharp and the grains are larger in size. There can also be a contribution from internal stress developed in the polycrystalline film and effective decrease in the imperfections at grain-boundary regions. Similar results on red shift of bandgap with annealing and hence on crystallization has been reported for WO3 films by Sivakumar et al [23].

![Figure 3.12(a) - (c) Extinction coefficient (κ) of the films as a function of substrate temperature for (a) pO2 = 0.066 mbar (b) 0.10 mbar (c) 0.15 mbar](image1)

![Figure 3.13(a)- (c) Extinction coefficient (κ) of the films as a function of substrate temperature for (a) pO2 = 0.066 mbar (b) 0.10 mbar (c) 0.15 mbar](image2)
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The thickness of the films deduced from their spectral transmittance data vary between 100- 230 nm depending on the deposition conditions [24]. The extinction coefficient of the as-deposited and annealed films as a function of oxygen pressure for each substrate temperature is shown in figure 3.12(a) - (c) and 3.13(a) – (c). The \( \kappa \) value increases with substrate temperature for the as-deposited films prepared at lower oxygen pressures (0.066 and 0.10 mbar) whereas a reverse trend is observed for films deposited at \( p_{O_2} = 0.15 \text{ mbar} \). The high value of extinction coefficient for the films deposited at \( T_s = 300 \text{ K} \) at 0.15 mbar oxygen pressure can be attributed to their porous nature revealed through their SEM and AFM images. Table 3.2 summarizes the optical constants of the as-deposited and annealed films.

3.3(e) DC Electrical Resistivity Measurements

![Graphs showing electrical resistivity vs substrate temperature](image)

**Figure 3.14 (a) & (b)** Electrical resistivity vs substrate temperature as a function of substrate temperature for (a) as-deposited films (b) films annealed at 773 K.

The earlier reported values of DC electrical resistivity for physical vapor deposited tungsten oxide films are already discussed in section 2.3(f) of Chapter 2 [25-28]. Figure 14(a) & (b) shows the room temperature electrical resistivity of as – deposited and annealed tungsten oxide films. In the present study the resistivity values of the investigated films lie between 0.1 \( \Omega \text{m} \) to \( 0.6 \times 10^2 \Omega \text{m} \). Variation of resistivity with substrate temperature is drastic for the films deposited at lower oxygen pressures. The conductivity of \( \text{WO}_3 \) is determined by the non-stoichiometry originating from oxygen vacancies [29]. The electrical resistivity of the as-deposited films (amorphous films) is
found to be lower than the annealed films. The electrical resistivity of crystalline thin films is generally derived from two competing factors such as carrier mobility and carrier density. Though post-annealing of films in air can enhance crystallization, leading to higher mobility, annealing in air at a temperature higher than deposition temperature provide oxygen to the tungsten oxide films and can possibly decrease the carrier density resulting in increased resistivity for the annealed samples.

3.4 Conclusions

To summarize, tungsten oxide thin films have been successfully synthesized from metallic tungsten target using reactive pulsed laser deposition technique. Structural analysis using XRD indicates amorphous like features for all the as-prepared samples irrespective of the ambient oxygen pressure and substrate temperature. Thermal annealing of the as-deposited films at 773 K turned them to polycrystalline in nature. A phase change from monoclinic $W_{18}O_{49}$ to triclinic $WO_3$ and then to hexagonal $WO_3$ is observed in annealed films which are deposited at a $T_s = 723$ K at different oxygen pressures 0.066, 0.10, 0.015 mbar respectively. Morphological analysis using SEM and AFM techniques revealed the transformation of smooth very fine grain-like morphology with the evolution of nanowhiskers, nanorods and nano-sized star/flower like features upon thermal annealing the as-prepared samples. The optical bandgap evaluated from transmittance measurements for the as-deposited films vary from 3.09 - 3.38 eV with a red shift in absorption edge with substrate temperature compared to films deposited at 300 K, whilst the optical bandgaps of thermally treated films vary from 2.89 – 3.22 eV with a blue shift in absorption edge with substrate temperature compared to films prepared at 300 K. Indirect allowed interband optical transition is found to prevail in both the as-deposited and annealed films of tungsten oxide. Tungsten oxide thin films with transparency $\geq 75\%$ and low resistivity 0.1 $\Omega m$ is attained for films grown at $T_s = 523$ and 723 K for $pO_2 = 0.066$ and 0.1 mbar.
Table-3.1  X-ray crystal structure and lattice parameter for the annealed films deposited at $p_{O_2} = 0.15 \text{ mbar}$ for different substrate temperatures.

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Table -3.2 Optical constants of as-deposited and annealed tungsten oxide films

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<td></td>
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References


[9] JCPDS Card No. 36-101

[10] JCPDS card No.33-1387


[13] JCPDS card No.5-388


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