A Review on WO\textsubscript{3} films prepared by various methods

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Recent developments in the synthesis of transition metal oxides in the form of thin films have opened up opportunities in the construction of electrochromic devices with enhanced properties. Transition metal oxides like WO\textsubscript{3} and MoO\textsubscript{3} have good electrochromic properties and these oxides can also change their optical properties when a voltage pulse is applied. These electrochromic materials are used for displays, gas sensors, rear-view mirrors and smart windows for energy saving applications. There are numbers of different techniques used for the deposition of stable thin films of these oxide materials. Tungsten Oxide (WO\textsubscript{3}) is the best suited material for energy conservation applications.

Keywords: Tungsten oxide; Sputtering; Sol-gel; Spray Pyrolysis; Electrochromic; Smart Window

INTRODUCTION

WO\textsubscript{3}[1], NiO[2], TiO\textsubscript{2}[3], V\textsubscript{2}O\textsubscript{3}[4] which are considered as inorganic EC material while viologen[5], polyaniline (PANI)[6], poly(3,4 ethylenedioxythiophene) (PEDOTs)[7] are common organic and polymer EC materials. Among all inorganic material WO\textsubscript{3} have high coloration efficiency, quick response time and long life[8]. Tungsten was first introduced in the 18th century by Peter Woulfe who was the first person to recognize this new element. He introduced this element as wolframite, so tungsten was originally known as wolfram, explaining the choice of “W” for its elemental symbol. In year 1841 Robert Oxland gave the first procedure for preparing tungsten trioxide and he found that tungsten trioxide (WO\textsubscript{3}) is a wide band gap metal oxide having good semiconductor property for various applications including electrochromic materials and gas sensors[8]. WO\textsubscript{3} films also possess good hydrophilic, gasochromic and photochromic properties. The first electrochromic study on tungsten trioxide was reported in 1969[9]. The most promising application of this coating is as a switchable glazing for a smart window, which can save energy for air conditioning.

Recently, WO\textsubscript{3} films have been considered for use as dielectric layers in multilayer heat mirror coatings on building and automotive glasses. For most of these applications, thin films of WO\textsubscript{3} with nanometer thickness are usually deposited on glass or polymeric substrates. A variety of conventional deposition methods have been used to prepare WO\textsubscript{3} films, such as direct current (dc) or radio frequency (rf) magnetron sputtering[10-18], sol–gel methods[19-21], plasma spraying method[22], electron beam evaporation[23,24], thermal evaporation [25,26] and hydrothermal methods[27]. Tungsten oxide has a cubic structure which is also described by “empty-perovskite” type structure formed by WO\textsubscript{3}. In octahedral structure atoms are share at corners[8,10]. The empty space which is available inside the cube is filled by an interstitial atom. In interstitial sites the guest ions can be inserted. It is observed that both an amorphous and crystalline WO\textsubscript{3} thin films exhibit electrochromic coloration property due to ionic insertion. In case of amorphous WO\textsubscript{3}, the absorptance modulation during ion and electron insertion occurs in the visible and near-infrared regions of the spectrum. In crystalline WO\textsubscript{3}, however, the injected electrons are to a significant extent delocalized and behave like free electrons. The free-electron like behavior results in a reflective optical modulation which can be described by a modified Drude model. It is generally believed that the color change in the films is related to injection and extraction of electrons and metal cations[28]. The general electrochromic phenomenon of WO\textsubscript{3} is due to the formation of tungsten bronze (M\textsubscript{x}WO\textsubscript{3}) according to the following equation:

$$WO_3 + xM^{+} + xe^{-} = M_xWO_3$$

where $M = $H, Li etc. At low x the films have an intense blue color caused by photo affected intervalence charge transfer (CT) between adjacent W\textsuperscript{V} and W\textsuperscript{VI} sites. At higher value of x, the metallic “bronce” is formed which is red or golden in color. By cathodic polarization process ion insertion and electron injection takes place. The ions which are inserted will expand the lattice of the guest oxide while the electrons modify its electronic structure and in turn change its optical properties[9]. In general the electrochromic devices are classified in two types. In first type, the electrodes used are made of conducting glass and wrapped by an organic or inorganic polymer or plastic. This type of configuration was used in electrochromic windows and is bistable. The main limitation of this type of devices
is that they show slow color change due to the small amount of migration rate of the ions in the bulk polymer. Bright color changes are not possible here. Dissolving two complementary electrochromic molecules in a solvent is the second type of electrochromic device. This type is simpler than first type, the dark and bright color achieved by the reaction of solvent. The main drawback of this type is that it requires an electrical current to maintain in the colored state. The colored molecules diffuse through the system and react to restore the bleached states. This type cannot be used for large area devices. To overcome these problems an electrochromic system is needed which is both bistable and changes color rapidly[29]. When a suitable colorless molecule in oxidized state and colored molecule in reduced state is attached onto the surface of a colorless semiconducting electrochromic material (present case, WO₃) on conducting glass Indium-doped tin oxide (ITO) substrates the above process can be accomplished. When a negative potential is applied to the conducting glass then it injects electrons into the conduction band of the semiconducting electrochromic material and reduces the absorbed molecules. When a positive potential is applied then the molecules get bleached due to this the electrochromic material coloration efficiency of the molecular systems gets increased. The ultimate interest in the electrochromic materials is the fabrication of electrochromic device, which can control the transmittance of the reflectance of the incident light.

Electrochromism has remained an active area for basic[30] and applied research with large possibilities for applications in emerging technologies since many years. Some of the applications are already developed at the technological level and are commercialized successfully whereas some are still in the developmental stage. Few of them are already available in market such as electrochromic windows, which are used in office windows, architectural and automobiles, rear-view mirror for car and vehicles, and large area EC display devices. Some other application like eyewear, visors of helmets, electrochromic paper will be available in near future. However, due to lack of manufacturing techniques and durability of the available devices the ECD are not so common in markets.

APPLICATION & ELECTROCHROMIC PARAMETERS

The principles of these devices are explained briefly in this section [29]. There are four main applications of electrochromic devices and are shown in fig. 1(a)-1(d).

1. Information Display: Researchers have been working on information displays since the discovery of electrochromic device [31]. The electrochromic display can act in either reflectance or transmissive modes; the majority of devices work in the reflectance mode. The EC display can be easily viewed from any angle so it is particularly useful where people are walking (on railway station, airport, traffic direction boards, etc). People have also put efforts to use it in television and digital watch display. Switching time and high color reproducibility over a large number of switching cycles are the major shortcomings in using such devices [fig.1(a)].

2. Mirror with variable specular reflectance: The electrochromic mirrors are (operated in a reflectance mode) one of the important applications of ECD. Reflecting intensity is reduced as an optically absorbing color is induced over the reflecting surface[32]. Here total opacity is to be avoided, to persist a slow reflection in the darkened state. The self-darkening EC rear-view mirror generally available for cars and other vehicles is one of its important applications. During daytime, the rear view mirror is adjusted in such a way that the electrochromic component is in the bleached state resulting in a reflection from the back-reflecting part of the mirror. At night, the mirror is adjusted in such a way that the headlights behind the car only hit a photosensitive sensor on the front glass surface of the mirror. Therefore, it resists the light from following vehicles and thereby improves driver’s comfort. The device needs to be able to switch at least 10⁴ - 10⁵ cycles without visible degradation, with a switching time of less than 5s [fig.1(b)].

3. Smart windows: One of the most important applications of ECD, which are available in market, is the EC window. This electrochromic window is also known as “Smart Windows” and it is new technological development which automatically controls the amount of light and solar energy in buildings and provides comfort [33,34]. It is also used in architectural glazing or skylights to control the solar heat entrance and to save energy for air-conditioning in summer and heating in winter[35,36]. Furthermore, it is also used in automobiles, airplane, and trains in order to avoid dazzling. Such a
device needs high transmittance modulation and lifetime of at least 20 years with switching time of few seconds to few minutes [fig. 1(c)].

4. Variable-emittance surfaces: Variable emittance surface device are special design with a crystalline tungsten oxide film [fig. 1(d)]. Intercalation/deintercalation ions make this surface infrared reflecting or absorbing whose thermal emissivity is high [29]. The following are some of the properties required for quantifying the ECD: high transmittance modulation, high-coloration efficiency, low-switching time, good-memory effect, and long cyclic life.

1. Transmittance Modulation ($\Delta T$): Transmittance modulation is one of the most important electrochromic parameter for electrochromic device applications. It is defined as the transmittance change in colored and bleached state. Since the transmittance modulation depends on the wavelength, the change in the transmittance is measured by the optical transmittance spectra of the bleached ($T_b$) and the colored ($T_c$) state of the sample as a function of wavelength ($\lambda$):

$$\Delta T = T_b - T_c$$

Generally, $\Delta T$, lying between 70 – 80 %, is particularly used for device applications [37,42].

2. Coloration Efficiency (CE): Another key parameter for the electrochromic devices application is the coloration efficiency (CE) also known as electrochromic efficiency. The CE is described as how large is the magnitude of optical modulation formed by per injected/extracted charge i.e., the change in the optical density ($\Delta OD$) per unit of injected/extracted charge density ($Q$) per unit electrode area:

$$CE = \frac{\Delta OD}{Q}$$

The $\Delta OD$ depends on the light absorption ability of electrochromic materials. The change in the optical density is measured from the optical transmittance spectra of the bleached ($T_b$) and the colored ($T_c$) state of the sample:

$$\Delta OD = \log \frac{T_c}{T_b}$$

The charge density i.e. the charge injected per unit electrode area of the film is obtained from integration of the corresponding current for total time:

$$Q = I \times t$$

where, $I$ is the current $(A)$, $t$ is the total time $(s)$ for which the current is passed and $A$ is the area of the electrode $(cm^2)$. CE is positive if coloration is generated cathodically and negative if coloration is generated anodically [37,42].

3. Switching Time: Switching time $(t)$ is the time required for coloring or bleaching process of an ECD. Coloration time $(T_c)$ is defined as the time required switching from the bleached state to the colored state (90 % to 10 %) and the bleaching time $(T_b)$ is the time taken to switch from the colored state to the bleached state (10 % to 90 %). Some applications do not require a rapid color change such as the electrochromic office windows, which requires a very slow response; however, applications such as display devices, require a more rapid response. The switching time is influenced by certain factors viz. ionic conductivity of the electrolyte, the applied electric field, device area, and film structure [37,42].

4. Memory Effect: Depending on the polarity of the applied voltage, the ECD can exist either in colored or bleached state, which will be retained by the ECD after removal of the voltage; this effect is called “open-circuit memory effect.” This is one of the excellent benefits of electrochromic devices. In open-circuit condition, when the inserted charge is self-removed from the electrochromic film, due to an electrical leakage current or ion diffusion it loses memory, this phenomenon is called self-bleaching. Therefore, the ion conductor plays crucial role for the optical memory effect. The electrochromic memory can be for several days or weeks even without any current. However, some EC devices may require small refreshing charges to maintain the charged state because side reactions or short circuits may change the desired color [37,42].

5. Cycle-Life: It represents the number of color-bleach cycles that can be performed by the ECD before any significant extent of degradation has occurred. The cycle-life is therefore a measure of the electrochromic durability testing. The maximizing of the cycle life is an obvious aim of device fabrication and a minimum 10,000 cycles are acceptable. ECD are generally used in window and display applications, deterioration is best gauged by eye vision, and the same illumination that would be employed for normal device operation. However, 50% degradation is often tolerable for display application. The three common reasons for the low cycle life or device failures are: The TCO layer failure, electrolyte failure, or one or both of electrochromic layers failure. Most common cause of TCO degradation is decomposition of TCO, which increases the resistance and decreases the transparency. The reason for electrolyte failure is due to solar irradiation and generation of hydrogen gas, when electrolytes use proton for conduction. In electrochromic layers failure, the layers gets dissolved when they come in contact with electrolyte and in other cases, layer changes volume during redox process [37,42].

6. Cyclic Voltammetry: In cyclic voltammetry a voltage is applied between tungsten oxide film and a counter electrode. The voltage was swept back and forth between two set points, usually triangular manner. The current flowing from film in and out. Cyclic voltammetry can be used non-quantitatively to give a "fingerprint" of the electrochemical processes, to trace reversible and irreversible effects, and to ascertain voltage levels that yield stable operation [109].

7. Raman Spectroscopy: Raman Spectroscopy gives the information [109].

THIN FILM PREPARATION METHODS

1. Sputtering Method

By the bombardment of a target material with accelerated ions, the evaporation of target material and its deposition on a substrate thin film formation is carried out. If a reactive species like oxygen or methane is present in the gas phase then the chemical reaction with the evaporated target material can occur, leading to the deposition of a chemical compound. In the past, reactive sputter deposition processes were widely used for the preparation of oxides, carbides, nitrides, silicides or oxy-nitrides. The surface and volume microstructure of the deposited compounds depend strongly on the preparation procedure. For industrial thin film preparation sputtering deposition is well known technique. The oxide film deposited by sputtering method can’t show the same composition and microstructures as the films made by evaporation technique. Tungsten oxide films were deposited by reactive DC magnetron sputtering on various substrates such as quartz, Cr coated glass and transparent conducting glass and were used for transmittance, raman scattering and electrochemical measurements [38] WO3 films were prepared by DC and RF sputtering by Kaneko et al. and Akram et al. respectively. Beyond certain amount of O2 content, the rate of
substrates were mounted on a holder and maintained at a constant
with a 5nm layer of amorphous carbon was used as substrates. Th e
MHz. Ultrasonically cleaned alumina and glass slides, over coat ed
The sputtering atmosphere was an Ar-10% oxygen mixture at a total
mm3>70mm3>50mm3>30mm3>10mm3 and the could reach
transmittance (ΔT, %) of the 400 WTiOx film between the bleached
improve with deposition power caused by the doping with Ti. The
coloration efficiency higher for 0.4Pa total pressure approxima tely
fast EC response.  The result shows that as pressure increases the
higher working pressure was rough and lower density, which offered
by the amount of tungsten oxide present in the film. The film a t
modulation and coloration efficiency of films are strongly affe cted
of Ar/O2 maintain 4 and the total pressure varied from 0.41 to 1.7
meter. The characterization of the sputter discharge parameters for tungsten oxide preparation it is
obtained the \( \text{WO}_3 \) film exhibits the optimal pore network for the diffusion of Li+, possessing an electrochromic property. The pore structure of the 500 °C annealed \( \text{WO}_3 \) film exhibits the optimal pore network for the diffusion of Li+
and colored states at 400 nm is 25.8%, at 550 nm is 52.5% and at
400 W. WTiOx film is the best for electrochromic applications. The
800 nm is 62.4%. Jow-Lay Huang et al. [48] has reported
electrochromic properties of tungsten oxide films deposited by
electrochemical anodized RF-sputtered. Tungsten oxide films of
various morphology, crystallinity, and porosity can be prepared by
carefully altering the anodization time (20–50 min) and annealing
temperature (450–550 °C). Porosity influences the diffusion of Li+ ions within the electrochromic material and thus affects the
electrochromic property. The pore structure of the 500 °C annealed
WO3 film exhibits the optimal pore network for the diffusion of Li+
ions and possesses the superior EC property. Thus the EC results
said that film deposited after 40 min anodization and 500°C
annealed temperature had good modulation of 43.6% and coloration
efficiency of 42.8 cm²/C. S.S. Kalagi et al [49] has reported that the
tungsten oxide films deposited by varying the sputtering time using
RF sputtering. The working pressure was maintained at 1x10⁻² torr.
Oxygen content maintain 40% by keeping applied power to target
constant 140W and substrate temperature 23.2°C constant. The
sputtering time varies from 30, 45, 60 min. It was observed that the
film deposited at 30,45,60 min sputtering time shows transmittance
modulation 18%,32% and 55% respectively. The result shows that
60min sputtering time shows higher transmittance modulation 55%.
the device shows a coloration efficiency (C.E.) of 46.45 cm² C⁻¹
and reversibility of 98%.

2. Sol-gel Method

Dipping, spin-coating or spraying is the method used for thin film
preparation using sol-gel method. Using poly-condensation process
the first colloidal oxide is produced either by acidification process
and organo-metallic compound is formed [50]. Chemseddine
[57-61] and Habib [62-66] used the sol-gel technique which
has been surveyed [51-56] as the most widely studied technique.
The acidification process done by puring a solution based on
sodium tungstate or potassium tungstate through a proton exchange
resin. In this method solution was applied to glass plate, either
directly as drop or by spin coating and spraying, after drying or by
heating the hard coating with good electrochromic and optical
properties obtained. W-PTA sols were prepared in 18 ml of (30%)
H₂SO₄ which reacted with small percentage of metallic powder
[5gm, 91%]. The mixture was stirred for 12 hours at room
temperature until tungsten powder was dissolved. Platinum net was
then added to the mixture to remove any unreacted H₂O₂. The sols
with a deep brown color were stored at -25°C to prevent gellati on
prior to dipping. This gellation process can be reversed by adding
small amount of H₂O₂ until the dark brown sol is reformed [67].
Films were obtained by heat treatment and their thickness were in
the range of 150 nm/dipping up to 5 dipping thereby yielding
600nm thick films [68]. Dip coating is the method in which a
solution of tungsten hexaethoxide or tungsten oxo-tetra has been
applied successfully by Bell et al. [68]. They dip coated substrate at
5mm/s speed and DTA/TGA analysis shows result of WO₃ gel gets
crystalline phase and by performing electrochemical characterization method, WO₃ film coated on ITO glass than
coloration was done by adding H⁺ ion. The thickness of WO₃ film
was found around 1250Å. P. S.Patil et. al [69] had reported sol-gel
method for synthesis and chemically grown electrochromic tungsten
oxide. They were used FTO coated glass substrate and washed with
laboline solution and then double distilled water then after it was
dipped in chromic acid for 20 min and rinsed with double distilled
water. Then substrates were etched in 0.1 M H₂SO₄ in order to
improve adhesion. Substrates were cleaned with double distilled
water and dried in alcoholic vapour. It was seen that at the terminal
growth of film, the film thickness remains constant after 15 min at

640 nm wavelength and there was no further increase in thickness observed. For electrochromic property measurement using three electrode cell configuration with 0.5 M LiClO4/propylene carbonate as the electrolyte, platinum as the counter-electrode, tungsten oxide as the working electrode and the saturated calomel electrode (SCE) as the reference electrode and -0.8 to +0.8 V potential applied with 100mV/s scan rate. The result shows maximum coloration efficiency 12.57 cm²/C at 630nm.In same year Wang W. et al [70] had reported sol-gel method for mesostructured tungsten oxide films for electrochromic properties. They were used tungstic acid, H₂O₂: 35%wt.water solution and the non-ionic surfactants Brij56 (C₈H₁₇O₇(OH)(C₈H₁₇)), OH, n=10), Tween 60 (C₈H₁₇O₆(C₃H₄O₅)n, n=20). Peroxotungstic acid (PTA) was prepared by the reaction between H₂WO₄ with hydrogen peroxide. The PTA and surfactant in mixed solvents of water and ethanol, with weight ratio PTA : Surfactant:H₂O:ethanol of 1:0.2:4.5:2.25. The sol prepared was used for dip coating on glass substrate. The deposited film was allowed to dry at room temperature and then, was further thermally treated at temperatures 100–450 °C for between 1 and 20 h to solidify the film and remove the template. For electrochemical properties three electrode configuration method was used in which the working electrode consisted of the dip coated TOFs deposited on ITO coated glass in 0.1 M aqueous solution of sulphuric acid. An Ag electrode (Ag/AgCl/saturated KCl) and a platinum needle were taken as the reference and counter electrode, the result shows that the coloration efficiency 44cm²/C and higher charge density up to 8.2 mC/cm² at 100nm.

Y. Djaoued et.al [71] has used sol-gel method for deposition of tungsten oxide film. They were used an acylation reaction between poly (propylene glycol), bis (2-aminopropyl ether) (2-APPG) with isocyanatopropyltrioxy-sil-ane (ICS) in tetrahydrofuran (THF) in the volume ratio 1: 0.1: 1. They were observed structure at various temperature 400,500,600°C they found grain size 10,19,25nm. They were also found that the transmission in bleached state 76.4% at 1100nm wavelength, when the coloration potential applied 2.5V and bleach voltage applied -1.0V.

R. S. Patil et.al [77] has reported electrodeposited method for tungsten oxide for electrochromic property. They were prepared tungsten electrolyte by dissolution of 3.74g tungsten powder in 40 ml H₂O₂ (30%). Then exothermic reaction conducted at 0°C and 10°C. Mixing this solution with anhydrous absolute ethanol and water in the ratio of 2:3 yielded the deep yellow-colored deposition sol, which was refluxed at 55°C for 1 h to decompose off excess peroxide. Then graphite was used as counter electrode and SCE used as reference electrode, then constant potential supplied for 15 min at room temperature. For measurement of electrochromic property they were take film in to 0.5M LiClO4-PC electrolyte at different scan rates with a potential window from +1.4 to -1.4V versus SCE. They observed the transmission modulation and coloration efficiency at 630nm wavelength 74% and 92cm²/C respectively. A. Duta et.al [78] have prepared tungsten oxide film for synthesis of electrochromic properties using pyrolysis method of deposition. They were prepare precursor solution by dissolving 2.2 g of WC6 powder) in ethanol which contain acetyl acetone with WC6 and acetyl acetone in a 1:2 M ratio. Hexadecyl- trimethyl-ammonium bromide (HTAB) and polyethylene glycol (PEG 400) were added in the spraying solution in different amounts. The film deposited at 0 ppm, 200ppm, 500ppm of HTAB and PEG400. The result obtained shows that the film deposited at 550nm shows were prepared electrolyte by adding 35.4 ml concentrated HF into 64.6 m1 concentrated H₃PO₄ finally to an 8 M HF concentration. The films were anodized for different time period 10min, 20min, 40min, 60min, 120min by applying circuit potential of 40V with sweep rate of 300mV/s. To analyses electrochromic properties of tungsten oxide film the film characterized in an aqueous solution of 0.1M HClO₄. The results shows that the film deposited at 2μm thickness was gave higher value of coloration efficiency 54.95cm²/C.

Figure 2. (a) WO₃ film thickness after different anodization time in a concentrated H₃PO₄ and 8 M HF electrolyte under the anodization potential of 40 V. The insets show the thicknesses of resulting films. (b-f) SEM top-views of the WO₃ films fabricated [76].

3. Spray- pyrolysis Method

Hurditch used spray aqueous solutions of metatungstic acid (H₃W₁₂O₄₀) [73]. Spray deposition, using solutions of WC₆ dissolved in ethanol or NN-dimethyl formamide, was carried out [74] where spraying took place in air on to substrates heated up to 500°C. The tungsten oxide films thus formed showed electrochromic property. XRD spectra gave evidence of some chlorine contamination in the film. XRD showed that films deposited at temperatures more than 300°C were crystalline. Sivakumar et al.[75] have deposited monoclinic WO₃ films at 250°C and at higher wavelength region observed the optical studies may be due to coloration effect on thin films. P. Schmuki et.al [76] had prepared thick porous tungsten oxide films by anodization of tungsten in fluoride containing phosphoric acid electrolyte. They
As the band gap increases, the material becomes a better insulation. The temperature of evaporation can be controlled by introducing N₂ gas and the substrate temperature was maintained around 5.0–6.5 x 10⁻² Pa [81]. Deposited WO₃ films were analyzed by X-ray diffraction and found to be amorphous. The deposition rate was 4–5 Å/s, the deposition angle was varied within 40° with a planetary rotation, and the evaporation process was controlled by introducing N₂ gas and the substrate temperature was usually maintained at 80°C after keeping at 110°C for 5 min. The total gas pressure in the chamber during the evaporation process was controlled by introducing N₂ gas and maintained around 5.0–6.5 x 10⁻² Pa [81]. Deposited WO₃ films were analyzed by X-ray diffraction and found to be amorphous. The packing density of the film, calculated from the film thickness and weight, was 38 g/cm³ [82]. Sivakumar et al. [83] have studied the opto-electronic properties of WO₃ films electron beam evaporated at different substrate temperatures and study shows that it transformed from amorphous to crystalline nature by increasing the temperature and from optical study it is found that they have good coloration effect and stoichiometric nature. Table 1 shows reviews observed for electrochromic and optical properties using various deposition methods which show at the end of the paper. Development of semiconducting oxide materials with controllable energy gap is necessary for the increased applications in electrochromic liquid crystal display and optoelectronic devices. Hence the absorption and transmission properties were studied in detail to calculate the band gap variations and the related optical properties. For heavily disordered evaporated WO₃ films band gap varied from 3.2 to 3.4 eV [97]. The band gap depends on the materials preparation conditions and the temperature of evaporation. Miyake et al. [98] reported a monotonic drop of E₉ with increasing temperature. The band gap

Table 1: Electrochromic Properties of WO₃ Films.

<table>
<thead>
<tr>
<th>Research Group/ Year</th>
<th>Deposition Technique</th>
<th>Variable Parameters</th>
<th>Electrochromic Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>K. Lee et al. (2013)</td>
<td>RF Sputtering</td>
<td>Power 100, 200, 300, 400 and 500 W</td>
<td>CE = 30.2 cm²/C</td>
</tr>
<tr>
<td>J. Chen et al. (2012)</td>
<td>Spray Pyrolysis</td>
<td>Voltage 20, 40, 60, 80, 100 V</td>
<td>CE =15.2 cm²/C</td>
</tr>
<tr>
<td>K. Weng et al. (2012)</td>
<td>pulsed magnetron sputtering</td>
<td>Power 100, 200, 300, 400 and 500 W</td>
<td>OD= 0.85</td>
</tr>
<tr>
<td>J.T. Chang et al. (2012)</td>
<td>Reactive DC magnetron sputtering</td>
<td>Current (0.3, 0.5, 1.5 A)</td>
<td>Not studied</td>
</tr>
<tr>
<td>M. Rao et al. (2011)</td>
<td>Evaporation</td>
<td>Voltage 303-603 K</td>
<td>Not studied</td>
</tr>
<tr>
<td>H. Kawasaki et al. (2009)</td>
<td>RF magnetron sputtering</td>
<td>O₂/Ar = 5:5:6:4:7:3, 8:2, 9:1</td>
<td>Relative density: 0.78, 0.85, 0.92</td>
</tr>
<tr>
<td>A. Rouvier et al. (2008)</td>
<td>RF Sputtering</td>
<td>Temp. RT to 400°C</td>
<td>Absorption coefficient : 0.1</td>
</tr>
<tr>
<td>K. Muthu Karuppasamy (2008)</td>
<td>DC magnetron sputtering</td>
<td>Temperature 250-350°C</td>
<td>CE =40 cm²/C</td>
</tr>
<tr>
<td>J. Augustynska et al. (2006)</td>
<td>Sol-gel Method</td>
<td>Temp. RT to 200°C, O₂ pressure = 0.2-0.8</td>
<td>Not studied</td>
</tr>
<tr>
<td>B. Almeida et al. (2002)</td>
<td>Reactive DC magnetron sputtering</td>
<td>Voltage 450, 490, 530 V</td>
<td>CE max= 59.9 cm²/C</td>
</tr>
<tr>
<td>M. Hepel et al. (2000)</td>
<td>Electrochemically</td>
<td>Potential different +0.5 to -0.5 V</td>
<td>CE= 25 cm²/C @ 633 nm</td>
</tr>
<tr>
<td>P.S. Patil et al. (2000)</td>
<td>Solution thermolysis</td>
<td>10, 20, 50, 100 mV/s</td>
<td>Not studied</td>
</tr>
<tr>
<td>A. Pennisi et al. (1992)</td>
<td>Electrochemically</td>
<td>No of Cycle - 60, 100, 150, 200</td>
<td>Not studied</td>
</tr>
</tbody>
</table>

4. Electron beam evaporation Method

Condensation of the vapour produced by sublimation from hot tungsten powder is the standard technique for making tungsten oxide film for laboratory study [59]. In this method heating can be done by a resistive boat (Ta, Mo and W) or by a reaction crucible or by an electron beam, sometime water free powder is also used as substrate for deposition and the substrate temperature kept up to a few hundred degrees in unheated condition. The evaporation takes place due to non-reactive gases. By this evaporation technique good electrochromism thin films are made. The deposition rate gets increased by placing the substrate nearer to the vapour source. The vapour produced during this method of heating does not contain any individual atoms but it contains molecular nature. The dominating species is trimetric W₃O₉ molecules, dependent on experimental conditions [81]. The deposition rate was 4.5 Å/s, the deposition angle was varied within 40° with a planetary rotation, and the evaporation process was controlled by introducing N₂ gas and maintained around 5.0–6.5 x 10⁻² Pa [81]. Deposited WO₃ films were analyzed by X-ray diffraction and found to be amorphous. The packing density of the film, calculated from the film thickness and weight, was 38 g/cm³ [82]. Sivakumar et al. [83] have studied the opto-electronic properties of WO₃ films electron beam evaporated at different substrate temperatures and study shows that it transformed from amorphous to crystalline nature by increasing the temperature and from optical study it is found that they have good coloration effect and stoichiometric nature.
was changed from 3.25 to 2.7eV. The decrease is strongest at temperature >300°C which indicates that crystallization is caving the band gap narrowing for sputter deposition, the band gaps have been reported 3.0<\textit{E}_g<3.4 eV [97, 99]. For sputter deposition the authors reported 3.0 to 3.4 eV with a tendency that a high pressure of the sputter gas and high O\textsubscript{2} mixture in reactive sputtering. This process gave a low \textit{E}_g[100]. Crystallized films produced by sputtering shows band gap of 2.9 eV [101] and by chemical vapour deposition showed a band gap of 3.2 eV [102]. A thickness dependent change in the crystalline or tungsten oxide films made by anodizing is observed with the band gap values of 3.05 and 3.73 eV [103]. Crystalline anodic films with monoclinic triclinic, and orthorhombic structure and different degrees of hydration had the band gap of 2.55<\textit{E}_g<2.79eV as observed by the photo electrochemical measurements [104]. Kubo and Nishikitani [105] reported that the optical band gap converges to a constant value between 2.8 and 2.7eV that was assigned to crystalline WO\textsubscript{3} film. The hydrogen tungsten bronze is a reasonable semiconductor at low values of x (x=0.3 to 0.5) of H\textsubscript{x}WO\textsubscript{3} [106]. Rottkay et al.[107] recorded the optical measurements with a variable angle spectroscopic ellipsometer from 280 to 1700nm. Upon colouration the agreement between effective medium theory and optical measurements deteriorates. The injected electrons are trapped at the energetically lower sites, thus giving the compound character of a preferred component, possibly the one with smaller atomic number. Films prepared in the sol-gel process showed good transmission modulation at wavelengths higher than 520nm, more that 50% and at lower wavelength the transmittance was very less [108]. All transmittance and reflectance spectra showed the typical interference structure caused by both ITO and WO\textsubscript{3} layers. As the injection charge of WO\textsubscript{3} increases the absorbance also get increased and due that the WO\textsubscript{3} will gets converted in tungsten bronze having blue color. The incomplete oxidation of evaporated tungsten oxide does not lead to the expected optical absorbance [109]. Azens et al.[110] reported that the ‘transmittance for as-deposited film increases strongly as one goes towards longer wavelengths in the luminous range. This feature was not typical for electrochromic tungsten oxide films. At the same time the luminous transmittance of unpolarized light is 40% at +60° and 35% at -60° in the as-deposited state whereas the corresponding numbers are 15% and 9% in the colored state. This clearly manifested that angular selectivity of the injected charge of WO\textsubscript{3} increases the absorbance also get increased and due that the WO\textsubscript{3} will gets converted in tungsten bronze having blue color. The incomplete oxidation of evaporated tungsten oxide does not lead to the expected optical absorbance [109]. Azens et al.[110] reported that the ‘transmittance for as-deposited film increases strongly as one goes towards longer wavelengths in the luminous range. This feature was not typical for electrochromic tungsten oxide films. At the same time the luminous transmittance of unpolarized light is 40% at +60° and 35% at -60° in the as-deposited state whereas the corresponding numbers are 15% and 9% in the colored state. This clearly manifested that angular selectivity may be of interest for applications of electrochromic smart windows, inclined windows. The reflectance spectra of WO\textsubscript{3} films showed significant reflectance variation in the infrared region which coincides to sputter deposited WO\textsubscript{3} films [111]. Golden and Steele [112] reported that in the normal transmission mode, the electrochemically lithiated WO\textsubscript{3} films showed brown coloration on high levels of lithiation. The transmission spectra for x=0.3 and 0.5 show a very broad peak in the near IR regions. Bader et al.[113] reported a theoretical outline for the reflection and transmission spectra obtained from spectroscopic ellipsometer technique on thin films deposited on a thick transparent substrate. The optical parameters are shown as a function of the wavelength for the as deposited WO\textsubscript{3} films before insertion of lithium. The observed optical variation in the tungsten trioxide films are comparable to the reported results for the tungsten trioxide films prepared by electrochemical and thermal evaporation techniques. In the potassium ion intercalation process, the transmission spectra of the WO\textsubscript{3} film deposited on TCO exhibits an extremely high degree of transmission (80%) in the as-deposited state [114].

CONCLUSION & DISCUSSION

Devices based on electrochromism with their tunable transmission for visible and infrared radiation will play an important role for architectural and automotive glazing. As WO\textsubscript{3} is thermodynamically stable at room temperature, it is considered as the most suitable material for the electrochromically active electrodes in the electrochromic devices. In this review paper the various methods used for deposition such as sputtering, sol-gel, spray pyrolysis, electron beam evaporation are studied and it is found that out of all these technique sputtering is most widely used for deposition. The materials properties, preparation techniques, colorations/bleaching efficiency and the electrochromic devices developed are elaborately presented in this review.

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REFERENCES

[32]. M.Green, Electrochromic displays Displays, 9 ,166-200 (1988).


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