



Effect of substrate on the electro chromic properties of tungsten trioxide thin films

K. V. Madhuri ^{1*}, P. V. Ashrit ²

¹ Vignan University, Vadlamudi, Guntur (Dt), Andhra Pradesh, India

² Thin Films and Photonics Research Group (GCMP)

*Corresponding author E-mail: kvmsvu@gmail.com

Copyright © 2014 K. V. Madhuri, P. V. Ashrit. This is an open access article distributed under the [Creative Commons Attribution License](https://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Abstract

Thin films of tungsten trioxide (WO₃) were deposited onto glass and Indium Tin Oxide (ITO) coated glass substrates using thermal evaporation technique under various deposition conditions. In the present work the effect of substrate on the structure and EC performance of WO₃ thin films has been examined using a dry lithiation method. The structural and optical changes occurring in these films with lithium insertion have been studied. It is found that the ITO coated substrate promotes the granulation and higher coloration efficiencies of the films. The peak efficiency is observed at higher infrared wavelengths where it is principally the reflectance modulation that brings about optical changes.

Keywords: WO₃ Thin Films, Electrochromism, Optical and Structural Properties, Effect of ITO Substrate.

1. Introduction

Today the role of various interactive materials and devices in which changes can be brought about in a precisely controlled and reversible manner has increased tremendously. A category of particular importance is the devices for the control of light absorption, transmission and reflection which employ optically active materials. Chromogenic materials in which a reversible optical property change can be induced by the influence of various stimuli have become the object of immense research recently. The electrochromic (EC) materials are one such type in which a reversible change in optical property can be induced through the application of a small electric field [12]. Devices based on these EC materials have attracted a lot of research attention in the last couple of decades due to their various potential applications such as in energy efficient smart windows, display devices and switchable mirrors [6], [11]. Hence, the study of this phenomenon has been attracting a sustained interest for the last couple of decades. Efficient light transmission control in throughput devices and light reflection control in displays and reflective mirrors as per need is an exciting challenge opening the way to innumerable applications. Recently, there has been a considerable interest in EC devices based on lithium intercalation in many Transition Metal Oxide (TMO) thin films. The main advantages with these TMOs are the high coloration efficiency, large material selection, reasonable stability and relatively low cost [6], [10], [14]. Decades of research carried out on the TMOs has confirmed Tungsten Trioxide (WO₃) as the most efficient and versatile EC material [3], [4]. The electrochromic (EC) performance of the well-known Tungsten Trioxide (WO₃) has become the subject innumerable studies in the recent years. The sensitive dependence of EC performance of WO₃ thin films on various deposition parameters is being studied profoundly in an effort to improve the coloration efficiency. In addition to exhibiting a crystalline phase dependent reflection or amorphous phase based absorption EC modulation, the WO₃ is also an interesting TMO with a high electrochemical activity, high work function, high lithium charge capacity and a fast response time [13], [18]. Its high chemical and physical stability has also led to its use as a very promising intercalation material in various solid state electrochemical devices [15]. In addition to this phase dependency, it is also found that the EC performance of these films depends very sensitively on the various film deposition conditions, including the humidity content, which in turn determine the film structure.

The electrochromic coloring of the WO₃ thin films occurs through synchronous up taking of electrons and ions (double injection) into the bulk of the film. Each coloring/bleaching cycle is a topotactic intercalation/ deintercalation process of ions with reversible changes of bond angles and lengths and therefore induces the mechanical stress within the thin film

matrix. Further, in its various crystalline phases the WO_3 films exhibits a reflection based reversible optical modulation with the insertion of lithium and electrons. With increasing free electron density the films exhibit a Drude type free electron reflection modulation with the plasma edge generally located in the higher near infrared wavelengths moving towards lower wavelengths [7]. In the amorphous form, on the otherhand, the optical modulation associated with the intercalation is attributed to the electrons inserted and localized on the W sites and to the intervalence transfer of these electrons, through light absorption, between the various W oxidation sites W^{+4} , W^{+5} and W^{+6} [9], [16]. The small polaron absorption model is generally accepted to explain this phenomenon, although, the actual mechanism of this absorption is yet to be understood further. Such absorption based optical modulation is generally centered on the lower near infrared and higher visible wavelengths. In all the cases (polycrystalline or amorphous), however, the coloration efficiency is known to depend sensitively on the humidity content and the microstructure of the film. It has been shown that the porous and nanostructured WO_3 films with a high open surface have the potential to show an improved EC performance [5], [8]. A vast amount of work seen in the literature is directed towards the improvement of the EC performance of the WO_3 thin films through a careful tailoring of all the above said parameters.

In the present investigation, our aim is to examine the role of the substrate in dictating the film structure and consequently the EC performance of the WO_3 thin films. These films deposited by thermal evaporation on glass substrates with and without an Indium Tin Oxide (ITO) coating and prepared under various conditions have been studied. The lithium intercalation is carried out by a dry in-situ method. In most of the work reported in the literature, the electrochemical method of EC studies restricts the film deposition to transparent conductor (TC) coated substrates. The dry lithiation method used in our case, however, enables us to study the structural evolution and optical changes occurring with lithium insertion on any type of substrate.

2. Experimental

Thin films of WO_3 were deposited onto chemically and ultrasonically cleaned glass and Indium Tin Oxide (ITO) coated glass substrates using the thermal evaporation technique. High purity (99.95%) Tungsten Oxide powder obtained from Johnson Matthey was used for the deposition of the films. The deposition was carried out in a chamber evacuated to a vacuum in the range of 10^{-6} Torr. Film deposition was carried out at a substrate temperature of 200°C and the samples were subsequently annealed at a temperature of 400°C in air for an hour to promote film crystallinity. The mass thickness of the films and the deposition rate were 200 nm and 0.2 nm/s, respectively, as measured by the quartz crystal thickness monitor. In order to examine the electrochromic properties of the WO_3 films a laboratory developed dry lithiation method [2] of controlled heating of Lithium Niobate (LiNbO_3) under vacuum, was used. The quantity of lithium inserted was measured in terms of the effective mass thickness deposited on the quartz crystal and the charge inserted (Q) was deduced from the electrochemical experiments carried out earlier. The dry method of lithiation is a convenient tool to examine the film structure and EC activity of films without always the need to deposit such films on transparent conducting (TC) electrodes. It is also a handy method to discern the effect of the substrate itself on the film properties. The coloration efficiency (CE) which is defined as,

$$\text{CE} = \Delta \text{OD} / Q$$

Where the optical density change, $\Delta \text{OD} = \log (T_b/T_c)$, is calculated as the logarithmic ratio between the transmissions of the film in the "as deposited" (T_b) and colored (T_c) states. The crystal structure and its evolution with lithium insertion was studied using a laboratory built X-ray diffractometer operating in reflection mode with Cu-K_α radiation ($\lambda = 0.1542 \text{ nm}$). A Digital Instruments (Dimension 2300) Atomic Force Microscope (AFM) was also employed to study the film structure and the changes. The optical transmission and reflection spectra of the films were obtained by the CARY5000 double beam spectrophotometer in the wavelength range 300 - 2400 nm.

3. Results and discussion

The micrographs of the WO_3 films deposited on glass and ITO coated glass substrates with no lithium and increasing quantity of lithium are shown in Fig. 1. The "as prepared" sample on glass substrate (with no lithium) exhibits a fairly smooth surface with a few dispersed embedded grains. With the insertion of lithium 2.5 nm (1.56 mC/cm^2) of lithium there seem to be some dynamic changes in the film morphology. The insertion of the highest amount of lithium studied i.e. 12.5 nm (7.81 mC/cm^2) gives way to the appearance of the intercrystal boundaries in the form of large cracks appearing in the film. At this level of lithium insertion and appearance of the boundaries one can estimate the crystals to be around a couple of microns in size. The micrographs of the films deposited on ITO coated glass in the "as prepared" state present a less smoother surface dotted with a few grains, as compared to the films on bare glass substrates. In this case the appearance of intercrystal boundary is evident even with the insertion of 2.5 nm of lithium. The separation of the crystals becomes even more predominant. From the micrographs it is estimated that the dimensions of the crystals are of the order of a micron.

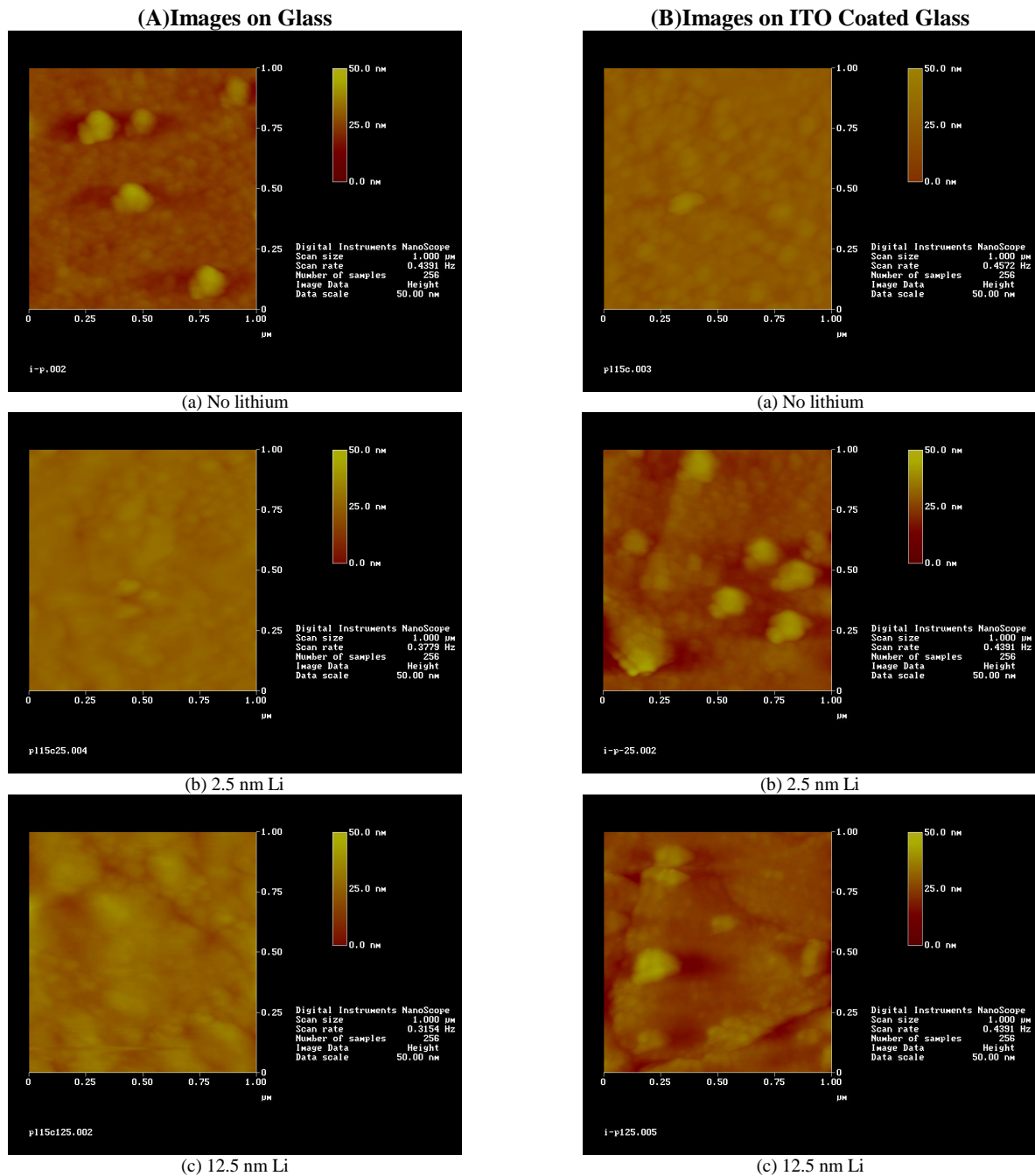


Fig. 1: AFM Images of WO_3 Films Deposited on (A) Glass and (B) ITO Coated Glass Substrates with the Insertion of Lithium

The XRD Patterns of the films deposited on glass and ITO substrates are shown in Fig. 2. From these results it was confirmed that both these films exhibit a reasonably high degree of crystallinity with different phase orientations. The crystallinity of the films improves in different orientations with increasing lithium concentration. The strong peaks seen in the XRD pattern of the films deposited on glass substrates indicate a hexagonal phase with a space group $P6/mmm$ as confirmed from the JCPDS data [2]. The basic structure of hexagonal WO_3 is an infinite plane of WO_6 octahedral sharing their corners and forming six-member rings in the (001) plane. The entire structure arises from stacking of such layers perpendicular to the c-axis. The hexagonal WO_3 is complicated because super reflections appear ($q = 7.2 \text{ nm}^{-1}$), indicating that the c-lattice must be doubled for the true cell [2]. As the content of lithium is increased, the absence of the (110) and (111) reflections at $q = 17.19$ and 23.56 nm^{-1} is observed. The peaks were found to be shifted to lower q values and the intensity of the peaks was increased with the lithium content in the films. This may be due to a change in the symmetry of the hexagonal WO_3 to a higher order, possibly orthorhombic [19], and [20]. The lattice parameters are calculated from the above data and the value of "a" is relatively constant at 0.735 nm and "c" decreases from 0.382 nm to 0.375 nm , which represents a contraction of the lattice volume, because the Li^+ ions at interstitial positions attract the

neighbouring O^{2-} ions in the lattice with increasing quantity of lithium in WO_3 films and which is consistent with the reported data [19], [20]. The unsolvated Li^+ ions are intercalated into the empty channels while retaining the hexagonal structure. The XRD spectra of WO_3 films containing different amounts of lithium deposited on ITO coated glass showing a tetragonal structure with a space group $P4/nmm$ is analogous to JCPDS data [2]. The peak positions of the tetragonal WO_3 and ITO substrates are marked by the line spectra below [20]. The diffraction peaks at $q = 16.11$ and 19.88 nm^{-1} related to (001) and (110) reflections reduce with increasing quantity of lithium in the films indicating an increasing symmetry of the structure. The lithium insertion into the films appears to induce a structural distortion similar to those observed by other groups [20]. In this case, the detection of lattice constant changes is difficult due to the overlap of several WO_3 and ITO peaks. The changes in the structure in both the cases may be because of the formation of Li_xWO_3 . From these studies, it can be concluded that the substrate texture influences more the structure of the films.

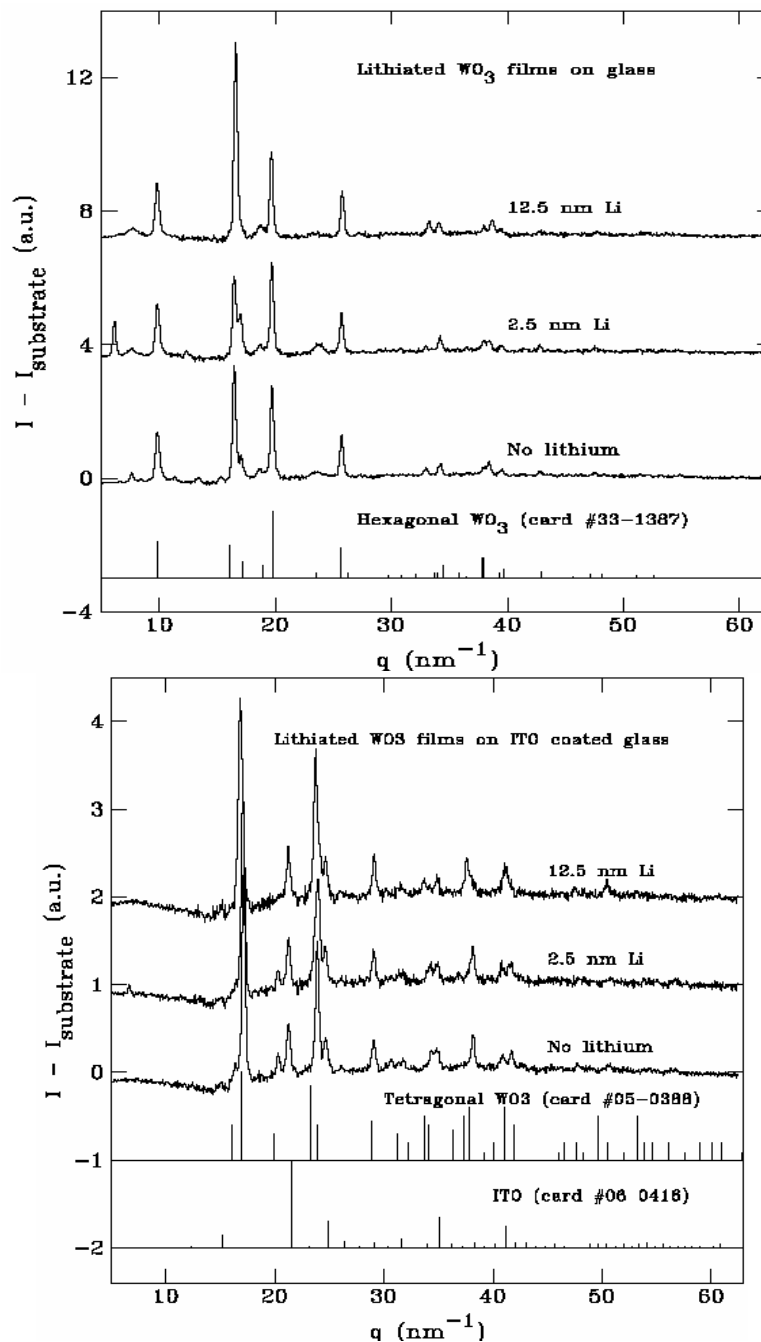


Fig. 2: XRD Spectra of WO_3 Films Deposited on Glass and ITO Coated Glass Substrates with the Insertion of Lithium

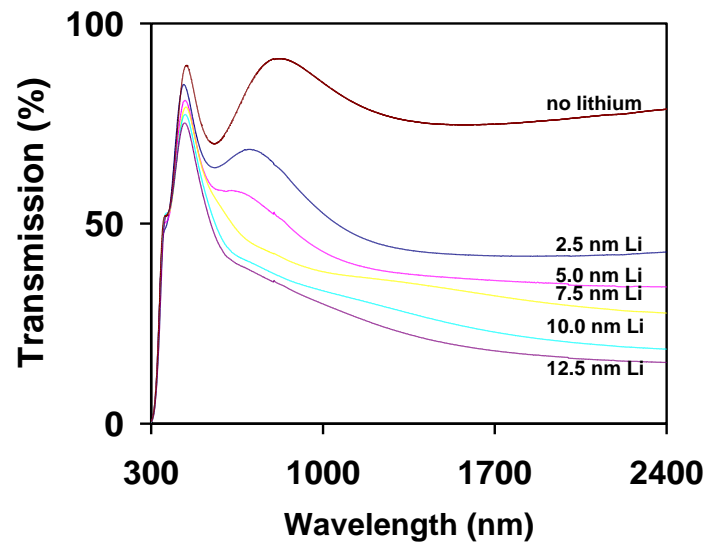


Fig. 3: Optical Transmittance Spectra of WO₃ Films Deposited On Glass Substrates with the Insertion of Different Quantities of Lithium

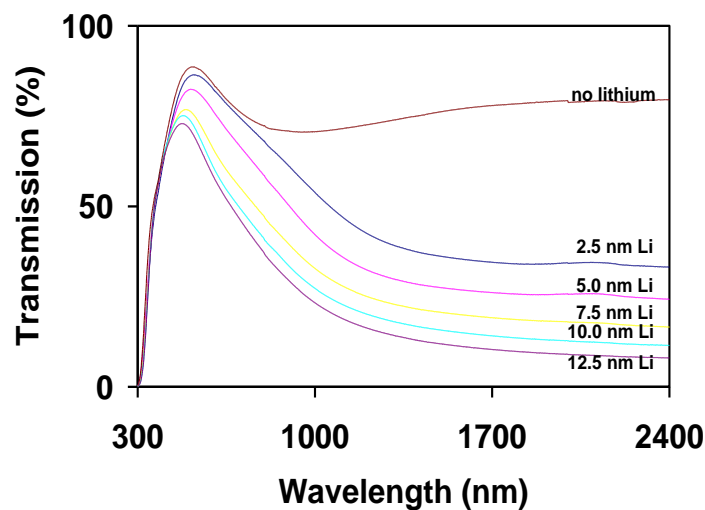


Fig. 4: Optical Transmittance Spectra of WO₃ Films Deposited on ITO Substrates with the Insertion of Different Quantities of Lithium

The transmission spectra of the “as prepared” and lithium inserted WO₃ film on glass substrate are shown in Fig. 3. The WO₃ film with no lithium (“as prepared”) shows a strong interference pattern with two peaks indicating the optical flatness of the two interfaces. With increasing lithium insertion there is a very effective transmission change through most of the spectral region studied. The coloration is quite drastic with the insertion of the first 2.5 nm of lithium. The subsequent coloration is of a much lower order. The change in the near infrared region is much more pronounced than in the lower visible region. Hence, the film shows a very selective optical modulation. The fast suppression of the second interference peak could be attributed to the coloration and reorganization of the film under lithium intercalation as is also evidenced by the AFM images. Generally, the high efficiency modulation in the infrared region is due to the reflection modulation predominance. As expected the most important changes occur in the early stage of insertion with a high density of W sites available for the inserted species. However, the broad range optical modulation seems to stem from the overlapping effects of Drude like reflection changes occurring in the polycrystalline phase where the inserted electrons are not localized as well as from the amorphous phase interspersed between the granular boundaries where the inserted electrons are localized on W sites exhibiting absorption modulation rooted in the intervalence charge transfer.

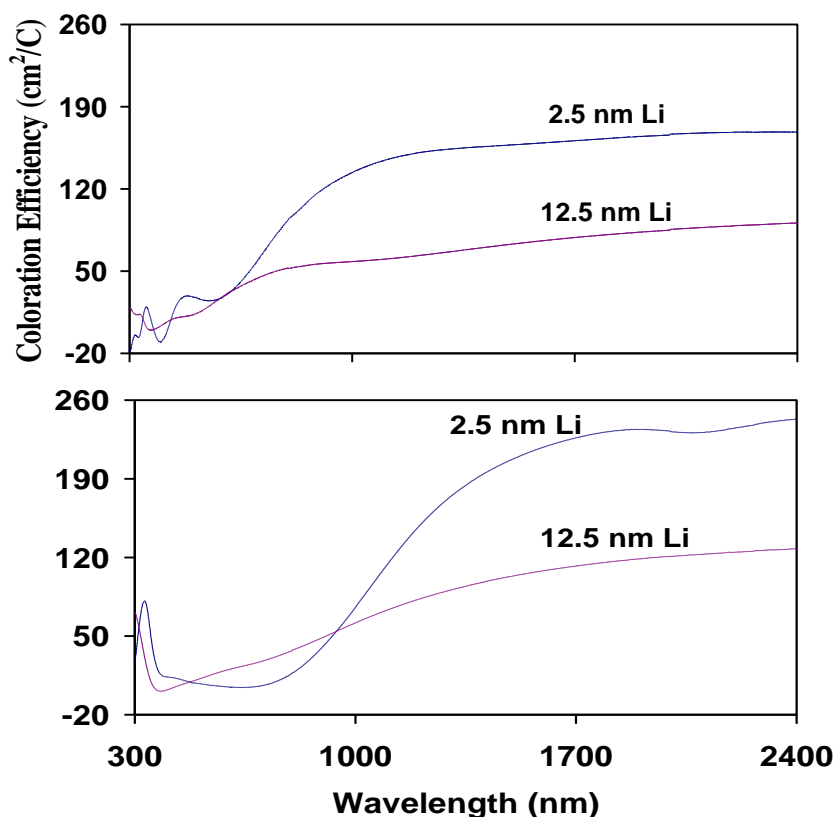


Fig. 5: Coloration Efficiency Spectra of Related Glass/WO₃ and ITO/WO₃ Films

The corresponding results for the WO₃ film deposited on ITO coated glass are shown in Fig. 4. In the “as prepared state” the film exhibits a less pronounced interference with a single peak. This diminution in the interference as compared to the film deposited on glass substrate can be attributed to a reduced film thickness in the case of ITO substrate. Although, both the substrates were deposited with 200 nm thick WO₃ films as measured from the quartz crystal due to the varying wetting effects of the two surfaces followed by the annealing effect which results in different surface morphologies of the two WO₃ films. A very effective coloration is seen here too with lithium injection. Bulk of the coloration is concentrated in the near infrared region indicating an even more predominant reflection modulation in the films deposited and annealed on ITO substrates. The initial change with 2.5 nm lithium insertion is very effective as in the earlier case. With increasing lithium the coloration in the near infrared region deepens even more effectively than the films deposited on glass substrate. Hence, the WO₃ films deposited on ITO substrates exhibit a much more pronounced selective optical modulation than the films deposited on glass substrates. Such effective and selective modulation is of great interest in the energy efficiency application of such films. The coloration efficiency (CE) spectra of the two films are given in Fig. 5. As expected the coloration efficiency with the initial intercalation of 2.5 nm of lithium is highly efficient in both the cases, i.e. WO₃ films on glass as well as on ITO coated glass. At this degree of coloration the efficiency is much more pronounced in the case of WO₃ film deposited on ITO coated glass where the peak value reaches around 240 cm²/C in the near infrared region. This film also exhibits a more distinct selective optical modulation with very little coloration in the visible region of the spectra. With higher degree of lithium intercalation (12.5 nm), however, the selective behavior in both the types of films studied is less evident. The films exhibit gradually increasing coloration efficiency towards the infrared region. The film deposited on ITO coated glass exhibits very high coloration efficiency for this level of intercalation with peak value reaching 120 cm²/C which is a significant improvement over the film deposited on glass substrate.

4. Conclusions

In this study undertaken to examine the effect of the ITO substrate on the optical, electrochromic and structural properties of polycrystalline WO₃ thin films, especially compared to the similar films deposited on plane glass substrate, the following conclusions can be drawn:

- i) For the deposition conditions used in this work, the WO₃ film granulation and polycrystallinity is promoted when the films are deposited on ITO coated glass substrates. This is inferred from the AFM and XRD studies of the films.
- ii) The surface and bulk structure of the WO₃ films deposited on ITO coated glass substrates lead to the suppression of interference effect.

- iii) The WO_3 films deposited on ITO coated glass substrates exhibit a much higher efficiency coloration compared to the films deposited on glass substrates. The efficiency increases gradually towards higher wavelength region. At lower levels of lithium intercalation these films also exhibit a highly efficient and selective coloration. Such optical modulation is of great interest in the energy related applications such as in smart windows, wherein the higher wavelength modulation can be brought about without compromising or changing the visible region behavior.

Hence, in this work it has been demonstrated by using the “dry lithiation” method that the polycrystalline WO_3 thin films deposited on ITO coated glass substrates exhibit better quality films from the electrochromic point of view and that such films have application potential for energy related applications.

Acknowledgements

Dr. K. V. Madhuri acknowledges DST (SERB/ET-0043/2013) for the financial Support to carry out this work. The partial support provided by the Atlantic Innovation Foundation (AIF) and the Natural Science and Engineering Research Council (NSERC) in carrying out this work is gratefully acknowledged.

References

- [1] Aird A, Donegheti MC, Mazzi F, Tazoli V, Salje EKH "Sheet Superconductivity in: Crystal structure of the Tetragonal matrix" (1998) *J Phys Codens Matter* 10:569.
- [2] Ashrit PV, Bader G, Girouard FE, Vo-Van Truong "Electrochromic materials for smart window applications" (1990) *SPIE* 1401:119.
- [3] Ashrit PV, Bader G, Truong VV "Electrochromic properties of nano Crystalline tungsten Oxide films" (1998) *Thin Solid Films* 320:324.
- [4] Bange K "Colouration of tungsten oxide films:A model for optically active coating" (1999) *Sol Energy Mater Sol Cells* 58:1.
- [5] Fang GJ, Liu ZL, Sun GC, Yao KL "Preparation and Electrochromic properties of nano crystalline WO_3 thin films prepared by pulsed excimer laser ablation technique" (2001) *Phys Stat Sol (a)* 184:129.
- [6] Granqvist CG (1995) *Hand book of Inorganic Electrochromic Materials*, Elsevier, Amsterdam.
- [7] Goldner RB, Haas TE, Seward G, Wong KK, Norton P, Foley G, Berera G, Wei G, Shultz S, Chapman R "Thin film solid state ionic materials for electrochromic window glass" (1988) *Solid State Ionics* 28:1715.
- [8] Granqvist CG (1993) *Electrochromic materials : Metal oxide composites with variable optical properties* *Mater Sci Eng A* 168:209.
- [9] Hashimoto S, Matsuoka H "Mechanism of electrochromism for amorphous WO_3 thin films" (1991) *J Appl Phys* 69:933.
- [10] Julien C, El Farh L, Balkanski M, Hussain OM, Nazri GA " The growth and electrochemical properties of metal oxide thin films :Lithium intercalation (1993) *Appl Surf Sci* 65/66:325.
- [11] Lampert CM *Smart switchable glazing for solar energy and daylight control* (1998) *Sol Energy Mater Sol Cells* 52:207.
- [12] Monk PMS, Mortimer RJ, Rosseinsky DR (1995) *Electrochromism Fundamentals and Applications* Wiley-VCH Weinheim 76.
- [13] Maruyama T, Arai S "Electrochromic properties of cobalt oxide thin films prepared by chemical vapor deposition" (1994) *J Electrochem Soc* 141:1021.
- [14] Murphy DW, Christian PA, Disalvo FJJ, Carides JN "Vanadium oxide cathode materials for secondary lithium cells" (1979) *J Electrochem Soc* 126:497.
- [15] Patil PS, Patil PR, Ennaoui EA "Preparation of mixed oxide MoO_3 - WO_3 thin films by spray pyrolysis technique and their characterization" (2000) *Thin Solid Films* 370:38.
- [16] Qiu H, Lu YF, Mai ZH *Nano structure formation on amorphous WO_3 thin films in Air by Scanning tunneling microscopy* (2001) *Jpn J Appl Phys* 40:6589.
- [17] Schollhorn R "Electronic / ionic conductors to superconductors: control of materials properties" (1988) *Angew Chem* 100:1446.
- [18] Solis JL, Saukko S, Kish L, Granqvist CG, Lantto V "Semiconductor gas sensors based on nano structured tungsten oxide" (2001) *Thin Solid Films* 391:255.
- [19] Hasan MM, Haseeb A S M A and Masjuki H H " Structural and mechanical properties of nano structured tungsten oxide thin films" (2012) *Surface Engineering* 28:10.
- [20] Hsi-Chao Chen, Der-Jun Jan, Yu-Siang Luo, and Kuo-Ting Huang "Electrochromic and optical properties of tungsten oxide films deposited with DC sputtering by introducing hydrogen" (2014). *Applied Optics* 53:321.