Chapter I

Introduction
In the current science and technology era, the branch of *Materials Science* has been evolving and fascinating by the researchers till to date and it opened doors for innovative design and fabrication of opto-electronic devices for future technologies. Materials science is briefly defined as the study of “*stuff*” and investigations of this branch narrate the relationship between the structure and properties of materials. Progress in the use of materials has marked civilization of mankind from the “Stone Age” and “Iron Age” to our age of semiconductors and polymers. Materials science and technology is a multidisciplinary approach to science that involves design, selection and utilization of three major classes of materials – Metals, Ceramics and Polymers (plastics). Materials science applies the analytical tools of physics as well as insights from chemistry and engineering (and even mathematics and computation) to forge this link between structure and properties as shown in the Fig. 1.1. This inter connection can lead to the improvement of the properties of known materials (such as steel or silicon), as well as new materials designed to meet new needs (superconductors, smart materials, nano structural materials etc.). The knowledge about materials properties, their impact and performance are more useful to make better, more economical and efficient “*stuff*” for ever.

![Diagram](image)

**Fig.1.1. Materials Science and Technology – A Multidisciplinary Approach**
In materials science, rather than haphazardly looking for and discovering materials and exploiting their properties, one instead aims to understand materials fundamentally so that new materials with the desired properties can be synthesized. The basis of all materials science involves relating the desired properties and relative performance of a material in a certain application to the structure of the atoms and phases in that material through characterization. The major determinants of the structure of a material and thus of its properties are its constituent chemical elements and the way in which it has been processed into its final form. In addition to industrial interest, materials science has gradually developed into a field which provides tests for condensed matter or solid state theories. Therefore studying about materials science can be a bridge to a career in any of these emerging technologies.

The foremost purpose of the contemporary material science is to tailor a material starting with its chemical composition, constituent phases and structure in order to obtain a desired set of properties suitable for a given applications. Among the materials that meet the current prerequisites, metal oxides with many interesting physical and chemical properties have been scientifically and technologically exploited in many fields like environmental science, electrochemistry, microelectronics, optoelectronics and relating fields. Depending upon their physical properties, they can be broadly categorized into the significant groups such as non-transition metal oxides and transition metal oxides. The non-transition metal oxides have a filled valence band which is derived from oxygen 2p atom and empty conduction band derived from the outer shells of metal atom. Transition metal oxides constitute a fascinating class of inorganic solids [1] that have been attracted the attention and constitute the backbone of solid-state/materials chemists aimed at realization of novel materials properties of technological importance [2, 3]. Among them, oxides of the early transition metals (periodic groups 4, 5, 6 and 7) containing d⁰ and d¹ electronic configuration are a special subclass, distinctly different from the other transition-metal oxides, showing several unique features. For example, the crystal structures of d⁰ metal oxides consist [4] of distorted metal-oxygen (MO₆) octahedra where the cation is displayed from the
centre of the octahedral. Several of the interesting features of these oxides can be
directly traced to this distortion. The occurrence of layered structures [5] and distinct
oxide hydrates for V₂O₅, MoO₃ and Re₂O₇ is a direct consequence of the distortion. The
high static relative permittivity and the consequent ferroelectric behavior and the
presence of soft phonon modes [6, 7] are the direct consequence of out-of-centre
distortion of MO₆ octahedra in d⁰ metal oxides [8].

Transition metal oxides exhibit a rich collection of interesting and intriguing
properties, which can be tailored for a wide variety of applications. Some of the
significant materials properties of current interest are spin-polarized metallic
ferromagnetism, negative thermal expansion, and second harmonic nonlinear optical
(NLO) susceptibility, fast ionic and mixed electronic/ionic conductivity for application
in solid state batteries, and last but not the least, high-temperature superconductivity. In
this regard many transition metal oxides have been prepared in bulk form or as thin
films, which paved the way for intensive research studies in the past several decades for
low-loss power delivery, quantum computing using cooper pairs, ultra-density magnetic
data storage and more recently spintronic applications.

Transition metal oxides exhibit a much wider range of electronic properties and
their electrical behavior ranges from the best insulators (e.g. Al₂O₃ and MgO) through
wide-band gap and narrow band gap semiconductors (TiO₂ and Ti₂O₃) to metals (V₂O₅,
Na₅WO₃ and ReO₃) and superconductors. Several Transition metal oxides exhibit
metal/non-metal transitions as a function of temperature. In case of non-Transition
metal oxides (exception of Sn)-have only one preferred orientation state. Other states
are inaccessible because too much energy is needed to add or remove an electron from
the cations where they are co-ordinate with O²⁻ ligands. Transition metal oxides behave
differently, in these the energy difference between a cation d⁰ configuration and either a
dⁿ⁺¹ or dⁿ⁻¹ configuration is rather small. The most obvious consequence is that many
transition elements have several stable oxides with different compositions [9].
The general formulae of the transition metal oxides are MO, M\textsubscript{2}O\textsubscript{3}, MO\textsubscript{2}, M\textsubscript{2}O\textsubscript{5}, MO\textsubscript{3}, M\textsubscript{n}O\textsubscript{2n-1} and M\textsubscript{n}O\textsubscript{2n+1}, where M represents the transition metal [10]. In simple metals, s - orbitals are main constituents of the conduction band whereas in the case of transition metal oxides, the s - electrons enter into deeper bonding orbitals. The conduction bands in the transition metal oxides are formed with oxygen 2p and metal d - orbitals. The oxygen 2p levels located in the lower energy leads to show ionicity [11]. Also, the directionality of ‘p’ and ‘d’ - electrons is manifested more directly in the transport phenomena. The presence of outer d - electrons in transition metal ions are the remarkable properties and these d - electrons can not be expelled either by a collective electron model (as in the case of s and p - electrons) or by localized electrons model (as in the case of f - electrons, which are tightly bound to the nuclei [12]). The weak interlayer forces of these materials offer the possibility of introducing foreign atoms between the layers which is the process of intercalation. Intercalation reaction is the basis on which the layered transition metal oxides are used as active layers/cathode materials in the design and fabrication of electrochromic/solid state micro-batteries. The insertion of lithium in transition metal oxides takes place topotactically with high theoretical energy density values which is a very interesting feature for their application in the field of electrochromic/electrochemical devices [13]. In recent years, the field of transition metal oxides has become a subject of intense study by the materials scientists in science & technology because of the novel characteristics and applications. A study of the prospective of these transition metal oxides not only seem as a challenging introduction to the solid state physics, chemistry and materials science and also provides a rich source of fascinating research problems for experimental and theoretical investigations and the application of these oxides to the energy device technology.

In addition, the transition metal oxides in thin films configuration have many striking properties. One of their most important features is that, their optical absorption can be switched reversibly under certain conditions, which is known as "chromism". By using this chromism phenomenon, it is possible to alter the transmission and reflection properties of glasses to regulate the radiated energy. This chromogenic
behavior is demonstrated most prominently in thin films of transition metal oxides, which are the most promising chromogenic materials for the fabrication of electrochromic windows (EC-windows) and large area passive displays. Recently great interest has been shown in the study of transition metal oxides as chromogenics, owing to their promising electro-, photo- and thermochromic properties. Unlike chromochromic, tinted, relative or photochromic coatings, which offer static modulation of incident radiation, but strikingly the optical properties of an electrochromic coating (the prime component of an EC windows) can dynamically modulate in response to the ever changing characteristics of solar radiation. The electrochromic effect in thin films of transition metal oxides has gained particular interest for the application of electrochromic windows (ECWs). These ECWs can allow variable throughput of luminous and solar radiation thereby energy saving benefits by controlling the fenestration performance by responding to the variation of the brightness of the environment. Nevertheless, electrochromic technology has remained as an active area for basic and applied research, with large possibilities for applications in emerging technologies. The interest was boosted with the realization that electrochromism was much of interest in fenestration technology as a means to achieve energy efficiency in buildings, and the concept of “chromism” was coined and captured the interest of researchers and general public. Therefore the study of electrochromics represents a very stimulating group of materials like transition metal oxides for scientific research curiosity and it is still to be expected great extent for technological break through in current science & technology.

Optically active thin film coatings can alter their optical properties as a function of changes in external conditions. The changeable optical characteristics can be obtained by different physical and chemical processes in a large number of materials, which are known as “Chromogenics” [14]. The chromogenic family of materials is ever expanding, with many types of new materials. Chromogenics cover any visibly switchable technology useful for glazing, mirrors, transparent displays and a variety of other applications. Materials with controllable light absorptance, transmittance or
reflectance possess a great technical relevance, because of their high potential applications. Single layers or multi-layers systems can be used for different types of devices that can modulate their optical characteristics as a function of temperature, intensity of irradiation, applied external potential, gases etc. In the near future, optically active thin films may be utilized to regulate the throughput of radiation energy for windows in buildings and cars, to maintain comfortable lighting and temperature, in sun glasses, as an optically active filter, or in systems with variable reflectance, as automotive rear-view mirrors, in displays, in sensors or detectors, as road signs and so forth [15 - 20]. The physical and chemical processes occurring in chromogenic materials and devices are of considerable scientific interest; because of electronic and ionic transport, changes in material composition, variation in structure or chemical potential, the formation of color centers, or small polarons and interfacial barrier effects, are all intercalated, i.e. the processes during the reversible optical switching are highly complex. The mechanisms responsible for the reversible variation of optical properties of films may basically divide into three categories:

Thermochromism:

The films change their optical properties as a function of substance temperature. The films alter their optical data reversibly when heated and return to their original properties when cooled to the starting temperature [21].

Photochromism:

A reversible absorption change triggered when a thin film is exposed to different irradiations and it regains the original properties with out irradiation, this phenomenon is known as Photochromism [22]. The induced optical absorption disappears spontaneously upon removal of the activation source. The photochromic phenomenon has been observed in various organic and inorganic substances in solid form or solution. The energy of the electromagnetic irradiation ($h\nu$), which induces the formation of the colored (activated) species, is usually situated in the blue region or UV range of the
spectrum. Although, the photochromism was first phenomenological observed in inorganic substances. Subsequently developmental work has reproduced the number of organic materials considerably. The photochromic processes of these organic substances are classified into “heterolytic cleavage”, “hemolytic cleavage”, “cis-trans isomerization” and “tautomesirn [23]. However the hemolytic cleavage is the most studied photochromic mechanism studied so far. The photochromism in inorganic materials invariably involves imperfections of the substances. Like localized defects, impurities, and dislocations are responsible for formation of electron – hole pairs in the excitation process and for forming color centers, by the trapping of free carriers. The energy for bleaching color centers can be obtained either by illumination with higher in the energy range of the induced absorption band of the color centers.

Electrochromism:

A unique property of thin films or thin film systems to change color, due to an applied potential, and change back to the original state by a potential reversal, is defined as Electrochromism. From a technological point of view, thin electrochromic films have been investigated extensively and they are the most promising candidates for various applications in the proximate future [24].

The substances which exhibit electrochromism are termed as electrochromic (EC) materials and in general both organic and inorganic oxide substances are identified as EC materials [25 - 27]. In the past decade, several numbers of organic materials were found to be exhibiting electrochromism. In particular, the Viologens were the best known materials, which have been investigated with regard to their application in electrochromic display devices. One attraction of the different types of Viologens is the possibility of choosing various colors by introducing different dopants into Viologen molecules. Electrochromism is also observed in groups, such as pyrazoline, pyridine or organometallics, such as poly tungsten anions and phthalocyanines of lanthanides. The group of organic materials also includes polymers [28], in these a chemical oxidation/reduction reaction occurs between the polymer and the dopant [29]. This
electrochemical oxidation/reduction causes a change of color; as a result these conductive polymers are useful as electrochromic materials. Comparatively, electrochromic polymers possess some disadvantages as mentioned given below in comparison to the inorganic electrochromic materials.

1. Organic polymer materials are known to be chemically unstable.
2. The organic polymers are generally affected by UV radiation; this UV instability is the responsible for short life time of polymer based devices used in outdoor applications. Because the UV light produces an undesired, irreversible side reaction of the weakly bound hydrogen and nitrogen ions.
3. The polymers do not adhere well onto the surfaces of inorganic transparent electrodes (ITO).

Inorganic materials are generally oxide films possessing both electronic and ionic conductivity. In these, the mechanism of coloration is described with a double injection of electrons and small ions to maintain charge neutrality. When an ionic species diffuse in the material, the driving force for macroscopic diffusion is the gradient of the chemical potential ($\mu$), which determines the working electrode potential as follows,

$$V = - (\mu - \mu_{\text{ref}})/e \quad \cdots \cdots \quad (1)$$

'\(e\)' stands for the positive elementary charge

'\(\mu_{\text{ref}}\)' = Gradient in chemical potential.

Electrochromic (EC) materials change their optical properties in response to an electric field and can be returned to their original state by a field reversal. The electrochromic materials promise to have major advances in energy-efficient window technology, helping to achieve the goal of transforming windows and skylights from an energy liability in buildings to an energy source for the nation's building stock. EC windows save energy by reducing cooling loads and reducing electric lighting energy consumption when dimmable lighting systems are used. However material
performance, optical characterization, colouration efficiency, durability and fabrication
research remain major foci of the electrochromic R & D community. The EC windows
have the following major advantages, such as

- A small switching voltage (1 – 5 V).
- Show specular reflection.
- Possess a gray scale.
- Require power only during switching.
- Exhibit adjustable memory, up to 12 – 48 hours.

Further, these inorganic transitions metal oxides are classified into (a) Anodic
electrochromic materials and (b) Cathodic electrochromic materials.

"Anodically coloring materials are those with an oxide colored state, i.e. they
color when a positive potential is applied"

\[
\text{Bleached} \quad \text{Colored} \\
\text{MO}_x + YA^- + Yh^+ \leftrightarrow A_y\text{MO}_x \\
A^- = F^-, CN^-, OH^-; 0 < Y < 0.3
\]

Many hydrous oxide films in group VIII (platinum group) exhibit anodically coloring
electrochromism [30]. The oxide films of Ir, Fe, Ni, Rh and Co were found to be
demonstrating anodic electrochromism. V_2O_5 films show a heavy anodic coloration in
the UV region (300 – 500 nm) and weak cathodic coloration in the NIR.

"Cathodically coloring substances possess a reduced colored state, i.e. they color
at negative potential".

\[
\text{bleached} \quad \text{colored} \\
\text{MO}_x + YA^+ + Ye^- \leftrightarrow A_y\text{MO}_x
\]

The transition metal oxides such as WO_3, MoO_3, V_2O_5, Nb_2O_5 and TiO_2 were
recognized as cathodic electrochromic materials and they show highest oxidation states.
Table – I: List of anodic electrochromic materials

<table>
<thead>
<tr>
<th>Sl.No</th>
<th>Substance</th>
<th>Bleached state</th>
<th>Colored state</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Iridium Oxide</td>
<td>Transparent</td>
<td>Blue-Black</td>
<td>31</td>
</tr>
<tr>
<td>2</td>
<td>Nickel Oxide</td>
<td>Transparent</td>
<td>Yellow, dark bronze</td>
<td>32</td>
</tr>
<tr>
<td>3</td>
<td>Iron Oxide</td>
<td>Transparent</td>
<td>Blue - black</td>
<td>33</td>
</tr>
<tr>
<td>4</td>
<td>Rhodium oxide</td>
<td>Yellow</td>
<td>Dark green</td>
<td>34</td>
</tr>
<tr>
<td>5</td>
<td>Rhodium oxide</td>
<td>Yellow</td>
<td>Brown purple</td>
<td>35</td>
</tr>
<tr>
<td>6</td>
<td>Cobalt Oxide</td>
<td>Red purple</td>
<td>Grey - Black</td>
<td>36</td>
</tr>
<tr>
<td>7</td>
<td>Vanadium Pentaoxide</td>
<td>Yellow</td>
<td>Green – Blue</td>
<td>37</td>
</tr>
</tbody>
</table>

Table: II List of cathodic electrochromic materials

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Substance</th>
<th>Bleached state</th>
<th>Colored state</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Tungsten trioxide</td>
<td>Transparent</td>
<td>Blue</td>
<td>38</td>
</tr>
<tr>
<td>2</td>
<td>Molybdenum oxide</td>
<td>Transparent</td>
<td>Blue</td>
<td>39</td>
</tr>
<tr>
<td>3</td>
<td>Vanadium pentaoxide</td>
<td>Yellow</td>
<td>Blue-black</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>Nb$_2$O$_5$</td>
<td>Yellow</td>
<td>Blue</td>
<td>41</td>
</tr>
<tr>
<td>5</td>
<td>Titanium Oxide</td>
<td>Transparent</td>
<td>Light yellow</td>
<td>42</td>
</tr>
<tr>
<td>6</td>
<td>WO$_3$/MoO$_3$</td>
<td>Transparent</td>
<td>Dark blue</td>
<td>43</td>
</tr>
<tr>
<td>7</td>
<td>WO$_3$/TiO$_2$</td>
<td>Transparent</td>
<td>Blue</td>
<td>44</td>
</tr>
<tr>
<td>8</td>
<td>Copper Oxide</td>
<td>Transparent</td>
<td>Light-black</td>
<td>45</td>
</tr>
</tbody>
</table>

It is note worthy that; the performance of electrochromics as active layers in smart windows significantly depends upon the structure of the EC material. Generally with respect to bulk crystalline structures the electrochromic oxides possess the following structures: (a) Perovskite – like structure, (b) Rutile – like structure, (c) Layer and block structure.
Perovskite structure:

The Perovskite structure, with a general composition CMeO₃ is represented in Fig. 1.2. The 'Me' ions occupy the corners of a primitive unit cell and 'O' ions bisect the unit cell edges. The central atom (C) is neglected at the moment since it is absent in the electrochromic oxides of most interest. The corresponding CWO₃ perovskite lattice

![CWO₃ structure diagram]

Fig.1.2. The representation of perovskite structure

(defective) perovskite MeO₃ configuration is often referred to as the rhenium oxide structure. In ReO₃ structure an infinite array of corner-sharing octahedral each with a metal ion is surrounded by six equidistant oxygen ions. In between these octahedral, there are extended tunnels that can serve as conduits and intercalation sites for small ions.

E.g. 1. Tungsten trioxide (WO₃), Molybdenum trioxide (MoO₃) and SrTiO₃.

Rutile-like structure: The rutile structure builds from almost octahedral MeO₆ units forming infinite edge-shared chains. These chains are arranged so that they form an equal number of ida vacant channels.
E.g.1. Titanium oxide (TiO$_2$) consist rutile like-structure, in which infinite planar double chains of TiO$_6$; these chains are connected by corner-sharing. Empty sites also form double chains or zig-zag tunnels.

2. Vanadium dioxide (VO$_2$) is of simple rutile-type, Inridium oxide (RuO$_2$).

**Layer and block structure:** The layer and block structures form a somewhat undefined group of electrochromic materials.

E.g. Hydrated nickel oxide shows pronounced anodic electrochromism, NiO, V$_2$O$_5$ and Nb$_2$O$_5$.

Therefore in spite of the substantial research effort from the birth of electrochromism, both tungsten and molybdenum trioxides have been recognized and continue to be the favorite candidates as the cathodically coloring primary EC materials in EC windows despite long standing efforts on polymeric and organic alternates. The reason is that, these oxides form a group of predominantly ionic solids that exhibit a wide range of optical, electrical, and chromogenic properties. In particular, tungsten trioxide is the most stable and best electrochromic material owing to its interesting physical and chemical properties. Similarly to tungsten trioxide, molybdenum trioxide also exhibits chromogenic properties for a given inserted charge. The close position of its optical absorption peak to the human eye sensitive peak makes this material very attractive for many applications. In addition to this, molybdenum trioxide has been recognized as best photochromic material due to its potential optical, electrical, catalytic and chromogenic properties. In view of the novel characteristics and multifarious applications of both tungsten and molybdenum trioxides, the present investigations are aimed to study the growth, characterization and chromogenic applications.

### 1.1 Importance of the Tungsten trioxide

Among several transition metal oxides, tungsten trioxide has been recognized as one of the best and alternative electrochromic material, owing to its exceptional
physical, chemical, structural, optical and electrochromic/electrochemical properties in comparison to other electrochromic materials [46]. Tungsten trioxide also exhibit different types of chromogenism, i.e thermochromism, photochromism and some non-reversible coloration processes. In addition, the physics and chemistry of many other optically active electrode oxides are fairly similar, so that tungsten trioxide can be served as a more convenient model for elucidating the salient properties of the whole class of optically active layers. Despite various inorganic compounds, tungsten trioxide in thin film configuration has significant and persisting electrochromic properties over the other on reversibility, stability; excellent response speed, durability with high coloration efficiency [47]. Tungsten trioxide possesses good chemical stability and requisite ionic as well as electronic conductivity imperative for switching between the colored and bleached states during electrochromic/electrochemical studies.

The tungsten trioxide demonstrates different optical modulations in amorphous and crystalline phases during electrochromic coloration process in the visible, near infrared regions in solar energy spectrum. It is generally accepted that the injection and extraction of electrons and ions represent a basic rule to interpret the electrochromism of this material with regards to optimization of the tungsten trioxide layer. In this regard, tungsten trioxide thin films exhibit appropriate absorption spectral range in the colored phase, high coloration efficiency in terms of absorption by means of low charge injection, fast response both in coloration and bleached states and low self bleaching speed when no potential is applied. Thin films of tungsten trioxide offer a number of other favorable properties such as, angle independence, continuously variable intensity of coloration, capability of storage of information with out energy supply, they exhibit an adequate coloration and bleaching rate with UV stability and they have a long operational temperature range. Tungsten trioxide (WO₃) in thin film configuration demonstrates superior characteristics of low power consumption and low stress for viewer’s eyes. In addition WO₃ offers better EC properties such as (i) Appropriate absorption spectral range in the colored phase, (ii) High coloration efficiency in terms of high absorption by means of low charge injection, (iii) Fast response both in
coloration and in bleaching steps and (iv) Low self-bleaching speed when no potential is applied. Due to these exclusive and intriguing electrochromic properties, tungsten trioxide thin films continue to be the favorite candidate as the cathodically coloring primary electrochrome active layer in electrochromic smart window technology despite long standing efforts on polymeric and organic alternates. When tungsten trioxide thin films are adapted in the smart windows as the primary active layer, they can adjust the room temperature by responding to the variation of the brightness of the environment dynamically modulating the optical transmittance [48].

1.1.1 Structure

The tungsten trioxides consist of WO₆ - Octahedra arranged in various sharing (Corners, edges, planes) configurations. The main differences between the phases are shifts in the position of the ‘W’ atoms within the Octahedral, and variations in W – O bond lengths [49]. The simplest form with a general composition, WO₃ or LiWO₃ is the (defect) perovskite structure as shown in the Fig. 1.3. As drawn, the ‘W’ ions occupy the corners of a primitive cell, and ‘O’ ions bisect the unit cell edges. The central atom is absent at the moment and will be denoted as Li or Na after intercalated ions occupying symmetric positions. Each ‘W’ ion is surrounded by six equidistant oxygen ions and each ‘O’ ion is bound to two tungsten ions in linear configuration, which can be represented as W⁶⁺ - O²⁻ - W⁶⁺. The stable Monoclinic WO₃ can have a ReO₃ - type structure (corner sharing arrangement of Octahedra). An infinite array of corner sharing WO₆ - Octahedra is formed like in Fig. 1.4 and the slight rotation of these octahedra with respect to each other, as well as unequal bond lengths in octahedral co-ordination, causes lattice distortions and reduces the symmetry [50, 51].

The displacement of the tungsten atom inside the octahedron is stabilized by an increase in covalence between the tungsten and oxygen atoms [52]. It is important that the octahedra are not strongly distorted, but the tungsten atoms are off-center and the octahedral are rotated to form diamond shaped cages channels. These Octahedras are in
J-Oc-

Fig. 1.3 Unit Cell for the perovskite lattice. (Part-I) and Octahedral symmetries (part-II) in the perovskite structure

Fig. 1.4 One layer of the Monoclinic WO$_3$ structure in the corner-sharing arrangement of Octahedra (ReO$_3$-type)

Fig. 1.5 The Monoclinic WO$_3$ structure ReO$_3$ type

Fig. 1.5a One layer of the Monoclinic WO$_3$ structure in the edge-sharing arrangement of Octahedra.
planes perpendicular to the [001] hexagonal axis and they form four numbered rings in the XY or [001] plane. These layers are stacked in arrangement and are held together by weak van der Waal’s forces. The stacking of such planes along the Z-axis are responsible to the formation of tunnels between the Octahedras as represented in Fig. 1.5. In the extended tunnels the small ions can stay or move in case of an exterior force, which leads to the possibility of ionic transport and intercalation in the structure, and mechanism for electrochromic materials.

The structure of the crystalline tungsten trioxide is based on corner sharing octahedral [53] and the basic building blocks are similar in the amorphous structure, although bond lengths and bond angles exhibit considerable disorder. The bonds are mainly of ionic character and in case of stoichiometric WO₃ can be pictured as being composed of W⁶⁺ and O²⁻ ions. An energy level diagram of the two oxides can be made as shown in Fig. 1.6. In that the atomic s, p and d levels of tungsten (W) are indicated, as well as the 2s and 2p levels of oxygen (O). The positions of these levels on the vertical energy scale are governed by their values for the isolated atoms as well as by the Madelung energies of the atoms when located in the pervoskite lattice. Each ‘W’ ion is octahedrally surrounded by six oxygen ions and each oxygen is linearly flanked by two ‘W’ ions. As a consequence of the arrangement, the ‘d’ level is split up into eₗ and t₂g levels as shown in the left hand part of the Fig. 1.6. The splitting arises because the eₗ orbitals point directly at the electronegative oxygen (O), where as the t₂g orbitals point away from the nearest neighbors into empty space and are hence lower in energy. Similarly the O 2p orbitals are split as indicated in the right-hand part of the Fig. 1.6. The 2pₓ orbitals are point directly at the nearest electropositive ‘W’ ions, where as 2pᵧ orbitals point into empty space. The number of states available for electron occupancy is fixed for each band i.e. the t₂g band has a capacity for six electrons (allowing for spin degeneracy), and the pₓ orbitals point into empty space. The number of states available for electron occupancy is fixed for each band i.e. the t₂g band has a capacity for six electrons (allowing for spin degeneracy), and the pₓ band has a capacity for twelve electrons (allowing for spin and electron degeneracy). Therefore tungsten trioxide has 24
electrons in the valence band, so that the Fermi energy lies in the gap between the $t_{2g}$ and $p_z$ bands. The band gap is wide enough for this material to render the material as transparent. Therefore in tungsten trioxide the excess electrons must enter the $t_{2g}$ band and the material, in principle transforms from a transparent to an absorbing depending on the localized states of electrons.

![Perovskite structure](image)

**Fig. 1.6** Schematic band structure for $\text{WO}_3 (\text{ReO}_3)$ defect perovskite structure.

If the film is in transparent state, the fermi level is in the band gap because the oxide has the same number of valence electrons, i.e. it has no conduction electrons. When small voltage is applied across the film, the fermi level moves upwards into the 5d orbitals of tungsten when external ions and electrons enter into the oxide, this process gives the blue coloration to the film. Similarly the fermi level moves downwards when the ions and electrons are removed, so the film becomes transparent again. In addition to the transparent oxide tungsten trioxide, there exist a number of sub-stoichiometric so called magneli phases of the forms $\text{W}_m\text{O}_{3m-1}$ and $\text{W}_m\text{O}_{3m-2}$ ($m = 1, 2, \ldots$) all the way down to $\text{WO}_2$ [54]. The color of crystalline tungsten trioxide ranges from blue to grayish as described in the following Fig. 1.7, when the O/W ratio decreases from $\sim 3.0$ [55, 56].
The color and color changes in thin films at different compositions are much weaker than in the bulk form due to much smaller thickness, and hence smaller absorption. A large interest in tungsten oxide materials in part, from the ability to join basic $\text{WO}_6$ building blocks together to give variety of crystal structures provided by different intercalation channels as shown in the following Fig. 1.8.
In particular, the monoclinic structure consists of corner-sharing distorted octahedra. Oxygen atoms are at the corners of an octahedron and a tungsten atom occupies a position slightly off center. This gives to a structure with infinite chains of alternating long and short W–O bonds running in all three crystallographic distortions as shown in the Fig. 1.9.

In thin film configuration, the structure of the tungsten trioxide is influenced by the temperature and it exhibits different crystal structures as reported in the following table - III.

Table: III The crystal structures of WO₃ thin films at various temperatures.

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Temperature</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>133 K - 223 K</td>
<td>Monoclinic (LT)</td>
</tr>
<tr>
<td>2</td>
<td>223 K - 290 K</td>
<td>Triclinic Phase</td>
</tr>
<tr>
<td>3</td>
<td>293 K - 673 K</td>
<td>Monoclinic (RT)</td>
</tr>
<tr>
<td>4</td>
<td>673 K - 1013 K</td>
<td>Orthorhombic Phase</td>
</tr>
<tr>
<td>5</td>
<td>&gt; 1013 K</td>
<td>Tetragonal Phase</td>
</tr>
</tbody>
</table>

1.1.2 Applications of WO₃ Thin films

Numerous applications of WO₃ thin films for EC and related devices make it one of the most versatile materials. Some of the current applications science technology, that are addressed here included as follows,

1. **PV powered EC-smart windows**: An integrated photovoltaic-powered (PV-EC) window is the obvious choice, particularly since PV technology is making a strong inroad in building facades. Moreover, the operational characteristics of both PV and EC technologies are generally compatible. A small area of PV cells can provide sufficient electric power to operate a large-area EC window.
2. **PEC device:** A dye-sensitized solar cell electrode was recently combined with an EC film to produce, which is known as a PEC window. The coloration process is equivalent to charging a battery; the photovoltage generated by the dye-sensitized electrode is used to charge the EC layer. The self-powered PEC cell has several advantages over the use of conventional PV for large-area window or display applications.

3. **Gas sensors:** The sensors are designed based on either the changes in electrical conductivity or optical properties. It is highly recommended for detection of environmentally sensitive gases such as H$_2$S, NO, Cl$_2$, O$_2$, O$_3$, NH$_3$, and organic vapors.

4. **Chemichromic WO$_3$ film for biosensor:** Photo-biological production of H$_2$ by green algae is actively pursued at NREL for the Hydrogen Energy Program. The research activity involves genetically selecting mutants of the green alga *Chlamydomonas reinhardtii*, which produces H$_2$ from water under increasing oxygen pressure. Based on the chemichromic effect of WO$_3$ thin film (coloration and bleaching in the presence of H$_2$ and oxygen, respectively) a screening procedure was developed to identify those H$_2$-producing mutants with enhanced O$_2$ tolerance.

5. **Solar energy conversion and storage cells:** A typical EC display device used white TiO$_2$ pigment dispersed in ethylene glycol and H$_2$SO$_4$ as a background electrolyte material. From the optical response characteristic of this device, the WO$_3$ thin film which is in contact with TiO$_2$ turns into blue due to irradiation of the film with UV light even without applying an external electric field, which was attributed to transfer of photo-generated electrons in TiO$_2$ to WO$_3$ films. This led to an extensive research and development effort on a solar conversion and storage device.
1.2 Importance of the Molybdenum trioxide

Molybdenum trioxide (MoO$_3$) is an alternative transition metal oxide semiconductor which received significant attention as an active electrode for electrochromic (EC) devices [57, 58]. The molybdenum trioxide is a wide band gap n-type semiconductor that acts as catalyst in many reactions involving hydrogen and oxygen molecules. It demonstrates electro-, photo-, and gaso-chromic effects by virtue of which the material is of much interest for the development of electrochromic display devices, optical switching coatings and smart window technology [59]. It forms non-stoichiometric thin films on vacuum evaporation owing to the decomposition and preferential evaporation of the lower vapour pressure constituent atomic species [60]. Such films are oxygen deficient materials (MoO$_{3-x}$) containing excess metal atoms, which act as doping centers, which can control the electrical and optical properties of MoO$_3$. The presence of non-stoichiometry is often associated with color centre formation, specifically by trapping the electrons at anion (oxygen) vacancies [61]. Therefore these non-stoichiometric MoO$_3$ thin films demonstrate new optical absorption bands (i.e. shows new color) after it is irradiated with UV light [62].

1.2.1 Structure

Molybdenum trioxide (MoO$_3$) crystallizes in layered orthorhombic structure and possesses an n-type semiconducting property [63]. The layered structure of MoO$_3$ consists of double octahedral sheets composed of edge-sharing octahedral MoO$_6$ units, which have six oxygen ions and one molybdenum ion on their vertex and centre respectively [64]. This layered semiconducting molybdenum trioxide has attracted much attention as interesting functional materials because of their unique properties, such as large surface area, guest molecule accommodation in their inter layers, delaminating and photocatalytic property [65]. MoO$_3$ exists in two crystalline polymorphous, the thermodynamically stable orthorhombic α-MoO$_3$ and metastable monoclinic β-MoO$_3$ phase. The two polymorphic phases of MoO$_3$ (α, β) are presented Fig. 1.10. The α-MoO$_3$ (Fig. 1.10a) crystallizes with orthorhombic symmetry
Fig. 1.10 Schematic representation of the structure of MoO₃ phases: (a) the layered α-MoO₃ phase with an orthorhombic lattice differs from the β-MoO₃ phase; (b) with a monoclinic lattice related to the three-dimensional ReO₃ structure.

(a = 1.3855 nm, b = 0.3696 nm, and c = 0.3963 nm) with four formula units per unit cell. The α-MoO₃ single-phase can be represented as double layers of linked distorted MoO₆ octahedra parallel to (010) planes. Within each double layer MoO₆ octahedra form edge-sharing zig-zag rows along the [001] direction and corner-sharing rows along [100] direction [66]. Successive layers are held together by weak interlayer forces with easy cleavage along (010) planes. The β-MoO₃ phase (Fig. 1.10b) with a monoclinic symmetry (a = 0.7122 nm, b = 0.5366 nm, c = 0.5566 nm, and β = 92.01°) does not contain the van der Walls gap of α-MoO₃. The orthorhombic unit cell of MoO₃ extends over two layers and contains four formula units and belongs to the space group of D₄h. It follows from the group theory those 48 eigen modes at the centre of Brillouin zones are described by atomic displacements either parallel or perpendicular to the c axis [67].
1.3 Literature Survey on Tungsten trioxide thin films

S. Penner et al. [68] prepared thermally evaporated WO$_3$ thin films onto vacuum-cleaved NaCl (001) crystals at various substrate temperatures. They explored the structure, morphology and composition of pure WO$_3$ thin films under different oxidative and reductive treatments in the temperature range 373 – 873 K. On set of crystallinity in the films was observed at substrate temperature of 430 K and XPS measurements were revealed the presence of W$^{6+}$ state in the film irrespective of the preparation conditions. The as deposited films were annealed in the temperature range 473 – 773 K and considerable changes were observed in crystallization of the oxidized WO$_3$ films at 673 K in an 1 bar O$_2$ which attributed to the monoclinic structure. At higher oxidation temperatures (773 K) the WO$_3$ films exhibited predominant hexagonal structure and persisted up to 873 K. The WO$_3$ – Ga$_2$WO$_3$ thin films were prepared at two different mixtures of WO$_3$ with Ga$_2$O$_3$ to suppress the structural modifications. They noticed that, irrespective of the Ga$_2$O$_3$ content, the reconstruction of the WO$_3$ thin films is completely suppressed. The reduction of the WO$_3$ thin films was performed in 1 bar H$_2$ in the temperature range 473 – 773 K and from the XPS measurements they observed the formation of sub-stoichiometric films and eventually induced the formation of the $\beta$ – W metal structure.

The tungsten trioxide thin films were grown using modified hot filament CVD technique on silicon substrates maintained at various substrate temperatures by S. Pal et al. [69]. The microstructural, surface morphological and optical properties of the deposited were explored as a function substrate temperature ($T_s$). The XRD measurements of the films revealed the amorphous nature of the films prepared at $T_s < 330^\circ$ C and exhibited monoclinic structured WO$_3$ films at $T_s = 430^\circ$ C. The broad band is observed at near 950 cm$^{-1}$ and no features in the 710 – 811 cm$^{-1}$ region of Raman spectra for WO$_3$ films deposited at $T_s = 30^\circ$ C, which attributed to amorphous nature of films. They observed the increase of intensity of the RS peaks in the region 710 – 818 cm$^{-1}$ with the increase of substrate temperature to the higher values.
(T_s > 130° C). From the AFM results, they reported that with the enhancement of substrate temperature the sample surface becomes smoother and films were composed of small grains. With the increase of substrate temperature the optical transparency of the films in visible region increased and absorption maximum shifted towards the UV region. The films were found to be sub-stoichiometric and exhibited small shoulder at binding energy 33, 34 and 35 eV in the XPS spectra of the films, which attributed to the presence of W^5+, W^4+ and W^3+ states. From their investigation they declared that fully stoichiometric WO_3 thin films were can be obtained at high substrate temperatures.

Y. Suda et. al [70] prepared tungsten trioxide thin films on the flexible indium tin oxide (ITO) substrates using pulsed laser deposition method. The temporal evolutions were examined from optical emission spectra (λ = 400 – 420 nm) from the plume produced by ablating WO_3 targets at an oxygen partial pressure of 10 Pa. They examined optical transmittance as a function of the oxygen/argon gas mixture. The films grown in O_2 (100%) gas were found to be high transparent and with the increase of argon gas percentage the transparency in the films was decreased. The films prepared at T_s < 300° C were amorphous in nature and with the increase of substrate temperature the crystallinity of the films was increased. They reported that the crystallinity of WO_3 thin films on glass substrates was independent of oxygen partial pressure. The compositional studies for the WO_3 films were carried out by XPS measurements and noticed the presence of spectral lines corresponding to W^6+, W^5+ and W^4+ states. They concluded that, the WO_3 films grown onto the flexible ITO substrates exhibited better electrochromic properties even the substrates were bent.

The W-Ti thin films were deposited by the Ar^+ sputtering of W (70%) – Ti (30%) target onto the silicon substrates by S. Petrovic et. al [71]. The surface structure and composition of W-Ti thin films were studied using XRD, STM and XPS respectively after exposing the samples to the air. They employed Grazing incidence X-ray diffraction technique for effective characterization at near the surface region of the film. From STM results the estimated lateral dimension of the grain was 32 nm and
the mean surface roughness of silicon substrate and deposited film roughness were found to be nearly equal, which indicates that prepared film followed the morphology of the substrate. The XPS results suggested that, sputtered W – Ti composite films had significantly different structure and composition with respect to surface of the film. From their investigation they reported that surface of the film had dominantly TiO₂ crystalline phase, in which the tungsten concentration is completely missing in the first atomic layer due to exposure of the samples to the air.

Y. Yamada et. al [72] deposited WO₃ thin films using RF sputtering and discussed the effects of structure and surface morphological features on photo/electrochemical properties. They observed that, the films prepared at low substrate temperature (T_s) or low total pressures were exhibiting (002) as predominant orientation and thick WO₃ films had (020) orientation at high T_s and total pressures. The SEM pictures of the films deposited at low substrate temperature displayed round shaped grains and with the increase of thickness the size of the grains became disk shaped particle. They summarized that current density increased with the increase of total pressure.

T. Takahashi et. al [73] deposited WO₃ thin films on glass substrates by radio frequency magnetron sputtering technique in presence of 80% Ar – 20% O₂. They investigated the influence of substrate to source distance (D_{T,S}) and working gas pressures (p_w) upon the structure, optical properties of the films. The deposition rate was observed to be decreased with the increase of (Ar + O₂) gas flow irrespective of the substrate to source distance. From the XRD measurements they reported that, the films grown at D_{T,S} of 70 mm showed amorphous structure and films prepared at D_{T,S} of 40 mm were found to be polycrystalline with monoclinic structure. They attributed the presence of compressive stresses caused to decrease the particle size in the films prepared at high gas pressures. The films exhibited lower optical transmittance prepared at lower gas pressures and noticed the shifting of fundamental absorption edge towards lower wavelength side with enhancement of both working gas pressure and D_{T,S}. They
concluded that, the WO$_3$ films grown at $D_{TS}$ of 40 mm and $p_w$ of 0.5 Pa exhibited comparatively higher efficiency than that of the films deposited at other conditions.

The nano structured intrinsic WO$_3$ thin films were deposited by reactive pulsed laser deposition technique and explored the influence of substrate temperature on their microstructural and optical properties by K.J. Lethy et. al [74]. The structural characterizations were carried out using both XRD and GIXRD techniques and from the obtained GIXRD data they reported the (001) as the predominant orientation. They evaluated average grain size of the nano particles as 40 nm for the films grown at $T_s = 300$ K. The micro Raman spectra for the films prepared at 300 K exhibited very intense RS bands at 807 cm$^{-1}$ and 710 cm$^{-1}$, which were attributed to the asymmetric stretching vibrations of O-W-O. The SEM figures were evidenced for the formation of well defined crystallites of dimensions around 50 nm for the films prepared at 300 K and observed the enhancement of grains size with the increase of substrate temperature to the higher values. They concluded that films prepared at higher substrate temperatures were exhibiting higher optical transmittance with an optical band gap in the range of 3.24 eV.

An electrochromic device with the configuration of (ITO/WO$_3$/Propylyne Carbonate (PC) + LiClO$_4$+HNO$_3$/NiO/ITO) was fabricated by Y.K. Fang et. al [75] and investigated it’s performance. They used (PC solution containing LiClO$_4$ +HNO$_3$) as electrolyte instead of (PC+LiClO$_4$). The optical transmittance spectra were recorded for ECD at different volume ratios of electrolyte and observed increase of optical switching speed of the device with the augmentation of HNO$_3$ volume ratio in the electrolyte. They reported 22 sec and 1 sec for coloring and bleaching transitions times respectively. From the results they attributed the improvements due to the injection of larger number of $H^+$ ions from the added HNO$_3$ gives more color centers in WO$_3$. Finally they optimized the volume ratio of HNO$_3$ 1/200 to attain good durability and switching speed.

The WO$_3$ thin films were deposited using reactive dc magnetron sputtering and investigated the emittance modulation of single layers of WO$_3$ films by A.-L. Larsson.
et. al [76]. In particular, they compared the infrared properties of amorphous, polycrystalline and nano crystalline WO$_3$ films prepared by gas evaporation technique. From XRD measurements they observed the formation of amorphous films at $T < 200^\circ$C and above $300^\circ$C the polycrystalline films were obtained. For 1.45 $\mu$m thick sputtered amorphous film, they noticed shifting of oscillations in reflectance spectra towards longer wavelength side with the increase of Li concentration. The reflectance spectra for nano crystalline films exhibited strong absorption at 10-25 $\mu$m due to the Reststrahlen band of tungsten oxide. At different intercalation levels, the reflectance spectra were recorded for crystalline WO$_3$ films and noticed increase of reflectance for $x \geq 0.14$. They noticed Reststrahlen band centered at 15-20 $\mu$m in all the spectra and its band shape was varied with the variation of microstructure of the films. The evaluated absorption coefficient is found to be more for nano crystalline films.

C.C. Liao et. al [77] developed a new composite WO$_3$ films based electrochromic device containing the nano structured WO$_3$ films as an electrochromic layer, which was fabricated by spray and electroplating techniques. The optical and electrochromic properties of the nano composite WO$_3$ films under lithium intercalation were studied using UV-Vis-NIR spectrophotometry and cyclic voltammetry. The WO$_3$ films were effectively coated onto the ITO nano particle layer and ITO coated glass substrates. The microstructural analysis for the films suggested that, both nano composite WO$_3$ film and WO$_3$ film deposited on ITO substrate were exhibiting similar results but differ in their surface morphologies. They showed the TEM evidence for the nano composite WO$_3$ films, which reflected the presence of mixed WO$_3$ and ITO particles. The triangular potential was used at a potential range -1.0 to 1.0 V for the investigation of coloring/bleaching kinetics at a sweep rate of 50 mV/s and reported that nano composite WO$_3$ films were demonstrated higher current density values. The nano composite film exhibited a better contrast in the spectra range of wavelength from 340 nm to 700 nm with a maximum value of $\Delta T = 58.7\%$ at 700 nm. They studied electrochromic device characteristics and measured the coloration/bleaching times for
both the films and suggested that the nano composite WO$_3$ films were demonstrating better switching stability than the other.

C.O. Avellaneda et. al [78] prepared amorphous WO$_3$ and WO$_3$:Li$^+$ thin films were prepared by employing the sol-gel method and investigated the kinetics and thermodynamics of electrochemical intercalation of lithium in to the films. They used galvanostatic intermittent titration technique (GITT) to evaluate kinetic properties of transport in solids. From the obtained data, the steady-state voltages of the galvanic cell were measured as a function of the stoichiometric coefficient ($x$) for pure WO$_3$ and WO$_3$:Li thin films and reported that higher quantity of lithium can intercalate into WO$_3$:Li films than the pure WO$_3$ films. The standard free energies ($\Delta G^\circ$) of lithium intercalation were estimated for both the films and suggested that the presence of Li in WO$_3$:Li films enhanced the $\Delta G^\circ$ values. The GITT measurements were revealed the enhancement of chemical diffusion and component diffusion coefficients with the increase of lithium concentration in the films. Finally they concluded that, the component diffusion coefficient values for both the films were two orders of magnitude lower than those of chemical diffusion coefficients.

The nano crystalline WO$_3$ films were prepared using modified sol-gel process at low temperatures and studied their microstructural properties by Y. Djaoued et. al [79]. Films were characterized by using Raman studies, TEM and SEM, in addition these an active electrode in an electrochromic device was tested and reported it's performance. From SEM investigation they observed the presence of brighter particulate water by consisting more WO$_3$, this observation was supported by EDS spectrum of the sample. Raman spectra were recorded at different positions on the sample and reported that crystallinity was varying from one point to another. The TEM image of the WO$_3$ sample exhibited large spots, which indicate the presence of nano crystallites of WO$_3$. From their observation they recommended the low temperature WO$_3$ films for the application of electro chromic windows as effective active layers.
C.M. Ghimbeu et al [80] deposited tungsten trioxide thin films onto a Pt-coated alumina substrate using the electrostatic spray deposition technique and explored the influence of substrate temperature on porous nature of the films. From their observation films deposited at $T_s = 200^\circ C$ were found to be smooth and exhibited some cracks in the films. They reported that films grown at $T_s = 400^\circ C$ were found to be highly porous by comprising very fine particles. The EDX of the films evidenced for the presence of peaks corresponding to the tungsten and oxygen. The annealed films at $500^\circ C$ were demonstrated characteristic triplet XRD peaks corresponding to monoclinic WO$_3$. The TEM photographs of the films exhibited the presence of nano sized particles, which was in agreement with the XRD results. They studied the electrical properties of the films and estimated the activation energy as 0.68 eV.

The tungsten trioxide films were prepared by H. Yang et al [81] using dip coating – pyrolysis method with PEG – 400 as the structure – directing agent. The TG – DSC analysis was carried out for the powder prepared from the precursor solution and found that $350^\circ C$ as the optimized annealing temperature for the film. The XRD results revealed the monoclinic structure of the films. The SEM pictures of the films showed the presence of non-characteristic grains over a 1 $\mu m$ scale with a non-uniform distribution of pores, which was favor for electrochromic properties. They noticed that films prepared by dip coating method were exhibiting notable reversible electrochromic properties up to 300 cycles. Finally they reported that dip coated WO$_3$ films demonstrated better transmittance modulation in the visible region.

M.G. Hutchins et al [82] deposited amorphous WO$_3$ thin films by thermal evaporation technique and explored electrical conductivity, dielectric properties in the temperature range 293 – 393 K. During dielectric loss measurements they do not observed any remarkable peaks during testing film and they obtained dielectric relaxation time from the imaginary part of the dielectric modulus. The evaluated activation energy from the dc conductivity and relaxation times were found to be very
They applied Hunt Theory for the interpretation to describe the electrical and the relaxation properties of a-WO$_3$ thin films.

Q. Wang et al. [83] prepared monoclinic WO$_3$ nano rods using solution based colloidal approach and investigated the Li-driven electrochemical properties in relation with the nano structures of the material. The XRD pattern of the WO$_3$ nano rods was similar to the bulk WO$_3$ XRD pattern and TEM results exhibited WO$_3$ nano rods of length 60 – 80 nm. They reported that both WO$_3$ nano rods and bulk WO$_3$ were demonstrating major differences within the region 3.5 – 1.5 V during voltage versus compositional studies. From the obtained voltage-compositional studies they observed the formation of different single phases with the increase of lithium insertion. The electrochemical impedance measurements were carried out for the films to obtain the information about the evolution of Li-driven relation Kinetics at different equilibrium states. The obtained charge-transfer resistance value of bulk WO$_3$ in the high frequency range was noticed to be strongly dependent on the applied voltage and it is remarkably larger than WO$_3$ nano rods. The cycling performance results revealed that WO$_3$ nano rods can accommodate up to 1.12 Li per formula unit, which is higher than the bulk WO$_3$. They reported that the unique rod-like structures were exhibiting enhanced electrochemical properties.

G.G. Belmonte et al. [84] prepared a-WO$_3$ thin films using electron beam evaporated technique and carried out detailed electrochemical characterizations of a-Li$_x$WO$_3$ thin films. A new phenomenological model was proposed to explain both the thermodynamic and kinetic - diffusion properties of the system over a broad range of intercalation levels. The chronopotentiometry measurements were performed and investigated the working electrode potential dependence on the Li driven level by measuring the constant current titrations. From titration experiments the chemical capacitance was evaluated and observed high capacitances for high insertion levels (x > 0.1). The dependence of chemical diffusion coefficient on composition of the film was observed and found to be nearly proportional to the reciprocal of composition.
They concluded that, a high value of the intercalation energy of an intercalated particle with the host provides the major contribution to the electrode potential variation with respect to the composition of the film.

N.M.G. Parreira et al. [85] deposited WO₃ coatings by DC reactive magnetron sputtering of a tungsten target and studied the influence of chemical & stoichiometric composition on structure and mechanical properties of the coatings. They studied the variation of oxygen content in the films as a function of oxygen partial pressure and noticed the formation of the stoichiometric WO₃ compound at p(O₂)/p(Ar) = 1:1. The influence of oxygen on structured transitions of WO₃ was analyzed using X-ray diffraction technique. They described mechanical properties of the films as a function of percentage of oxygen in the films and reported that, both hardness and Young's modulus values were found to be decreased with the increase of oxygen percentage in the sputtering atmosphere.

Electrochromic WO₃₋ₓ films of low internal stress were synthesized by electrochemical deposition and etching procedure by Hepel et al. [86]. They used electrochemical quartz crystal nano balance technique (EQCN) technique for characterizing the electro etching properties and employed isotopic method for the confirmation. The significant changes in color center distribution wane not noticed during etching process. From AFM results, they identified nearly mono dispersed spherically shaped nano particles of WO₃₋ₓ and estimated their average size as (27 ± 4) nm. Using EQCN, they evaluated stress contribution during intercalation of H⁺ and D⁺ ions intercalation and reported that they were approximately equal in the charge range from 2 to 3 mC. They studied isotopic effect during intercalation of H⁺ and D⁺ ions and evaluated the value of Δfₑ₀ = 38.9 Hz. The EC switching kinetics of WO₃₋ₓ films were examined using repetitive potential step experiments in 10 mM H₂SO₄ and 10 mM D₂SO₄ solutions. The evaluated bleaching times during deintercalation of H⁺ and D⁺ ions in 337 nm thick WO₃₋ₓ film were 1.3 sec and 1.9 sec respectively. Finally they concluded that, the low stress EDE films exhibited a fast switching behavior.
G. Leftheriotis et. al [87] deposited WO₃ thin films at room temperature using electron gun and investigated the influence of scan rate on Li⁺ ion diffusion coefficient during Li⁺ intercalation studies. They carried out electrochemical characterization of the cell using both cyclic voltammetry (CV) and the Galvanostatic intermittent titration technique (GITT). The CV experiments were performed at different scan rates and investigated the variations in diffusion coefficients. The evaluated diffusion coefficients were observed to be decreased from 11.4 cm²/s to 3.79 cm²/s with the decrease of scan rate in the order 50 -2 mV/s respectively. From the experimental observations, they reported that I_{peak} deviates from the square root law and I_{peak} is directly proportional to the scan rate. They compared the results deduced from the GITT experiments carried out on the same WO₃ film and observed that the voltammetric diffusion coefficient was found to be up to 67% higher than that by GITT. Finally they reported that the evaluated ‘D’ values by CV peaks with use of the Randles-Servik method must be treated with cation and low scan rates were required for credible results.

Thin films of WO₃ were deposited using pulsed DC magnetron sputtering by A. Subrahmanyam et. al [88] and studied the influence of oxygen sputter gas on structural and electrochromic properties. They observed that, with irrespective of the sputtering pressure all the films exhibited amorphous nature. Films deposited at higher oxygen sputtering pressure exhibited higher optical transmittance of 70 - 85% and they studied the relation ship between optical band gap to oxygen sputtering pressure. The evaluated refractive index values were decreased from 1.99 to 1.97 and then noticed to be increased to 2.04 with sputtering pressure at higher wavelengths. Films prepared at higher sputtering oxygen gas pressures were exhibiting higher coloration in the visible region and the peak at λ =372 nm was shifted to longer wavelength side with the increase of sputtering gas pressure. They concluded that, films prepared at higher oxygen partial pressures were exhibiting better coloration efficiency of 141 cm²/C and less switching time at λ = 550 nm.
R. Sivakumar et. al [89] deposited WO$_3$ thin films on glass and SnO$_2$:F coated glass substrates using electron beam evaporation technique. They observed differences in crystallinity of the films deposited on different substrates. The annealed films at 200° C exhibited monoclinic structure with crystallites of sizes in the order of nano size. SEM images revealed the amorphous nature of the films deposited at room temperature. Films coated on glass substrates and annealed at 300° C exhibited needle like textured grain morphology. They observed that, films prepared at room temperature on SnO$_2$:F substrates showed uniform sized grain morphology. They reported that, the evaluated optical band gaps were decreased from 3 eV to 2.72 eV with the increase of annealing temperature from 30 to 300° C.

Thin films of WO$_3$ were prepared using the electron beam evaporation technique by A.A. Joraid et. al [90] and investigated the influence of annealing on microstructural and electrochromic properties of the films. The XRD patterns of the annealed films indicated monoclinic structure and noticed a dramatic change in crystalline structure at higher annealing temperatures. With the increase of annealing temperature from 573 – 873 K the grain size was increased from 4.3 nm to 25.42 nm. They reported that, films annealed in air consisted greater grain size than the films annealed in vacuum. From optical transmittance studies, they observed decrease of energy gap with the increase of annealing temperature.

Fibrous reticulated WO$_3$ films were prepared by pulsed spray pyrolysis method and studied their electrical, optical and electrochromic properties by S.R. Bathe et. al [91]. The XRD pattern of the as deposited films did not displayed any peaks and SEM images of the film revealed multi-layered fibrous nature. They evaluated thermal activation energy for the films from Arrhenius law and found to be 4 X 10$^{-4}$ eV. From optical absorption studies, the estimated optical band gap energy was 3.1 eV. The cyclic voltammograms were recorded fro WO$_3$ thin films between +500 mV to –500mV and measured corresponding anodic charge density and cathodic charge densities as 4.2 mC/cm$^2$ and 5.6 mC/cm$^2$ respectively. From chronoamperometry investigations of
the films they measured coloration and bleaching response times as 5.5 sec and 3.8 sec. They carried out chronocoulometry studies at ± 0.7 V for the step of 10 sec and calculated electrochromic reversibility of the films as 75%. Finally they concluded that, using spray pyrolysis technique, better EC-WO$_3$ films of coloration efficiency of 34 cm$^2$/C at 630 nm can be produced for electrochromic device applications.

G. Beydaghyan et. al [92] investigated electrochromic properties of porous nano structured WO$_3$ thin films, deposited by using the technique of glancing angle deposition in a thermal evaporation. They observed increase in rms roughness with the enhancement of substrate tilt and film thickness. The as deposited nano structured WO$_3$ films were observed to be exhibiting granular and porous morphologies. They studied the effect of substrate tilt on refractive index and extinction coefficient of the films. The films deposited at tilt angle of 70° were noticed to exhibiting normal state transmission, along with open structure. With the increase of lithium concentration the optical transmittance was noticed to be decreased but films prepared at tilt angles of 70° were saturated with insertion of a very small amount of lithium. They observed the strong correlation that, nano structured films exhibiting significant coloration with charge insertion.

P.K. Shen et. al [93] prepared Cobalt and Nickel doped tungsten trioxide thin films using co-electrodeposition method and investigated their electrochromic properties. The cyclic voltammetric studies were carried out for WO$_3$, Co/WO$_3$ and Ni/WO$_3$ films in 0.5M H$_2$SO$_4$ solution at a scan rate of 50 mV/sec and reported that, Nickel doped WO$_3$ films were exhibiting high coloring currents than pure WO$_3$ and Co/WO$_3$ films. Using XPS analysis, they confirmed the presence of nickel or cobalt in the films. The deposited films at current density ranging from 0.3 to 1 mA/cm$^2$ were found to be crack free and active. The response times for coloring and bleaching of the films were evaluated by performing double potential pulse measurements. From the experimental observations both the transient coloring current and bleaching currents were observed to be proportional to the pulse bias. Finally they concluded that the
coloring currents from tungsten trioxide films doped with cobalt or nickel were much higher than undoped films.

Thin films of tungsten trioxide were prepared by sputtering onto heated and unheated substrates by A. Georg et al [94] and they compared two kinds of mechanisms of coloration electrochemical and the coloration by oxygen deficiency. The electrical conductivity as well as transmittance and reflectance were measured for sub-stoichiometric films in the temperature range 300 – 100 K. They observed similar optical behavior in two mechanisms but different electrical conductivity properties. The sputtered films were constituted by crystallites with the size in the range of the film thickness and with the increase of substrate temperature the number of the crystallites was enhanced rather than the size. By considering the stability and homogeneity of the sub-stoichiometric samples they evaluated optical constants (‘n’ and ‘k’) for different degrees of coloration and crystallinity.

J. Wang et al [95] studied the influence of deposition temperature on the electrochromic properties of reactively sputtered WO₃ films. The WO₃ films were electrochemically cycled with a constant current source and observed the increase of voltage drop on the WO₃ films with the rise in deposition temperature. The observed coloration efficiency increased with increase of substrate temperature (47 – 400°C) in the wavelength range 1000 – 2500 nm. The solar optical modulation was not affected significantly by the increase of deposition temperature but optical modulation in the visible region decreased rapidly with the temperature greater than 300°C. Finally they reported that, the crystallization of the WO₃ starts at 300°C in a low degree and it was enhanced rapidly after 350°C and change in optical and electrochromic properties were attributed to the increase in crystallinity of the films.

D.J. Kim et al [96] investigated hydrogen transport through rf-magnetron sputtered amorphous WO₃ film/indium tin oxide glass. The cyclic voltammetry, ac-impedance technique and potentiostatic current transient techniques were carried out to study the presence of hydrogen trap sites. They determined semi-quantitatively the
amount of the deep trap site based upon the Mott-Schottky relation. From the experimental results they distinguished three kinds of hydrogen injection sites existing in the rf-magnetron sputtered amorphous WO$_3$ films. Based upon build-up and decay current transients they numerically simulated under the impermeable boundary condition in the presence of the hydrogen trap sites.

P.S. Patel et. al [97] prepared tungsten trioxide thin films using a simple and inexpensive solution thermolysis technique. Thin film samples of different thickness were grown by varying the quantity of ammonium tungstate solution sprayed onto the preheated conducting glass substrate. They investigated the effect of the film thickness on the electrochemical and electrochromic properties using cyclic-voltammetry (CV) and chronoamperometry (C-A) techniques. From the experimental results, they observed that the coloration time was found to be almost independent of the film thickness, but bleaching time was found to be dependent on the film thickness. The evaluated coloration efficiency at $\lambda = 633$ nm was increased with an increase of film thickness. They concluded that the films prepared with the precursor quantity of 40cm$^3$ were exhibited maximum coloration efficiency of 56 cm$^2$/C at $\lambda = 633$ nm and all the samples were stable up to 1 X $10^3$ coloring/bleaching cycles.

M. Deepa et. al [98] prepared nano structured tungsten trioxide films with an interconnected frame work of grains and pores using Sol-gel deposition method. The as deposited films were annealed at different temperatures and films annealed at 500$^0$ C were found to be exhibiting triclinic structure. The XRD measurements were carried out for the films and the net ramification of lithium ion intercalation/deintercalation process is observed to be decreased some extent with crystallite size of the Virgin WO$_3$ film. The bright field micrographs of the as-deposited film showed glazy contrast suggestive of the amorphous structure and annealing at 250$^0$ C caused pore shrinkage to yield a microstructure with well-connected large and coarser grains. They observed that FTIR spectra were identical for the films both in Virgin and bleached states. The effect of lithium ion intercalation on the chemical composition of the WO$_3$ was examined
from the XPS spectra of the samples annealed at 250° C and colored under lithium insertion levels of x = 0.04 to 0.25. The electrochromical Li-ion insertion studies were carried out at different scan rates for WO₃ films. The evaluated ion storage capacity-per-unit thickness increased and observed to be acquired a maximum value between 100 to 500 cycles and declined gradually. The photodiode response vs. time transients at 632.8 nm were recorded between potential of the working electrode of E = +2.0 V and E = -2.0 V. The coloration time was observed to be increased nearly by an order of magnitude after cycling the film 500 times.

Tungsten trioxide (WO₃) thin films were deposited by DC magnetron sputtering in O₂/Ar atmosphere and investigated microstructure and electrochromic properties by T.S. Yang et. al [99]. The XRD pattern of the film did not revealed any characteristic peaks. The ratio of W=O/W-O is influenced by the increase of O₂ flow rate and found to be maximum at O₂ flow rate of 24 sccm. They considered the ratio of the W=O bond at 950 cm⁻¹ to the O-W-O bond in the region of 600-850 cm⁻¹ to estimate the crystallite size. From the experimental observations, they reported that the films deposited at 16 sccm O₂ supply were nano crystalline films. The electrochromic properties of the WO₃ films were studied by cyclic voltammetry at voltages between -1.0 and 0.6 V relative to Ag/AgCl with a scan rate of 10 mV/sec. Post annealed films at 200° C exhibited induced larger charge capacity, transmittance variation and coloration efficiency. Finally they concluded that larger internal volume with optimal nano crystallite size is essential to conduct ions and electrons for electrochromic intercalation.

J. Wang e. al [100] deposited WO₃ thin films using reactive DC magnetron sputtering and investigated the relationship between the electrochromic properties and deposition temperature. The XRD analysis revealed that the crystallization of the WO₃ initiated at Tᵦ = 300° C and exhibited tetragonal structure at Tᵦ > 350° C. Films deposited at Tᵦ = 47° C exhibited greater optical modulation in the visible region 450 – 800 nm and small optical modulation in the range 1000 – 2500 nm. Where as
WO$_3$ films prepared at $T_s = 400^\circ$C demonstrated less optical modulation in visible region and higher in the wavelength range 1000 – 2500 nm. The process resistance of films was noticed to be increased with the enhancement of substrate temperature. The films deposited at $T_s = 47^\circ$ – 400$^\circ$C were showed almost constant satisfactory solar modulation of 48% suitable for the use of smart window systems. The graph between optical density versus photon energy displayed a broad absorption peak at 1.3 eV for the films deposited at $T_s < 350^\circ$C, which represented the amorphous nature of the films and with the increase of substrate temperature the absorption peak shifted towards lower energy side. They reported that, the evaluated colouration efficiency of the sputtered films and observed increase of colouration efficiency in the wavelength ranges from 1000 nm to 2500 nm, while decreased in the visible region.

J.L. He et. al [101] prepared Tungsten trioxide (WO$_3$) thin films by reactive sputtering technique and investigated the influence of oxygen concentration on their microstructural and electrochemical properties. They noticed abrupt decrease in deposition rate, when $O_2$/Ar gas flow ratio was above the 0.1. The XRD patterns of all films deposited at different $O_2$/Ar flow ratios exhibited the amorphous nature. From the AES analysis they obtained stoichiometric WO$_3$ films at $O_2$/Ar flow ratio of 0.5. A chemical shift was noticed for binding energy of W 4f$_{7/2}$ with the increase of $O_2$/Ar flow ratio, during the ESCA studies. The evaluated diffusion coefficient values were found to be decreased with the increase of $O_2$/Ar flow ratio. They optimized that, films deposited at an $O_2$/Ar flow ratio of 0.3 – 0.5 demonstrated maximum transmission changes for coloring and bleaching states and enhancement of coloration efficiency was observed with the increase of $O_2$/Ar flow ratio.

The electrochromic WO$_3$ thin films were deposited using pyrolysis method and investigated influence of nature of the substrate on structural, morphological and optical properties by J.M. Oretega et. al [102]. Films grown onto soda-lime glass exhibited polycrystalline nature associated to the hexagonal WO$_3$ phase, along with monoclinic structure. They reported that, structures of WO$_3$ films were independent of sheet
resistances of the different FTO substrates. During proton insertion/extraction the monoclinic structure of WO$_3$ film noticed to be changed to tetragonal structure. The electron diffraction patterns for WO$_3$ films deposited on different FTO substrates correlated to the XRD results. From SEM results, the particle sizes in WO$_3$ films prepared on glass substrates were observed to be bigger than the particle sizes when films grown on ploy crystalline substrate. The rms roughness and surface area were higher for the WO$_3$ films grown on high resistance FTO substrates. They optimized the scan rate as 600 mV/s and potential was swept between -1.1 and 1.8 V to obtain better results during cyclic voltammetry studies. The optical transmittance spectra were recorded for as deposited and colored films to investigate the electrochromic properties.

M. Deepa et al [103] investigated a comparative study on microstructural, optical and electrochemical properties of spin and dip coated WO$_3$ thin films. The XRD pattern of the dip coated film annealed at 250$^\circ$ C exhibited triclinic crystalline phase, whereas spin coated films showed hexagonal phase. SEM analysis for the dip coated film revealed a crack free morphology and its spin coated counterpart was characterized by dominant cracks. For dip coated film, they noticed pore size in the range 55 to 100 nm and grain size varied from 55 to 80 nm. In case of spin coated films, the observed pore size varied roughly within a narrow range of 60 - 70 nm. The bright field micrographs of annealed (at 250$^\circ$ C) spin and dip coated films were appeared as glazy contrast corresponding to amorphous structure. The as deposited dip coated films's FTIR spectra was characterized by a doublet at 976 cm$^{-1}$ and 986 cm$^{-1}$, but FTIR spectrum of spin coated film exhibited a single peak at 970 cm$^{-1}$. They focused their attention on electrochemical and optical properties of nano structured spin and dip coated films obtained by annealing process. They reported highest transmission modulation of 70% at 640 nm for dip coated films, where as spin coated film exhibited optical modulation of 65% at 725 nm. During first 10 cycles, the coloration efficiency of dip coated films increased from 41.8 cm$^2$/C to 47.6 cm$^2$/C at $\lambda = 550$ nm. For spin coated films colouration efficiency at $\lambda = 550$ nm was noticed to be decreased from 41.1 cm$^2$/C to
34.7 cm²/C. They concluded that dip coated WO₃ films were exhibiting superior characteristics than the spin coated films for the application of smart windows.

The tungsten trioxide thin films were deposited onto different substrates using thermal evaporation and annealed in the temperature range 350° - 450° C to investigated the electrochromic properties by E. Ozkan et. al [104]. They noticed onset of crystallization in the films at 390° C and films annealed at 450° C were exhibited monoclinic structure. For as-deposited WO₃ films Raman spectra displayed broad peak at 770 cm⁻¹ corresponding to W⁶⁺ - O bands and another strong peak at 950 cm⁻¹ associated to the W⁶⁺ = O band stretching modes. With the increase of annealing temperature the intensity of RS peak associated to W⁶⁺ = O band decreased significantly. They noticed that, amorphous WO₃ films were exhibiting wide absorption band having peak at 1.3 eV. The evaluated optical band gaps were decreased as a result of enhancement of annealing temperature. The absorption peak of the films annealed at 390° C was abruptly shifted towards lower photon energy by indicating the crystallinity in the films. From deconvolution of the absorption spectra they suggested two different polaron transitions in amorphous WO₃ films.

Effect of substrate temperature and sputtering gas pressure on optical and electrochromic properties of WO₃ films deposited through RF sputtering, were examined by E. Washizu et. al [105]. The XRD pattern of the films deposited at room temperature indicated the amorphous nature of the films. They observed the enhancement of crystalline growth with the increase of substrate temperature and composed of crystallites of size of 45 nm at 50 m Torr and 500° C. The as-deposited amorphous films exhibited maximum optical band gap of 3.15 eV and decreased with the increase of substrate temperature. With the increase of substrate temperature the evaluated refractive index values of the WO₃ films were increased. The coloring and bleaching times were observed to be decreased with the decreasing the substrate temperature. Finally they summarized that, short response times below 1 minute were obtained for the films consisting the optical band gap of 3.1 eV.
The WO₃ thin films were deposited by a laser ablation technique and studied the effect of film deposition conditions and the influence of various substrates on microstructural of films by O.M. Hussain et al [106]. The color of the films deposited at less than 100 m Torr were appeared as light blue in color. From the XPS analysis of the films, they reported the binding energies of characteristic W4f peaks about 36.1 eV and 38.2 eV respectively. The WO₃ films prepared at 100 m Torr were observed to be transparent and nearly stoichiometric. The WO₃ films grown on pyrex glass substrates at Tₛ < 573 K were observed to be amorphous and at higher substrate temperatures they exhibited triclinic structure. They reported decrease of crystallinity in the films with the increase of oxygen partial pressures greater than 100 mTorr. The films deposited onto ITO-coated glass substrates were demonstrated monoclinic structure and cubic perovskite type structure for the films grown onto the single-crystal SrTiO₃ substrates.

H. Kamal et al [107] deposited amorphous/crystalline WO₃ films on heated/unheated substrates using RF-sputtering technique. The obtained XRD patterns for a-WO₃ films during coloring/bleaching processes revealed an increase in the microstrain caused by EC reaction. The WO₃ films deposited at Tₛ = 573 K and at total pressure of 7.5 X 10⁵ pa were exhibited triclinic structure. The change in degree of crystallinity was observed for deep colored films and corresponding XRD spectrum of hydrogen bronze film exhibited the tetragonal structure. They noticed that, both a-WO₃ and c-WO₃ films showed remarkable bleaching and coloration effects and attained saturation condition after 5 and 10 cycles respectively. The a-WO₃ films demonstrated relatively larger optical modulation in visible region than the crystalline WO₃ films. Self bleaching test was conducted with respect to time at λ = 633 nm. They concluded that, coloration persistence in air is much better than aqueous solution and water.

R. vijayalakshimi et al [108] prepared WO₃ films by electro deposition technique and investigated their microstructural and electrochromic properties. Films deposited at optimized conditions exhibited triclinic structure. The cyclic voltammetric studies were carried out in the applied potential range -1.0 to 1.0 V at different scan
rates and they noticed neither coloring nor bleaching speeds were affected by number of cycles. They reported that, thicker films were exhibited the higher coloration but coloring speed was independent of the film thickness. The evaluated diffusion coefficients were observed to be increased with the increase of solution concentration. FTIR studies revealed the presence of broad peak in the region of 5300 - 3780 cm⁻¹ corresponding to the O-H stretching vibration. From their experimental observations, the electrodeposited WO₃ films were highly stable in H₂SO₄ electrolytes.

I. Porqueras et. al [109] deposited WO₃ layers onto various substrates like silicon wafers, glass and fused silica by using thermal reactive evaporation technique and explored their optical properties in the IR and UV-Visible regions. The as-deposited WO₃ layer of thickness 300 nm was exhibited high optical transmittance in the range 400 - 800 nm. They inserted Li⁺-ion in WO₃ layer through dry methods and studied their optical properties and observed the enhancement of absorption. The Li-doped WO₃ films were exposed to atmosphere to investigate the effect of humidity in the atmosphere and mentioned that, for long time exposure to the atmosphere caused to decrease the optical transmittance.

The crystalline WO₃ films were prepared by dc reactive sputtering and investigated their microstructural and infrared reflective characteristics by Y.S. Huang et. al [110]. The XRD pattern of the WO₃ films deposited on Si-wafers at Tₛ = 40° C revealed the amorphous nature of the films, but with the increase of substrate temperature (Tₛ = 350° C) films were found to be completely crystallized into monoclinic structure. The cyclic voltammetry studies were out for c-WO₃ films at a scan rate of 50 mV/s in the -500 to +1000 mV range. The Raman spectra were recorded for as deposited c-WO₃ and after intercalation with different amounts of ions. The obtained Raman spectra displayed two sharp peaks at 765 and 895 cm⁻¹ corresponding to (O-W⁶⁺-O) vibration and no sharp was displayed around 950 cm⁻¹. After intercalation Raman spectra of the films exhibited new peaks at 315, 410 cm⁻¹, which were attributed
to the (O-W$^{2+}$-O) vibration. They reported that, the emissivity of WO$_3$/ITO/glass configuration was observed to be modulated between 0.261 and 0.589.

The optical, electrical and structural properties of spray deposited polycrystalline WO$_3$ thin films were studied by M. Regragui et al [111]. The as deposited WO$_3$ films were exhibited 80% of optical transmittance and in colored state it reduced to the 5%. They noticed that, the variation of optical transmittance was independent of the spray rate. The colored films were exhibited higher reflectivity and absorption in the near-infrared region. The electrical conductivity measurements were carried out for the films and observed an increase in the conductivity for colored films. The evaluated activation energies ($E_a$) were found to be high for as deposited WO$_3$ films prepared at higher spray rate, but in case of colored films $E_a$ values were decreased from $1.1 \times 10^{-2}$ to $0.8 \times 10^{-2}$ eV. The structural investigations were carried out by XRD and noticed structural phase transformation from monoclinic to cubic during coloration process. The current density – time characteristics of WO$_3$ films (prepared at different spray rates) were investigated during Li intercalation/deintercalation studies. They concluded from electrochemical measurements that, the cyclic voltammograms for the films were reproducible after five cycles.

A. Subrahmanyam et al [112] fabricated a fast protonic solid state device having similar structure: glass/ITO/WO$_3$/Ta$_2$O$_5$/NiO/ITO. The non-stoichiometric WO$_3$ layer was deposited on ITO coated glass substrate using DC magnetron sputtering technique at an ambient deposition conditions. Ion-storage and electrolyte layers were formed on WO$_3$ film using electron beam evaporation technique. As deposited WO$_3$ film on glass substrate at room temperature exhibited the presence of amorphous phase and for the same film they noticed 83% of optical transmittance along with 60% of optical modulation during ion-intercalation studies. The cyclic voltammetric studies were carried out for the as deposited WO$_3$ films at a scan rate of 50 mV/s and recorded the corresponding cathodic and anodic currents. With the ion-intercalation, the change
in the Fermi level in WO$_3$ film was investigated by evaluating the work function using Kelvin-probe for both colored and bleached films. They measured the response times for the fabricated protonic device and obtained 6 and 5 sec response times for colored and bleached times respectively.

A. Antonaia et. al [113] studied the electrochromic properties of thermally evaporated tungsten trioxide thin films and studied the influence of annealing temperatures on electrochromic properties of the films. Films prepared at room temperature were exhibited amorphous nature and the nano crystalline films were obtained at T$_{a}$ = 80° C. They reported that, WO$_3$ films grown at 80° C and annealed films annealed at 465° C were demonstrated an orthorhombic crystalline structure with a preferred orientation along (200) reflection. From XRD analysis they stated that WO$_3$ films deposited at 300° C were exhibited a monoclinic structure with a columnar growth. The WO$_3$ layers annealed at 465° C had different colouration levels and exhibited tetragonal crystalline structure for hydrogen tungsten bronze. The surface morphology of the deposited films at 80° C showed very smooth surface and after annealed at 465° C they noticed micro granular with an average grain size of 450 Å. The transmittance versus time measurement was carried out and noticed advancing coloration front. The electron diffusion coefficient was evaluated for the film annealed at 465° C and found to be 1.22 cm$^2$/V. Self bleaching process investigations were carried out for the films prepared at 80° C and subsequently exposed to water and air, from this study they reported that, the transmittance at $\lambda$ = 633 nm was increased more rapidly due to exposure of the film to the air. From the experimental results the annealed films showed minimum coloration persistence either in air or pure water. The optical switching tests were carried out for both nano crystalline and crystalline WO$_3$ layers and concluded that both the layers exhibited good reversibility for the electrochromic process even after 1000 cycles.

Thin films of WO$_3$ were prepared by A.K. Srivastava et. al [114] using electrodeposition method for the application of electrochromic windows. The as
deposited films were annealed at 100° C. The XRD studies revealed the amorphous nature of the annealed films at 100° C but TEM results for that sample indicated the presence of nano structured state of the film. The selected area electron diffraction studies were carried out and spotty electron diffraction pattern of the film reflected hexagonal crystalline structure of WO₃ film along [0001] zone axis. Surface morphological features of the films were studied from SEM micrographs at different magnifications. They estimated the pore sizes present in the films and found to vary from 20 to 300 nm. The microstructural evolution of the annealed films was investigated from FTIR studies and did not noticed any considerable changes in modes associated to oxygen and water molecules upon annealing. The optical transmittance spectra were recorded within 300 ≤ λ ≤ 850 nm wavelength range for annealed WO₃ films in their respective bleached and colored states and observed 65 - 71% optical modulation in the 600 - 850 nm. The obtained maximum coloration efficiency for the films was 96 cm²/V at 850 nm. Cyclic voltammetry studies were performed at different scan rates and evaluated Li-ion diffusion coefficient for the intercalation was (3.7 ± 0.3) × 10⁻¹⁰ cm²/s for the annealed films at 100° C and ion-storage capacity was decreased from 24 mC/cm² to 21 mC/cm² after 10⁴ cycles.

A. Antoniaia et. al [115] studied electrochromic properties of amorphous/crystalline double layers of WO₃ with respect to amorphous and crystalline single layers of WO₃ films. They deposited WO₃ films on glass substrates by thermal evaporation process using cryogenic pump and observed that respective films were exhibiting poor electrochromic properties. The WO₃ films prepared in a more oxidative atmosphere were found to be demonstrating stable structural properties both in coloration and annealing processes. The XRD results revealed the presence of nano crystallites in an amorphous matrix of the film. They noticed the transformation of amorphous WO₃ phase to nano crystalline WO₃ phase due to illumination with electron beam for different time intervals. TEM results supported the presence of nano crystalline phase in the film. The XRD pattern of the WO₃ films grown at Tᵣ = 80° C and anr = 1.1 at 500° C w. showed an orthorhombic crystalline structure with (200) as
preferred orientation. The cyclic voltammetric studies were carried out between +400 – 600 mV for different WO₃ structures, in which the amorphous/crystalline double layer displayed insignificant peaks. They reported that, amorphous/crystalline double layer was exhibiting faster coloration response and deepest coloration level than the amorphous single layers.

P.R. Bueno et. al [116] prepared amorphous WO₃ films by using dip-coating method on glass substrates. They utilized transient time, frequency techniques to evaluate the improvements in Li⁺ charge and mass intercalation kinetics of amorphous WO₃ host material by adding the LiCF₃SO₃ during film synthesis. From XRD and optical transmittance investigations they suggested that, doping 20 mol% of LiCF₃SO₃ to pure a-WO₃ did not show any effect on structural and optical properties of the films. The UV-Visible spectra of doped a-WO₃ films were exhibited higher electronic reversibility and the amount of doping (LiCF₃SO₃) lowered the time response in the bleaching process. Doped a-WO₃ films showed higher absorptance in the range of 70 – 800 nm compared with pure film. From cyclic voltammetry measurements, they noticed higher cathodic, anodic charge values and higher charge reversibility for doped WO₃ films than the pure a-WO₃ films. Li-ion intercalation/deintercalation processes were observed to be more easily in modified a-WO₃ thin films. Finally, they concluded that, the enhancement of the charge, mass, optical absorption kinetics and the reversibility of a-WO₃ (as a host material for Li⁺ - ion intercalation) were observed by the addition of LiCF₃SO₃ dopant.

Tungsten trioxide and vanadium doped tungsten trioxide thin films were deposited by sol – gel spin coated method and optical, structural properties were investigated by E. Ozken et. al [117]. The optical transmittance was observed to be decreased with increase of number of layers. The evaluated refractive index and extinction coefficients of the spin-coated films were increased from 1.84 to 1.89 and 1.37 X 10⁻³ to 1.42 X 10⁻³ respectively with the increase of film thickness. The AFM results revealed that, the surface roughness of WO₃ film increased with the increase of
film thickness. Vanadium doped tungsten trioxide thin films showed higher transmittance value compared to pure WO₃ films. The refractive index and extinction coefficient values were observed to be lower for vanadium doped WO₃ films comparatively with pure WO₃ films of same thickness. The evaluated optical band gap values of WO₃ and vanadium doped WO₃ films were found to be 3.1 eV and 2.77 eV respectively. From experimental observations, they concluded that the optical properties of sol-gel deposited WO₃ and V-doped WO₃ films were depend on film thickness.

M.G. Hutchins et. al [118] deposited amorphous tungsten trioxide thin films by thermal evaporation process. As deposited films were annealed and investigated their structural and optical properties as a function of film thickness. The XRD pattern for as deposited films displayed broad peak at 2θ = 23° by indicating the amorphous nature and after annealing the film at 723 K for 2 hours, the XRD pattern indicated the polycrystalline monoclinic WO₃ phase. They recorded optical transmittance and reflectance spectra for as deposited and annealed films, from the spectra they evaluated the optical constants. From the plot (n²-1)¹ versus E² of amorphous and crystalline film, they evaluated the oscillator energy (Eₒ), dispersion energies (E_d) and found to be 18.18, 5.95 eV and 11.13, 2.92 eV for amorphous and crystalline films, respectively. The evaluated optical dielectric constant was noticed to be increased with the enhancement of annealing temperature. From the plot of n² versus λ² they evaluated lattice dielectric constant (E_L) and observed the disagreement between the values of the optical dielectric constant and lattice dielectric constants. With the increase of annealing temperature the evaluated band gap values were varied from 3.27 eV to 3.05 eV for amorphous and crystalline films respectively.

Mixed Vanadium tungsten trioxide thin films were grown using pulsed laser deposition technique and investigated the influence of Vanadium content on the electrochromic performance of films by A. Rougier et. al [119]. At room temperature XRD pattern of the films revealed the high degree of amorphous nature with the irrespective of Vanadium content. With the increase of Vanadium content in the films
up to 20%, the films exhibited a more Yellowish color and appeared as homogeneous. With the increase of vanadium content, the shape of cyclic voltammetry differed from homogeneous linear evolution and noticed an extra peak at -0.1 to -0.2, whose intensity increased with the increase of Vanadium content. They observed constant reduction in capacity and decrease of reversibility of the cell due to addition of vanadium up to 10%. During CV measurements, the V-W-O system demonstrated a better reversibility with the decrease in capacity as a function of Vanadium content. They concluded that, with the increase of Vanadium content (>4%) the observed optical transmittance decreased and leading to a smaller contrast, which was associated to the decrease of coloration efficiency.

M. Regragui et al. [120] prepared WO₃ thin films using spray pyrolysis and studied their optical and electrical properties intensively in the colored state of the films. The XRD results revealed the monoclinic phase of the films annealed for 60 min. They observed significant surface roughness for the films from SEM micrographs. The obtained optical reflectance spectra were normalized with respect to substrate temperature and observed broad reflectivity domain in the near-infrared region. At room temperature, they evaluated the conductivity, carrier density and Hall mobility of the annealed films and observed the enhancement of conductivity values by indicating the nature of degenerated semiconductor. Finally, they explained discrepancy between the conductivity, optical and Hall measurements by considering the grain-boundary model and tunneling contributions to the electrical conductivity.

R. Sivakumar et al. [121] prepared WO₃ thin films using electron beam evaporation technique on FTO coated glass substrates maintained at various temperatures (T[subscript]s). The compositional, electrochromic and electrochemical studies were carried out for as deposited and annealed films. The XRS spectra for WO₃ films grown on glass substrates were exhibited characteristic peaks of W and O by enumerating the compositional purity and quality. The evaluated binding energies of W4f doublet for all the films were observed to be in good agreement with WO₃ powder. They observed the
formation of oxygen deficiency in the films with the increase of substrate and annealing temperatures. During electrochemical analysis, they noticed enhancement of cathodic spike current, anodic peak current with the increase of scan rates. The calculated diffusion coefficient values of WO₃ films during H⁺-ion intercalation/deintercalation process from 0.05 M H₂SO₄ electrolyte solution, varied between 5.4 X 10⁻¹⁰ to 1.42 X 10⁻⁷ cm²/s, where as its value varied between 8.72 X 10⁻¹⁰ to 1.75 X 10⁻⁸ cm²/s for 0.1 M electrolyte solution. The films cycled in 0.1 M H₂SO₄ electrolyte solution were exhibited good electrochromic coloration both in colored and bleached states. They observed higher optical modulation in the visible region and lower optical modulation in infrared region of the spectra. They concluded that, the films produced a lower substrate temperature had higher coloration efficiency than the films prepared at higher substrate and annealing temperatures.

M. Deepa et. al [122] prepared amorphous WO₃ films through sol-gel method and obtained nano crystalline films after annealing at 600°C. They investigated the effect of nano scaled rods, pores and grains on optical properties of the films. The XRD measurements indicated the formation of nano crystalline with pseudocubic triclinic structure up on annealing at 600°C. TEM bright field micrographs of WO₃ films exhibited nano rods of different diameters, which were overlapped with nano particles in annealed WO₃ films. The as deposited nano structured WO₃ films exhibited about 73% of optical transmittance in the visible region. The evaluated coloration efficiency values were increased from 15 to 73 cm²/C as λ increased from 450 to 750 nm. They noticed the straight line behavior of (ahv)² versus hv and (ahv)¹/² versus hv for all the films, which was associated to the direct allowed and indirect permitted transitions for nano crystalline WO₃ films. During coloration process, both direct and indirect gaps were shifted towards higher energy side. The cycle life of the electrochromic device was determined by using cyclic voltammograms at a scan speed of 20mV/s and recorded the photodiode response versus time transients at λ = 632.8 nm. They conclude that, the nano crystalline films exhibiting higher diffusion coefficients value of (2 ± 1) X 10⁻¹⁰ cm²/s and these nano crystalline films showed insignificant decline up to
1000 cycles. The observed coloration time increased moderately from 164 – 179 seconds and bleaching rate increased from 15 to 60 sec for 1000 cycles. They reported that ion storage capacity of the films was decreased from 21 mC/cm² to 10 mC/cm² after 1500 cycles.

A.A. Mohammed et. al [123] prepared vacuum evaporated WO₃ thin films onto Al₂O₃ substrates and investigated the effect of annealing on grain size and crystallographic structures. They identified three temperature domains (20-100° C, 100 – 250° C and 250 – 400° C) in which the WO₃ films exhibited more phases. The significant structure and morphology changes were not observed during annealing between temperature ranges of 20 – 100° C. The TED pattern of the films annealed at 100 – 150° C demonstrated the coexistence of monoclinic WO₃ + WO₃.1/3H₂O phases and later WO₃.1/3H₂O crystallization in an annealing temperature of 180° C and the hydrated oxide WO₃.1/3H₂O phase is changed into hexagonal WO₃ structure. In the annealing temperature range of 200 – 250° C, the spotty TED pattern for the films revealed the slight enhancement of grain size. For WO₃ films annealed at 350° C demonstrated both monoclinic structure with typical contrast and hexagonal structure by the stacking of thin layers with poor contrast. They concluded that, microstructural properties and crystallographic structural changes were influenced by the annealing process.

The WO₃ thin films were deposited through the method of W (CO)₆ pyrolysis and investigated the effect of deposition and annealing temperatures on film structure by A. Szekeres et. al [124]. Using the single layers model film thickness and mean refractive indices were evaluated from the experimental ellipsometric data. The RHEED measurements for the grown films supported the observation of used models and indicated the monoclinic structure for WO₃ films prepared at 300° C. As deposited films were exhibited higher refractive index values and noticed to be decreased with the increase of substrate temperature. They reported the optical band gap values for the amorphous films in the range 3.25 – 3.4 eV.
G.J. Gang et al [125] deposited single and double layers of WO₃ and V₂O₅ by pulsed laser deposition technique at ambient film processing conditions and investigated their structural properties and variations in chemical composition. The optical transparency in the films was noticed to be increased with the increase of oxygen partial pressure. The XRD pattern for as deposited WO₃(V) and V₂O₅(Ti) films at Tₓ = 200° C on ITO substrates exhibited the amorphous.

A. Baserga et al [126] prepared WO₃ thin films by using pulsed laser deposition technique as a function of back ground inert gas pressures and carried out Raman scattering investigations for different types of WO₃ films. Films grown at very low pressures (<10 pa) were found to be amorphous in nature and they noticed the enhancement of crystalline domains of increasing size with the increase of inert gas pressure. The observed Raman peaks at 183, 207, 275, 718 and 810 cm⁻¹ were associated with the monoclinic phase of WO₃. SEM photographs indicated the influence of back ground gas pressure on surface morphology of the films. The compact structure of the films deposited at 1 pa was observed to be changed to a nano particle – composed web-like network at very high deposition pressure of 1000 pa. For the films deposited in He atmosphere, the high frequency band in Raman spectra exhibited blue shift (towards 870 cm⁻¹) and low frequency band is observed to be more structured. They concluded that Raman spectroscopy can be employed to study the dependence of WO₃ phase transitions on the structure and organization.

J.P. Matthews et al [127] reported the effects of temperature on electrochromic device switching voltages. The WO₃ electrochromic films were deposited onto (10 X 10 cm) LOF TEC8/3 glass substrates using the of Sol-Gel dip coating method. From the results they observed decrease of magnitude of the applied voltage as the increase of temperature throughout both coloring and bleaching states. The maximum coloring voltage was found to be decreased with the increase of temperature and this relation was obtained by a linear plot of log V_c versus 1/T. They used the voltage limited constant current charge injection method for charge injection and extraction into
the WO₃ films at higher temperatures. Obtained results revealed that, the voltages required for coloration were decreased with the increasing temperature. From the analysis of the emf and \( V_c \) response to temperature enabled to estimate the maximum applied voltages required to color the electrochromic films for safe switching conditions.

Thin films of WO₃ and MoO₃ and mixed WO₃/MoO₃ were prepared by thermal evaporation and investigated their optical properties by E.E. Khawaja et. al [128]. They achieved the derivation for the refractive and absorption indices from the measured normal incidence transmittance of the films. The WO₃ and MoO₃ films were found to be homogeneous and films prepared from the mixed oxides were chemically inhomogeneous. Rutherford Backscattering spectrometry (RBS) measurements on the films revealed that the films of WO₃ and MoO₃ were fairly uniform but the films prepared from mixed oxides were chemically inhomogeneous. They determined average refractive indices for the mixed oxides films in the spectral region in which they were absorbing.

M.D. Ingram et. al [129] prepared electrochromic devices of the general type of configuration (ITO)/WO₃/(PEO)-H₃PO₄/(H)ITO. For this device a typical chronoamperometric trace was obtained during bleaching and the voltage was stepped from its rest potential of -0.2 to +0.5 V. For small voltage steps from 0.0 to -0.4V, the chronoamperometric traces were found to be essentially smooth and continuous. Analysis of the cell transmittance was carried out during coloration and observed respective peak respective peak representing the color forming processes. They studied current-time behavior from the following obtained peak and thereby implying that ion movement across the WO₃/electrolyte interface is rate limiting at moderate to high ‘x’. Finally, they reported that electron movement through the electrochromic film is rate limiting.

Orthorhombic WO₃ films has been prepared by using Vacuum evaporation technique and studied the effect of the substrate temperature and post annealing on the
surface morphology of the films by M. Sharon et. al [130]. The optical gaps for the orthorhombic WO$_3$ films was evaluated for as deposited, annealed and for hydrogen reduced films. The films deposited at $T_s < 300$ K were found to be amorphous with a band gap of 3.7 eV (direct) and 3.2 eV (indirect). From the experimental observation they reported that there is no effect of hydrogen reduction on the band gap of films. Finally they concluded that hydrogen reduction caused to decrease the resistance of the film and it did not produce any hydrogen tungsten bronzes ($H_n$WO$_3$).

J.V. Gabrusenoks et. al [131] prepared amorphous tungsten trioxide thin films and investigated by Raman scattering method. The investigation of Raman spectra of a-WO$_3$ films showed the presence of terminal-oxygen and ordinary W-O-W bonds in the structure of the film. From the obtained RS result, they reported that the terminal oxygens in a-WO$_3$ film are connected with the presence of (WO$_3$)$_n$.mH$_2$O clusters. ESR spectrum of the samples revealed the presence of W$^{5+}$ states (color centers) in a-WO$_3$ films, which are connected with the electron localization in axially distorted WO$_6$ octahedra, containing terminal oxygen (W=O). They used intervalence charge transfer transition between two localized W$^{5+}$ and W$^{6+}$ states to explain the optical absorption of the color centers in the colored a-WO$_3$ films.

B.W. Faughnan et. al [132] prepared WO$_3$/MoO$_3$ mixed – oxide thin films and studied their electrochromic properties. They reported that, the optical absorption peaks of all the mixed-oxides are higher in energy than the either of pure WO$_3$ and MoO$_3$ oxides. They assumed that an electron trapped on a Mo$^{6+}$ ion lies at an energy $\Delta E$ below the energy; it would have trapped on a W$^{6+}$ ion. Therefore three different optical transition energies for this electron, which ($E_{ww}$) electron transition between two tungsten ions, ($E_{mm}$) transition between molybdenum ions and ($E_{mw}$) transition between molybdenum ion and tungsten ion. From the evaluated values, they mentioned that ($E_{mm}$) is greater than ($E_{ww}$) by the amount of $\Delta E$. With the increase of crystallization the optical transition ($E_{mm}$) in amorphous WO$_3$ films was shifted towards lower energy side, the similar phenomena was observed in mixed oxides. The calculated diffusion
coefficient values decreased exponentially with the increase of Mo concentration up to \( c = 0.3 \) and at this concentration it is found to be \( D_e = 2 \times 10^{-5} \text{ cm}^2/\text{sec} \), which is 1/250 that in pure WO\(_3\). They attributed this lower diffusion coefficient value with the electrons being trapped at deeper sites that are present in WO\(_3\).

D. Dini et al. [133] investigated the importance of mechanical effects in electrodes during electrochromical reactions in the tungsten trioxide (WO\(_3\)) system. The deposited WO\(_3\) films were characterized with the laser beam deflection method (LBDM) in order to compare the mechanical effects of H\(^+\), Li\(^+\) and Na\(^+\) intercalations in the host structure. They reported that, stress in WO\(_3\) during intercalation of H\(^+\), Li\(^+\) and Na\(^+\) is compressive and linearly dependent on the inserted charge with a slope about 3 Mpa per mC/cm\(^2\). From the linear stress vs. inserted charge relationship, they observed the presence of an elastic, reversible mechanical strain of the host oxide. A large deviation from the linear stress-strain relationship is attributed to the plastic deformation. The linear increase of stress in the films is observed to be strongly depending upon the rate of the electrochemical reaction. Finally, stress measurements revealed the non-homogeneous distribution of inserted ions when guest diffusivity was considerably lower than insertion rate in the Na\(_x\)WO\(_3\) samples.

Thin metal oxide films for a WO\(_3\)-based symmetric electrochromic system with a nickel oxide layer as the counter electrode have been prepared by E. Zelazowska et al. [134] using spray pyrolysis on SnO\(_2\):F coated soda-lime float glass, at a temperature of 670 – 720 °C and using metal acetylacetonates as precursors. The films have been characterized for composition and morphology by scanning electron microscopy equipped with an X-ray energy dispersive analyzer (SEM/EDAX), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). Electrochromic properties have been examined in the electrochemical cells of a smart window arrangement using lithium ion doped sol–gel derived organic–inorganic hybrid materials as electrolytes. Hybrids with room-temperature ionic conductivities of \( 10^{-4} - 10^{-3} \Omega^{-1} \cdot \text{cm}^{-1} \) have been synthesized from tetraethyl orthosilicate (TEOS) with an addition of 35 mass % of organic compounds.
1.4 Literature Survey on MoO₃ thin films:

Thin films of MoO₃ were prepared on Quartz and Si(100) substrates by reactive dc magnetron sputtering of a 'Mo' target in an oxygen and organ atmosphere. The structural, compositional and optical properties of grown MoO₃ thin films were studied systematically as a function of post-growth annealing by S.H. Mohamed et. al [135]. The RBS studies for the films revealed that the composition of deposited films at an oxygen partial pressure of 0.4 Pa was MoO₃.90 which is equal to MoO₃. Significant change in chemical composition of the films is not observed as a function annealing temperature. The XRD patterns of the films indicated that, the as deposited MoO₃ films exhibited the amorphous nature. The films annealed at 300° C showed polycrystalline (α + β) mixed MoO₃ phase. They reported (011) as preferred orientation for the films prepared at oxygen partial pressure of 0.19 Pa and (200) as preferred orientation for the films grown at 0.4 Pa. The optical transmittance of films deposited at 0.19 Pa, was increased with the increase of annealing temperature up to 200° C, after that decreased noticeably. No change in optical transmittance was observed for the MoO₃ films deposited at 0.4 Pa and annealed at 200° C and above 200° C drastic and continuous decrease in optical transmittance is observed. Finally they summarized that, the estimated band gap (Eₐ) values of the films deposited at 0.19 Pa are small than those obtained for the films prepared at 0.4 Pa.

S.S. Mahajan et. al [136] synthesized Niobium (Nb) doped MoO₃ thin films using spray pyrolysis deposition technique. The undoped MoO₃ thin films prepared at 350° C were demonstrated the polycrystalline nature with α - Orthorhombic phase. For 3 % Nb doped films, they observed drastic change in crystalline and that led to the formation of an amorphous phase. From scanning electron microscopy results, films grown at 350° C on glass substrate demonstrated micro thread like reticulated morphology with large grains of size about 1 – 2 µm. With the increase of Nb doping percentage crystalline threads disappeared and become very small grains by indicating the rupturing of crystalline. They reported increase of optical band gap value with the
increase of Nb doping percentage. From the obtained cyclic voltammograms they observed bulging of voltammograms with the increase of Nb doping and maximum area under the curve was obtained for higher Nb doping concentration. Moreover the electrochemical stability of pure MoO$_3$ in H$_2$SO$_4$ solution is slightly less than the Nb doped one. Finally they reported that, 9 % Nb doped MoO$_3$ thin films demonstrated higher coloration efficiency of 32 cm$^2$/C at the wavelength of 630 nm than the pure MoO$_3$ films.

R. Sivakumar et. al [137] prepared MoO$_3$ thin films using electron beam evaporation technique. The films were deposited on glass and fluorine doped tin oxide (FTO) coated glass substrates. They investigated the influence of substrate temperature on microstructural and optical properties of MoO$_3$ thin films for electrochromic devices. The XRD studies revealed that MoO$_3$ films prepared on glass substrates maintained at substrate temperature (T$_s$) less than 200$^\circ$ C exhibited amorphous nature and noticed increase of crystalline at T$_s$ > 200$^\circ$ C. But formation of polycrystalline MoO$_3$ thin films deposited onto FTO coated glass substrates maintained at T$_s$ = RT. The SEM pictures of MoO$_3$ films prepared on glass substrates at T$_s$ = 100$^\circ$ C demonstrated Whisker-like structure with almost independent of clusters. But in the case of films deposited on FTO glass substrates at the same condition demonstrated pearl like structure with platelets piled one over the other corresponding to a layered structure. The MoO$_3$ films deposited at T$_s$ = RT on glass substrates showed higher optical transmittance of about 95 %. They noticed shifting of absorption edge towards the higher wavelength region with the increase of substrate temperature. Based on the obtained results, they concluded that $\alpha$ - MoO$_3$ films deposited at T$_s$ = RT on FTO substrates have layered structure to adapt them efficiently for efficient electrochromic devices.

Thin films of MoO$_3$ were prepared by electron beam evaporation technique on microscopic glass and FTO coated glass substrates and studied their compositional and electrochromic properties of MoO$_3$ thin films by R. Sivakumar et. al [138]. The XRD investigation revealed that, the MoO$_3$ films prepared at T$_s$ < 200$^\circ$ C demonstrated
amorphous nature. From XPS spectra, no additional peaks were observed other than the characteristic peaks of 'Mo' and 'O' by indicating the compositional purity. The characteristic doublet peaks were observed at binding energies of 232.22 eV and 235.44 eV. During electrochemical analysis, the optimized MoO₃ films prepared on FTO substrates were used as working electrodes. The cyclic voltammograms of MoO₃ films were recorded in the potential range between -1.2 and +1.2 V SCE. From the CV results, all the films are demonstrating better reversibility and reproducibility in their electrochemical analysis. The optical transmittance spectra of MoO₃ films prepared at Tₛ = RT demonstrated good electrochromic coloration in the visible region.

C.V. Ramana et al [139] deposited MoO₃ thin films by magnetron sputtering in a reactive atmosphere of an argon – oxygen gas mixture. They explored the influence of substrate temperature and oxygen partial pressure on growth and microstructural properties of MoO₃ films. From the Reflectance high-energy electron diffraction (RHEED) patterns, they came to some conclusions that all the films are exhibiting well textured – polycrystalline structure irrespective of the deposition conditions. The choice of p- and n- type substrates has no effect on the structure dependence and oxygen partial pressure has significant effect on the phase or crystalline. The RHEED measurements suggested that the 62.3 % of oxygen partial pressure is the optimum to obtain phase pure MoO₃ polycrystalline films. The RBS results suggested that the MoO₃ films prepared at 445º C with 62.3 % of oxygen partial pressure were nearly stoichiometric. The optimized MoO₃ films exhibited elongated crystals with lower surface roughness as indicated by SEM micrographs. The absence of any other peaks except peaks corresponding to 'Mo' and 'O' in EDAX spectra was the evidence for existence of MoO₃ phase. Finally they summarized that, the sputtered MoO₃ films were more useful for electrochemical applications.

M. Zuluaga et al [140] prepared MoO₃ thin films using CO₂ laser operating on a continuous wave mode. They investigated the influence of intensity of laser intensity on microstructural and optical properties of MoO₃ thin films. The XRD patterns of the
films revealed the growth evolution of the films with the increase of laser intensity. The films grown at substrate temperature of 350° C and laser intensity of 4.3 W/mm² demonstrated mixture of α and β phases of MoO₃. The refractive index and absorption coefficients were evaluated from the obtained optical data recorded for the films prepared various laser intensities. They reported that, refractive index noticed to be decreased with the increase of laser intensity. The absorption spectra for all the films exhibiting an absorption center located at 750 nm. Finally, they concluded that, the intensity of CO₂ laser beam affects the crystallographic and optical properties of MoO₃ films.

T.S. Sian et. al [141] prepared amorphous and crystalline MoO₃ thin films on ITO coated glass substrates using thermal evaporation. They aimed to investigate the effect of oxygen deficiencies on electronic, optical properties of unintercalated amorphous MoO₃-x thin films and the correlation between optical absorption process and XPS data. The XRD spectra of as deposited films and annealed at 100° C demonstrated diffused pattern by indicating the amorphous nature and noticed on set of crystalline at 350° C. They recorded transmittance and reflectance in visible and near – infrared regions for films annealed at various temperatures. The observed transmittance value decreased steeply at 400 nm wavelength indicating a strong absorption due to band to band transition. The estimated refractive index values do not change as a function of annealing temperature and extinction coefficient values of all the films showed a peak between 200 nm and 1100 nm. They estimated optical absorption coefficients and confirmed the existence of direct band (since α > 10⁴). The calculated optical gap values are 3.27 eV and 3.16 eV for crystalline and amorphous films respectively. The XPS core level studies revealed the presence of Mo⁴⁺ and Mo⁵⁺ oxidation states in amorphous films, while Mo⁶⁺ states only in crystalline films.

S.S. Sunu et. al [142] prepared polycrystalline MoO₃ thin films onto alumina substrates and studied their gas sensing properties. From XRD investigations, they observed that amorphous nature of MoO₃ thin films deposited at substrate temperature
below 673 K. SEM pictures of $\eta - Mo_3O_11$ and $\chi - Mo_4O_{11}$ demonstrated nearly spherical morphology with an average grain size of about 300 – 500 nm. But as a function of post-annealing the grown films demonstrated needle like morphology. They studied the variation of conductance of the annealed films in air as a function temperature in the range 500 – 605 K. The cross – sensitivity studies were reported for LPG and H₂ and from their observations, they reported that thin film based sensors were relatively more selective compared to those using porous pellet structures in the temperature range 508 - 555 K.

H. M. Pathan et al [143] prepared MoO₃ thin films on stainless steel substrates using electro-deposition from aqueous solutions. For the deposited films cyclic voltammetric studies were performed in molybdic acid electrolyte solutions of various concentrations. From CV observations, they noticed nonlinear increase in peak current with the increase of solution concentrations. They reported that, cathodic peak current and voltages decreased with the enhancement in composition of citric acid in the solution. The XRD pattern revealed the amorphous nature of the MoO₃ films prepared at lower concentrations. From SEM picture, they observed surface with composed of small spherical grains with estimated average grain size about 10 – 20 nm.

O.M. Hussain et al [144] deposited MoO₃ thin films by reactive pulsed laser deposition on Corning 7059 glass substrates. They investigated the influence of oxygen partial pressure and deposition temperature on the structure, surface morphology and optical properties of MoO₃ films to understand the growth mechanism of the films. The films prepared at 473 K in an oxygen partial pressure of 100 mTorr exhibited predominantly a (0k0) orientation, corresponding to an orthorhombic layered structure of $\alpha - MoO_3$. The evaluated optical band gap of the films was 3.24 eV. The films deposited at an oxygen partial pressure of 100 mTorr and at a deposition temperature greater than 700 K exhibited both (0k0) and (0k2) orientations, representing $\alpha - \beta$ mixed phases MoO₃. The investigations revealed the growth of polycrystalline and single crystalline orthorhombic layered structure of $\alpha - MoO_3$ thin films with composition nearly approaching the nominal stoichiometry at moderate substrate temperatures in an oxygen partial pressure of 100 mTorr.
1.5 Scope of the present work

In view of the novel material characteristics of transition metal oxides (TMOs) by virtue of their fascinating and promising properties in the current nanoscience and technology era, the investigations are intended to work on these materials. In particular owing to the enduring and impending chromogenic properties of tungsten trioxide, it seems to be paramount as an active layer for the next major advances in energy-efficient window technology (Smart windows) and also its applications in opto-electronics, electronic displays and optical memory devices. Consequently by considering the potential applications of tungsten trioxide, the methodical investigations are necessitated about the growth and respective systematic characterization of the grown tungsten trioxide thin films. However, the efficiency of tungsten trioxide thin films as an active layer essentially depends on density, stoichiometry, and internal porosity of the deposited films, which in turn depend upon the type of thin film deposition technique and film processing parameters. Literature survey revealed that much work has been reported on the growth and properties of tungsten trioxide thin films. Most of the researchers intensively discussed about the preparation of amorphous/polycrystalline tungsten trioxide thin films and characterization of their microstructural and opto-electrochromic/electrochemical properties only. Various chemical and physical vapour thin film deposition techniques are employed to deposited tungsten trioxide thin films. Despite various physical vapor deposition techniques, activated reactive evaporation (ARE) is one of the plasma assisted physical vapor thin film deposition techniques to grow nearly stoichiometric thin films with better uniformity at relatively lower substrate temperatures with higher deposition rates. In this deposition technique, the reaction occurs predominantly in plasma; as a result chemical composition of the films can be controlled by changing the ratio of reacting species.

Therefore in the present investigation, the tungsten trioxide thin films are deposited onto ITO coated glass substrates, by using home build activated reactive
evaporation technique and studied the influence of respective film processing parameters on composition, microstructural and optical properties of the grown films. A comparative study on electrochromic/electrochemical properties of amorphous, nano and poly crystalline tungsten trioxide has been carried out to check the endurance and adaptability of the films as an active layer. In extension to the present work, an effort has been made to grow both tungsten trioxide and molybdenum trioxide thin films onto flexible ITO coated Kapton substrates and studied about their microstructural properties and electro - photochromic properties to employ them as active layers for future based flexible electrochromic windows.

1.6 Objectives of the present work

The main objectives of the present investigations are

- Deposition of tungsten trioxide thin films by activated reactive evaporation technique under various deposition conditions.
- Structural, compositional and optical properties in relation to the deposition conditions.
- Study of electrochromic and electrochemical properties of the deposited tungsten trioxide thin films.
- Investigations on the growth of tungsten trioxide thin films on flexible Kapton substrates using activated reactive evaporation technique.
- Growth, characterization and electrochromic properties of tungsten trioxide films grown on flexible substrates.
- Electrochromic and photochromic performance of molybdenum trioxide thin films prepared onto flexible Kapton substrates.
1.7 Organization of the Thesis

The results of the present investigations carried out and detailed discussions on the results obtained are presented systematically in the thesis. The thesis consists of five chapters.

➢ The first chapter deals with the scientific and technological importance of the tungsten trioxide and molybdenum trioxide thin films, the literature survey and scope of the present work,

➢ The second chapter deals with the details of experimental techniques employed for the growth and characterization of the films.

➢ The growth of tungsten trioxide thin films, characterization and a detailed discussion on the obtained results along with electrochromic/electrochemical properties of tungsten trioxide thin films are presented in the third chapter.

➢ The fourth chapter describes the growth, electrochromic and photochromic properties of Molybdenum trioxide thin films.

➢ The fifth chapter deals with the summary of the results and conclusions drawn on the basis of the conglomeration of all the results of the present investigations.
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