PYROLYTICALLY SPRAY DEPOSITED ELECTROCHROMIC WO₃ FILMS

by

Zhou Guanghui
B.Sc. (Honours), Hunan Normal University, 1982

THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE
in the Department
of
Physics

© Zhou Guanghui 1987

SIMON FRASER UNIVERSITY
July, 1987

All rights reserved. This work may not be reproduced in whole or in part, by photocopy or other means, without the permission of the author.
APPROVAL

Name: Zhou Guanghui
Degree: Master of Science
Title of Thesis: Pyrolytically Spray Deposited Electrochromic WO3 Films

Examinining Committee:

Chairman: L. E. Ballentine

K. Colbow
Senior Supervisor

R. Frindt

S. R. Morrison

B. P. Clayman
Examiner
Professor of Physics
Simon Fraser University

Date Approved: 23. July 1987
PARTIAL COPYRIGHT LICENSE

I hereby grant to Simon Fraser University the right to lend my thesis, project or extended essay (the title of which is shown below) to users of the Simon Fraser University Library, and to make partial or single copies only for such users or in response to a request from the library of any other university, or other educational institution, on its own behalf or for one of its users. I further agree that permission for multiple copying of this work for scholarly purposes may be granted by me or the Dean of Graduate Studies. It is understood that copying or publication of this work for financial gain shall not be allowed without my written permission.

Title of Thesis/Project/Extended Essay

Pyrolytically Spray Deposited Electrochromic WO3 Films

Author:

(signature)

Zhou Guanghui
(name)

August 13, 1987
(date)
ABSTRACT

Pyrolytically spray deposited WO₃ films on various transparent SnO₂:F substrates were investigated by means of X-ray diffraction and the results were correlated to the electrochromic behavior of the films.

The SnO₂:F films with thicknesses greater than 5000Å were also pyrolytically spray deposited onto glass slides, using a solution containing stannic chloride and stannous fluoride. The polycrystalline SnO₂:F films, used as the substrate for electrochromic WO₃ films, were highly conducting.

The WO₃ films of thicknesses 400 to 4200Å were deposited onto the SnO₂:F substrates using a tungsten chloride solution. Through X-ray diffraction studies, the deposition parameters (crystallinity of substrate, carrier gas flowrate, substrate temperature during the deposition and deposition time) for controlling the crystallinity and preferential crystallite orientation of the WO₃ films, were qualitatively determined.

The electrochromic performance revealed that polycrystalline WO₃ films with a larger crystallite size and more randomly oriented crystallites showed a larger transmittance change on applied voltage during coloration. These results partially support the hypothesis proposed by Svensson et al. [15], that injected electrons in polycrystalline
WO$_3$ films with larger crystallite size are likely to show free electron behavior. The effects of the crystallite preferential orientation on the electrochromic behavior of the WO$_3$ films, were also discussed.
To

my motherland, my Alma Mater and my family.
ACKNOWLEDGMENTS

I wish to express my sincere thanks to my senior supervisor, Dr. K. Colbow, for his encouragement, supervision and financial support throughout this research. Thanks also to Dr. R. F. Frindt and Dr. S. R. Morrison for acting as the members of my supervisor committee and examining committee, and to Dr. B. P. Clayman from the Physics Department for acting as my examiner.

My special thanks go to Dr. S. Wessel, for her concrete guidance and helpful discussions and for her kindness in correcting the hand-written manuscript of my thesis which occupied a great deal of her time. I sincerely thank J. Hickman and D. Craigen for their technical help during the experiments.

Finally, a scholarship from the Chinese Government and the TA'ships from the Physics Department of SFU were also very much appreciated.

-vi-
TABLE OF CONTENTS

Approval ................................................................. i
Abstract ........................................................................... ii
Dedication ....................................................................... v
Acknowledgments .......................................................... vi
List of Tables .............................................................. ix
List of Figures .............................................................. x

1. Introduction .............................................................. 1
   Aims and structure ..................................................... 4

2. WO₃ Thin Films and EC Cell ........................................ 6
   2.1 Electrochromic cell ............................................... 6
   2.2 The physical properties of WO₃ films ................. 8
   2.3 Electrochromism of WO₃ films ....................... 12
   2.4 Reflection modulation of WO₃ film ............ 16

3. Materials and Methods ............................................... 23
   3.1 Preparation of SnO₂:F films ............................. 23
   3.2 Apparatus and procedures of pyrolytic
       spray deposition ............................................. 24
   3.3 X-ray diffraction studies .................................. 25
   3.4 Measurement of film thickness ....................... 27
   3.5 Measurement of film sheet resistance ............ 28
   3.6 Electrochromic measurement ....................... 28

4. Results and Discussion ............................................. 34
## List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>SnO₂:F films deposited onto glass slides with N₂ flowrate 38 l./min</td>
<td>51</td>
</tr>
<tr>
<td>4.2-1</td>
<td>WO₃ films deposited onto amorphous SnO₂:F substrate</td>
<td>52</td>
</tr>
<tr>
<td>4.2-2</td>
<td>WO₃ films deposited onto low polycrystalline SnO₂:F substrate</td>
<td>53</td>
</tr>
<tr>
<td>4.2-3</td>
<td>WO₃ films deposited onto highly polycrystalline SnO₂:F substrate</td>
<td>54</td>
</tr>
<tr>
<td>4.2-4</td>
<td>WO₃ films deposited onto intermediate polycrystalline SnO₂:F substrate</td>
<td>55</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>2.1</td>
<td>The sandwich structure of an electrochromic cell</td>
<td>19</td>
</tr>
<tr>
<td>2.2</td>
<td>The oxygen octahedron packing of theWO₃ crystal structure</td>
<td>20</td>
</tr>
<tr>
<td>2.3</td>
<td>The monoclinicWO₃ structure showing the distortedWO₆ octahedra projected along the y axis</td>
<td>21</td>
</tr>
<tr>
<td>2.4</td>
<td>Normal reflectance spectra computed for the electrochemically coloredWO₃ film</td>
<td>22</td>
</tr>
<tr>
<td>3.1</td>
<td>Diagram of the pyrolytic spray deposition oven</td>
<td>31</td>
</tr>
<tr>
<td>3.2</td>
<td>Diagram of the cross-sectional geometry of the experimental cell</td>
<td>32</td>
</tr>
<tr>
<td>3.3</td>
<td>Block diagram of electrochemical measurement</td>
<td>33</td>
</tr>
<tr>
<td>4.1</td>
<td>X-ray diffraction patterns of four types of SnO₂:F films deposited onto glass slides with N₂ flowrate 38 l./min</td>
<td>56</td>
</tr>
<tr>
<td>4.2</td>
<td>Transmittance spectra of highly polycrystalline SnO₂:F film with thickness 5380Å and WO₃ film deposited onto above SnO₂:F with thickness 440Å</td>
<td>57</td>
</tr>
<tr>
<td>4.3</td>
<td>X-ray diffraction patterns of WO₃ deposited onto glass at Tₛ = 450°C with a N₂ flowrate of 16.5 l./min for 7 minutes, H₂WO₄ powder before and after heated at 450°C for 10 hours</td>
<td>58</td>
</tr>
<tr>
<td>4.4</td>
<td>X-ray diffraction patterns of WO₃ films deposited onto highly polycrystalline SnO₂:F at Tₛ = 400°C with different N₂ flowrate</td>
<td>59</td>
</tr>
<tr>
<td>4.5</td>
<td>X-ray diffraction patterns of WO₃ films deposited onto four different types of SnO₂:F (shown in Fig.4.1) at Tₛ = 400°C with N₂ flowrate 16.5 l./min</td>
<td>60</td>
</tr>
<tr>
<td>4.6</td>
<td>Dependence of crystallite size on substrate temperature of WO₃ films</td>
<td>61</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>----------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>4.7</td>
<td>Dependence of crystallite size on thickness of WO₃ films deposited onto amorphous and highly polycrystalline SnO₂:F</td>
<td>62</td>
</tr>
<tr>
<td>4.8</td>
<td>Dependence of crystallite size on thickness of WO₃ films deposited onto polycrystalline SnO₂:F</td>
<td>63</td>
</tr>
<tr>
<td>4.9</td>
<td>Diffraction peak intensity distribution with thickness of WO₃ films deposited onto polycrystalline SnO₂:F</td>
<td>64</td>
</tr>
<tr>
<td>4.10</td>
<td>Dependence of intensity ratio on thickness of WO₃ films deposited onto polycrystalline SnO₂:F</td>
<td>65</td>
</tr>
<tr>
<td>4.11</td>
<td>Dependence of intensity ratio on thickness of WO₃ films deposited onto polycrystalline SnO₂:F</td>
<td>66</td>
</tr>
<tr>
<td>4.12</td>
<td>Transmittance change vs thickness of WO₃ films deposited onto polycrystalline SnO₂:F</td>
<td>67</td>
</tr>
<tr>
<td>4.13</td>
<td>Transmittance change vs thickness of four WO₃ films with thicknesses 2550, 2600, 2780 and 3100Å</td>
<td>68</td>
</tr>
<tr>
<td>4.14</td>
<td>I-V characteristics of a typical experimental ECC</td>
<td>69</td>
</tr>
<tr>
<td>4.15</td>
<td>Dependence of white light transmittance on the voltage applied of the same cell in Fig. 4.14</td>
<td>70</td>
</tr>
<tr>
<td>4.16</td>
<td>Time response of the same cell as in Fig. 4.15</td>
<td>71</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

Electrochromism is exhibited by a number of materials, such as transition-metal oxides (WO$_3$, MoO$_3$ and V$_2$O$_5$). Electrochromism is a reversible color change in a material caused by an applied electric field or current. This change can be due to the formation of color centers (or defect complexes) or to an electrochemical reaction that produces colored compounds [1]. Among these electrochromic materials, tungsten trioxide (WO$_3$) is one of the best examples, and has been widely studied. Since the electrochromic properties of WO$_3$ thin films were reported by Deb in 1973 [2], many investigations have been carried out on both properties and preparation methods of the film for the purpose of display devices and radiation controlled "smart windows".

Both amorphous and polycrystalline WO$_3$ thin films show the electrochemical coloration and that the optical properties of the films change during the coloration. Basically, amorphous film can be used in display devices because of its fast time response of coloration, and polycrystalline film can be used in windows due to its high infrared reflectance during
Vacuum evaporated WO$_3$ films were produced by Fanghnan et al. in 1975 [9]. They constructed some electrochemical cells based on these films to perform electrochemical coloration and proposed a double injection model of positive ions and electrons for the mechanism of WO$_3$ electrochromism. Miyake et al. [10] carried out systematic measurements of the physical, optical and electrochromic properties of vacuum evaporated WO$_3$ films in 1983. They concluded that the properties of these films depend considerably on the substrate temperature during the deposition which determines the formation of amorphous or polycrystalline films; films prepared at a substrate temperature higher than 400°C have a resistivity of $10^{-9}$ to 10 Ωcm and the films prepared at a substrate temperature lower than 350°C were amorphous and transparent with a resistivity of $10^2$ to $10^3$ Ωcm. Both amorphous and polycrystalline films showed electrochromic behavior [10].

Another method, rf sputtering from a compressed WO$_3$ target under Ar–O$_2$ atmosphere, was used by Goldner et al. in 1985 [4]. They found that the films prepared at the substrate temperatures higher than 325°C were polycrystalline in structure and showed a high infrared reflection during the coloration. Later, Kaneko et al. [11] investigated a number of properties of the rf sputtered WO$_3$ films. In addition to the similar results of evaporated films, they found the properties of the rf sputtered films depended on the O$_2$ concentration and
total pressure of the atmosphere.

Other WO₃ thin film preparation methods, such as electrolytic precipitation, solgel [12] and chemical vapour deposition [13] have been tried recently. A pyrolytic spray deposition technique was reported by Craigen et al in 1986 [14]. In this method WO₃ films were deposited onto a SnO₂:F film substrate by pyrolytically spraying a WCl₆•nH₂O solution in an open-air atmosphere. They primarily investigated the the structure and electrochromic behavior of the films prepared by this method and found that at a substrate temperature of 400°C, WO₃ deposited onto glass was amorphous, and deposited onto polycrystalline SnO₂:F layer was polycrystalline in structure itself. They also reported that WO₃ films prepared by this method showed similar electrochemical coloration to the WO₃ films prepared by other methods. Comparatively this method is simple and inexpensive, and has the potential to produce large area electrochromic coatings with low capital and production costs.

Coated window glass is being used on an increasing scale for gaining energy efficiency. Essentially, if the onset of high reflectance of the coatings occurs at a wavelength of about 0.7 μm, such coatings can be used for decreasing the inflow of infrared solar radiation therefore diminishing the need for air conditioning in a warm climate. If the onset of the high reflectance is instead at a wavelength of about 3.0 μm, the coatings provide low thermal isolation desired in a
cold climate. Many authors [4], [7], [15], [16] proved that electrochemically double injected polycrystalline WO₃ films show a metallic, i.e. an approximate free-electron behavior resulting in a high adjustable infrared reflection with different density of injected electrons and satisfy the above condition. Based on the double injection model, Svensson et al. computed the visible and infrared reflectance of ideal crystalline WO₃ films as function of electron density. Their theoretical result give twice the experimental value of reflectance for an rf sputtered polycrystalline WO₃ film in a deeply colored state reported by Goldner et al. [4]. This discrepancy was interpreted by Svensson et al. [15] as a poor crystallinity of the film, which produces grain boundaries, neutral defects, dislocations, etc.

AIMS AND STRUCTURE

The aim of this thesis is to investigate the pyrolytic spray deposition parameters for controlling the degree of the crystallinity, such as crystallite size and preferential orientation of the WO₃ films, and the correlation between crystallinity and electrochromic behavior of the WO₃ films.

Chapter 2 describes the basic considerations of an electrochromic cell. WO₃ crystal structure, the structure of WO₃ in the form of thin films and the models of
electrochromism are discussed. A computation of theoretical reflectance modulation of polycrystalline WO$_3$ film is also introduced.

Pyrolytic spray deposition apparatus and materials as well as experimental methods are described in chapter 3.

Chapter 4 presents the results of this research and gives a detailed discussion of the deposition parameters for controlling the degree of the crystallinity of the WO$_3$ films. The electrochromic behavior of the WO$_3$ films is explained in relation to their crystallinity. The conclusion follows in chapter 5.
2.1 ELECTROCHROMIC CELL

Fig. 2.1 shows the sandwich structure of a typical electrochromic cell (ECC) [5], [6]. Generally, an ECC operates between two electrode layers. These can be semi-transparent metals, such as a 50 to 100\% thick gold film or transparent doped semiconductor layers, such as indium-tin-oxide (ITO) or F doped tin oxide films. For the purpose of larger area window shutter, the two electrode layers should be as transparent as possible in the visible region of the solar spectrum and highly conductive. It is important to keep the electrical resistance of the electrodes as low as possible to minimize current loss and heating of the window [18]. In both liquid and solid electrolyte cells, it is important that the electrolyte or fast-ion conductor should not react chemically with the electrodes. The ions needed in the electrochromic reaction are provided by the ion storage and are injected in the coloration process into, or withdrawn in the bleaching process from, the electrochromic layer through the ion
conductor. The electrons needed in the coloration process are provided by the electrochromic substrate layer. For cells using liquid electrolytes, the electrolyte can serve as both storage and conductor for ions. While in all-solid-state cells the ion conductor can be an appropriate dielectric and the ion storage can be another electrochromic layer (preferably anodic if the base electrochromic layer is cathodic, or vice versa). One may also combine the conductor and storage media into one layer [6]. The electrochromic layer which has been widely studied is a WO$_3$ thin film because of its appropriate characteristics. Other inorganic partially hydrated transition metal oxides such as MoO$_3$ [19] and organic substances such as C$_{10}$H$_8$N$_2$ [18], also have been tried.

The optical properties of ECC for windows are continuously switchable between colored and bleached states. The nature of this switching can be different depending on the basic requirement on the cell, i.e. whether the main goal is to achieve control of the energy flowing through the window, or if daylighting and glare control are of prime importance. Under certain conditions, it may also be possible to have variable thermal insulation.

There are two general approaches to achieving variable transmittance: modulation of absorptivity or of reflectivity. Either form of the modulation would result in benefits of thermal stability of interior space. However,
reflection modulation is highly desired for window purposes. The optical properties of the polycrystalline WO₃ film are conveniently treated in terms of modulated reflection because the injected electrons exhibit an approximately free-electron behavior, whereas amorphous WO₃ films are treated in terms of modulated absorption because the injected electrons are highly localized in W⁺⁺ sites [6], [9], [16], [18].

2.2 THE PHYSICAL PROPERTIES OF WO₃ FILMS

The structure exhibited by a material in the form of a thin film depends on the film preparation conditions. For the WO₃ thin film prepared by the methods described in the introduction, the substrate temperature, the crystallinity of substrate, the pressure of the atmosphere and the carrier gas flowrate are important parameters. Especially, the substrate temperature can result in an amorphous or polycrystalline structure of the films prepared. Both uncolored amorphous and uncolored polycrystalline films are transparent. In visible and infrared regions the refractive index is about 2.2 [2], [10], [11], [20], and the extinction coefficient before coloration is about 0.1 which results in small absorption before coloration [20]. During coloration, the optical density of electrically colored amorphous films increases about 7 times and for polycrystalline films the
optical density increases only 2 times in the near infrared region (1.5eV) [16]. X-ray diffraction and electron microscope observations revealed that the films prepared by the methods described above are composed of a tungsten mixed oxide with the composition of WO$_{2.33}$, W$_{20}$O$_{55}$ and WO$_3$, and are mainly WO$_3$ in composition [2], [4], [10], [14].

Since Brakken found that WO$_3$ has perovskite-like structure [22], many authors have investigated WO$_3$ with a view to understanding its physical properties [17], [23], [24], [25], [26], [27], [28], [29]. On the basis of the cubic approximation of the WO$_3$ lattice, Kopp et al. calculated the energy band structure of WO$_3$ using the Green’s function method [23]. The calculated band gaps were about 50% smaller than the optical measured values of about 2.6 eV for the indirect gap and 3.5 eV for the direct gap reported by Koffyberg et al. [24].

WO$_3$ single crystals are thought to exhibit at least five phases in the temperature range from 900 to -180°C, changing through the sequences tetragonal, orthorhombic, monoclinic, triclinic and monoclinic during cooling [17], [25]. Salje found that WO$_3$ exhibits orthorhombic symmetry with the unit cell dimensions of a=7.341Å, b=7.570Å and c=7.754Å in the temperature range from 467 to 680°C [28]. Tanisaki found WO$_3$ to be of monoclinic symmetry with unit cell parameters of a=7.30Å, b=7.53Å, c=7.68Å and $\beta=90.54^\circ$ at room temperature [25], but the $c$ axis length is twice that
reported by others [30]. WO$_3$ thin films prepared at substrate temperature from 350 to 500°C were found to be the mixture of monoclinic, triclinic and orthorhombic in structure [10], [14]. However, these types of structure are perovskite-like based on the corner-sharing and packing of WO$_6$ octahedra as shown in Fig.2.2 [17]. The structure analyses of WO$_3$ have revealed considerable deviations from the ideal cubic perovskite type. For the orthorhombic symmetry, the deviation from the ideal perovskite structure is characterized by a zigzag displacement of the W atom in the \( \vec{b} \) and \( \vec{c} \) crystallographic directions as well as a tilt system with tilt angles around the \( \vec{a} \) crystallographic direction [28]. On the other hand, the distortions of the monoclinic structure correspond to displacements of W atoms and mutual rotations of the oxygen octahedra. As shown in Fig.2.3, the W-O bonds of the monoclinic structure form zigzag chains along the three crystallographic axes, with W-O-W angles of 158±2.3° and O-W-O angles of 166±5.6°. In the \( \vec{a} \) crystallographic direction the W-O bonds are of roughly equal length (1.9Å), while in the \( \vec{b} \) and \( \vec{c} \) crystallographic directions the W-O bonds are alternately long and short (2.1Å and 1.75Å respectively). As in most perovskite-like structure substances, the magnitude of the above deviations from the cubic symmetry depend on temperature [17].

The structure of amorphous WO$_3$ in the form of thin films has also been widely investigated [8], [29]. It is composed
of a spatial oxygen network of tightly bound \((\text{WO}_3)_m\text{H}_2\text{O}\)
clusters with a large number of terminal oxygen \(\text{W}=\text{O}\) and \(\text{W}-\text{O}-\text{W}\)
bonds between clusters. Using Raman scattering, Gabrusenoks
et al.\[29\] found that the clusters with dimensions not larger
than 20 to 30\(\%\) (to preserve X-ray amorphousness) are linked
together in such a manner as to guarantee a porous structure of
the amorphous \(\text{WO}_3\) films. The clusters in the amorphous \(\text{WO}_3\)
films contain at least two types of \(\text{WO}_6\)-octahedra: one with
a oxygen terminal and one without it, which represents an
axially distorted and a generally distorted octahedron,
respectively \[29\].

The crystal structure of tungsten bronze has been studied
extensively \[18\], \[30\], \[31\]. By the injection of different
cations, one can form different tungsten bronzes such as
\(\text{Li}_x\text{WO}_3\), \(\text{Na}_x\text{WO}_3\), \(\text{K}_x\text{WO}_3\) and \(\text{H}_x\text{WO}_3\) \[18\], where generally
\(0<x<3\). Wiseman et al. used a deuterium analogue to determine
the structure of \(\text{H}_x\text{WO}_3\) \[31\]. From neutron diffraction
studies the authors concluded that the crystal structure of
\(\text{H}_x\text{WO}_3\) has a similar structural progression from distorted \(\text{WO}_3\)
to the cubic perovskite type structure at high \(x\) value. The \(\text{W}\)
atoms are arranged on a simple cubic lattice and are
surrounded by almost regular octahedra of \(\text{O}\) atoms linked
together by corner sharing. The octahedra are tilted 11° and
form the \(\text{W}-\text{W}\) direction, producing an \(\text{O}-\text{O}\) distance between
adjunct octahedra of 3.264\(\AA\). Statistically the deuterium atoms
are attached to all \(\text{O}\) atoms with a bond length of 1.1\(\AA\) long
and a displacement of 11.8Å off the straight line to the neighbouring O atom. The deviation from a normal O-H bond length (1.0Å) may be significant since it is quite feasible that the O atoms are relaxed from their average positions whenever a deuterium atom is attached. So by analogy the atoms in H₃WO₄ form an OH bond with one of its surrounding O⁻² neighbors, so that the chemical formula of the hydrogen bronze should be (OH).WO₃₋ₓ. In the limiting case of x=3, a tungsten hydroxide W(OH)₃ would result and the "hydrogen tungsten bronze structure" was indeed found for the trivalent hydroxides In(OH)₃ and Sc(OH)₃ [31].

2.3 ELECTROCHROMISM OF WO₃ FILMS

Many investigations have been carried out in the effect to understand the electrochromism of WO₃ films. Until about 1975 it was believed that a current applied to WO₃ produced a redox reaction to form a blue-colored oxide product. The reaction was proposed to be [32]:

\[ xWO_3 + 2yH^+ + 2ye^- \rightarrow W_xO_{3x-y} + yH_2O \]  \hspace{1cm} (2.1)

A similar model for this system was suggested at the same time by Hurditch et al. [33], which discusses the formation of a complex of WO⁺ and OH⁻, i.e. the extraction of oxygen.
according to the following reaction:

$$\text{WO}_3 + y\text{H}^+ + ye^- \rightarrow \text{WO}_{3-y}(\text{OH})_y \quad (2.2)$$

Another model proposed by Faughnan [9] fits most experimental data [34]. It involves intervalence transition absorption for electrocoloration of \(\text{WO}_3\). Coloration of the film was achieved by simultaneous injection of cations and electrons into interstitial sites in the \(\text{WO}_3\) atomic lattice, forming a tungsten bronze, according to the following equation:

$$\text{WO}_3 + x\text{M}^+ + xe^- \rightarrow \text{M}_x\text{WO}_3 \quad (2.3)$$

where \(M\) is a positive ion, in the simplest case a proton, \(\text{H}^+\). In amorphous films this model accounted for coloration by intervalence transfer absorption [8], stated as:

$$\text{W}^{8+}(A) + \text{W}^{6+}(B) + h\nu \rightarrow \text{W}^{6+}(A) + \text{W}^{8+}(B) \quad (2.4)$$

where \(A\) and \(B\) are two different lattice sites. Another model closely related to Faughnan's theory suggests that the presence of a polaron, which is an electron loosely bound to its accompanying lattice distortion, causes coloration of the \(\text{WO}_3\) films [16]. In both models coloration is attributed to the tight localization of conduction band electrons to \(\text{W}^{8+}\) sites.
The $W^{5+}$ species form a defect band that is localized within the $WO_3$ bandgap. However, coloration could also be explained by delocalized electrons and free electron plasma absorption [18]. This effect has been ruled out because in amorphous films a broad absorption peak is noted over the range of 1.2 eV to 1.5 eV, rather than the sharp peak characteristic of a plasma [16].

Some of the experimental results supported the double injection model. Nishimura et al. [35] measured the infrared absorption spectra of $WO_3$ cells at coloration, they observed a rather strong absorption at shorter wavelength and ascribed the peak to $W^{5+}$, which peaks at approximately 1.0 $\mu$m. A weak but clear absorption peak at 4.3 $\mu$m is observed only in the colored samples, which can be ascribed to the O-H stretching vibration [35]. Dickens et al. studied the enthalpy changes for hydrogen insertion into $WO_3$ film by using solution calorimetry [36]. The results supported the double injection model. Schirmer et al. [16] pointed out that since all tungsten sites are not equivalent in an amorphous material, the injected electrons will be preferentially trapped at deeper sites. This variation in trap depths will add an additional term $E_0$ to the energy of the transition. This is supported by the fact that the optical absorption shifts to lower energy in crystalline $WO_3$ films [16]. Crandall et al. [37] measured the variation of the chemical potential ($\mu_H$) of hydrogen in amorphous films of H$_x$WO$_3$ and reported that as the coloration
proceeds an internal electromotive force appears which is a function of the stoichiometric parameter x value in HxWO3.

Some of the experimental results could not be explained by the double injection model, for instance, coloration under UV illumination and annealing in a vacuum without hydrogen (or cation) injection [2]. Muramatsu et al. [38] compared SIMS (Secondary Ion Mass Spectroscopy) results of electrochemically colored and bleached WO3 films and found that the spectra peak heights of hydrogen atoms were the same in both cases, and the OH- and H2O contents were also the same in both cases. In addition, they compared the XPS (X-ray Photoelectron Spectroscopy) results of WO3 films colored and bleached by the same method and showed that the stoichiometry of the films from the peak height ratio of oxygen to tungsten were the same in both cases, and there was no extraction of oxygen from the WO3 during the coloration at least at the surface of the film [37]. Recent electron resonance studies argued against both intervalence transfer and small polaron models [38]. In this point electrons are not uniquely localized in HxWO3 in either amorphous or polycrystalline films. If W5+ is formed during coloration, the donated electrons must be delocalized over a number of tungsten sites [16]. In the fine grained polycrystalline film a model was proposed by Dautremente-Smith et al. [39] which follows the double injection model with consideration of localized electrons in deep donors in grain boundaries [39]. Although the
understanding of the mechanism of the coloration of WO₃ films is not completed now, the double injection and intervalence transfer model which was first proposed by Faughnam et al. [9] seems the most reasonable explanation and is widely accepted.

2.4 REFLECTION MODULATION OF WO₃ FILM

On the basis of the double injection theory, the theoretical reflectance of polycrystalline WO₃ film was first computed by Svensson et al. [6], [7]. Introduction of electrons and positive ions into the WO₃ film gives an electron density $N_e$ and an equal density of ions $N_i$. Electrons with $N_e$ in excess of the Mott critical density [40] are assumed to occupy the WO₃ conduction band in the form of an electron gas. Damping of the free electrons occurs, in principle, from scattering by ionized impurities, neutral point defects, dislocations, crystallite boundaries etc. For a sufficiently ideal film one may neglect all but the ionized impurities — an unavoidable consequence of the double injection model [7], [9]. The dielectric function can be written as [5]:

$$\epsilon = \epsilon^{W_0} + \frac{i}{\epsilon_{\infty} \omega \rho} \quad (2.5)$$
Here $\varepsilon_{\infty}$ is the dielectric constant of the WO$_3$ host lattice, 
$\hbar \omega$ is the photon energy, $\varepsilon_0$ is the permittivity of free space, 
$\rho = \rho_r + i \rho_i$ is the complex dynamical resistivity of the damped 
electron gas, and $Z$ is the charge of the point-like defects, 
which are screened by a dielectric function $\varepsilon^t$. $\varepsilon^t$ is 
dependent on wavevector $k$ and frequency $\omega$, and can be given 
by the random phase approximation [41]. $\omega_p$ denotes the plasma 
frequency.

Fig. 2.4 illustrates the reflectance at normal incidence 
of a 2000Å thick crystalline WO$_3$ film with electron density $N_e$ from $10^{21}$ to $10^{22}$/cm$^3$ computed by Svensson et al. 
according to equations (2.5) and (2.6). In Fig.2.4 the 
dashed curve represents the reflectance of an rf sputtered 
polycrystalline WO$_3$ film with high densities of H$^+$ and e$^-$
state as measured by Goldner et al. [4]. Cogan et al. reported 
the reflectance of this film with injected Li ions [42], and 
obtained the similar result as Goldner et al.[4]. The 
experimental values were lower than the theoretical computed
values. This difference was interpreted by some researchers [4], [6], [7] as being caused by the assumption of ideal ionized scattering. The actual film is of polycrystalline structure and the crystallinity, such as crystallite size and morphology may affect the electron scattering mechanism and the electrochromic behavior of the films.
Fig. 2.1 The sandwich structure of an electrochromic cell.
Fig. 2.2  The oxygen octahedron packing of the WO$_3$ crystal structure

- : W atoms
○ : O atoms
Fig. 2.3 The monoclinic WO₃ structure showing the distorted WO₆ octahedra projected along the y axis.

Only W atoms between y±0.3b are shown; atoms at y≈0 are solid, atoms at y≈+1/4b are dashed, those at y≈-1/4b are dotted [17].
Fig. 2.4 Reflectance spectra computed for the configuration given in the inset.

The electrochromic \( \text{WO}_x \) layer has the shown magnitudes of electron density \( N_e \). The shaded area denotes the luminous efficiency of the eye and the thin curve represents a typical solar irradiance spectrum. The dashed curve represents the reflectance measured by Goldner et al. [4],[17].
Luminous efficiency of the eye

Solar spectrum (AM1)

Computed reflectance

Measured reflectance (from Goldner et al.)

Wavelength (µm)
CHAPTER 3

MATERIALS AND METHODS

3.1 PREPARATION OF SnO$_2$:F FILM SUBSTRATE

The method of preparation of SnO$_2$:F films is exactly the same as that used for WO$_3$ films and will be described in detail later. 20 SnO$_2$:F films (substrate: 7.5X2.5 cm$^2$ microscope glass slides) were prepared at a time.

For each type of SnO$_2$:F substrate, 30 grams of hydrated stannic chloride powder (SnCl$_2$.5H$_2$O, 97.5%, BDH Chemical Ltd.) and 2.4 grams of stannous fluoride powder (SnF$_2$, BDH Chemical Ltd.) were dissolved in distilled water to produce 80 ml solution. This solution was then sprayed using an ultrasonic nebulizer, which was designed and assembled in our laboratory.

Pyrolysis of SnCl$_2$ is the basic reaction involved in the process:

\[
\text{SnCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{SnO}_2 + 4\text{HCl} \quad (3.1)
\]

The substrate temperature was controlled between 300 °C
and 500 °C to obtain different types of substrates for the WO₃ films. The spray time was sufficiently long to make films thick enough to eliminate the size effect on electrical conductivity of SnO₂:F films.

3.2 APPARATUS AND PROCEDURES OF PYROLYTIC SPRAY DEPOSITION

For each WO₃ film sample, 3 grams of WCl₆ powder (Johnson Matthey Inc.) were weighed using a triple beam balance in a dry box. The powder was then dissolved in 50 mls of N-Dimethyl formamide (CON(CH₃)₂, 98.415%, BDH Chemical Ltd.) solution. The solution which was dark red in color was then immediately sprayed.

The chemical reaction may be written as:

\[ \text{WCl}_6 + \frac{3}{2}O_2 \rightarrow \text{WO}_3 + 3\text{Cl}_2 \uparrow \]  

(3.2)

Fig. 3.1 shows the design of the pyrolytic spray deposition oven which was built in our lab. An EN 145 electronic nebulizer (Medigas Pacific Ltd., Burnaby, B.C.) was used as the aerosol generator. The spray tube was a stainless steel cylinder with a 16x0.3 cm² spraying slit. The distance between spraying slit and the electric heater was about 3 cm, and the angle of the slit with respect to the film substrate was about 45°. A 3PN116 powerstat variable transformer was used to supply
power for the electric heater. The temperature of the electric heater was varied by changing the voltage of the transformer. The spray tube and the electric heater were contained in a wooden box with a glass window through which the substrates and the $\mathrm{WO}_3$ samples can be taken in and out respectively. $\mathrm{N}_2$ was passed through an airflow meter and used as the carrier gas.

Prior to spraying, the heater with tin bath was heated to the required temperature which was measured using an infrared galvanic detector. The $\mathrm{SnO}_2$:$\mathrm{F}$ substrate was then placed on the heater for 20 minutes heating prior to spraying. The tin bath served as thermal contact between heater and substrate to be sprayed.

3.3 X-RAY DIFFRACTION STUDIES

The X-ray diffraction experiments were carried out using a computerized diffractometer with CuKα line radiation. The diffraction patterns were compared with the results of published literature [9], [43] and the diffraction peaks were predicted by

$$\frac{1}{d^2} = \frac{i^2}{a^2} + \frac{j^2}{b^2} + \frac{k^2}{c^2}$$

(3.3)

and the Bragg condition
\[ \lambda = 2d \sin \theta \]  

(3.4)

The average crystallite size \( t \) of \( \text{WO}_3 \) films was calculated by the Scherrer formula [44]

\[ t = \frac{0.9 \lambda}{B \cos \theta} \]  

(3.5)

where

\[ B^2 = B_w^2 - B_s^2 \]  

(3.6)

and \( \theta \) is the diffraction angle, \( B_w \) is the broadening (radians) of the diffraction peak measured at half its maximum intensity. There are two factors contributing the broadening \( B_w \): one is the instrumental broadening \( B_s \) (0.2°) and the other is pure diffraction broadening \( B \) when the crystallite size of the film is less than about 1000Å (0.1 μm). Pure diffraction broadening increases with decreasing crystallite size and at sizes less than 100Å the back-reflection peaks disappear entirely and the low-angles peaks become very wide and more diffused [44].

It was worth noting that the crystallite size calculated by this method leads to a determination of the average crystallite size only.

In order to check the structure of the pyrolytically spray deposited \( \text{WO}_3 \) films, X-ray diffraction
measurements were carried out on a few samples of the tungsten chloride solution sprayed onto glass slides, H₂WO₄, powder heated in the pyrolytic spray deposition oven for a few hours and pure untreated H₂WO₄ powder (98%, BDH Chemical Ltd.). The chemical reaction of heating H₂WO₄ is thought to be:

\[ \text{H}_2\text{WO}_4 \rightarrow \text{WO}_3 + \text{H}_2\text{O} \quad (3.7) \]

By comparing the diffraction patterns of the tungsten chloride solution sprayed onto glass slide with the heated H₂WO₄ powder we can identify the characteristic diffraction peaks of the pyrolytically spray deposited tungsten trioxide films.

3.4 MEASUREMENT OF FILM THICKNESS

The thicknesses of the SnO₂:F and WO₃ films were measured by an interference step method using a microscope with an interferometer attachment (Wild Heebrugg Ltd., Switzerland). A hole step was made on the sample by placing a small amount of Zn powder on the film and adding a small amount of concentrated HCl acid. After the reaction the film was rinsed from with distilled water. A few films were re-measured using a mechanical "taly-step" technique (Taylor-Hobson, Model 3) and approximately the same results were obtained.
3.5 MEASUREMENT OF SHEET RESISTANCE

The electrical resistance of SnO$_2$:F films was measured by two methods. Using indium-gallium eutectic and two copper wires to make two ohmic contacts to the film, the resistance between these two contacts of the film were measured using a multimeter. Following calibration, a two-point probe method (the separation of the probes was 1.0 cm) was used to measure the sheet resistance of the films.

3.6 ELECTROCHROMIC MEASUREMENT

The fabrication of the experimental ECC is shown in Fig.3.2. It consisted of a working electrode (WE), a counter electrode (CE) and an Ag/AgCl reference electrode (RE). The CE was a highly conductive SnO$_2$:F film (with sheet resistance of 20$\Omega$/□) and the WE was polycrystalline WO$_3$ film on the SnO$_2$:F substrate. These two electrodes were fixed parallel to each other in a plexiglass frame leaving a 2 mm thick space, into which the electrolyte (10% H$_2$SO$_4$ in water
by volume) was placed. The RE was made by immersing a Ag wire in saturated KCl solution and applying a voltage of 1.0 to 1.5 V to the Ag wire with respect to a carbon counter electrode in the solution.

The electrochemical properties of the experimental ECC were studied using an instrumental arrangement of a lock-in amplifier (model HR-8); a potentiostat (model 173); an universal programmer (model 175); and an electrometer probe (model 178), all are produced by Princeton Applied Research Co.. A x-y recorder (7000 AR, Hewlett Packard) and a monochromator (Industries Co., Metuchen, N.J.) were also used in the experiments. A PIN-6LC Scottky barrier silicon pin photodiode (United Detector Technology Inc., Santa Monica, Cal.) which has a linear response to visible and near-infrared lights was used to measure the light intensity transmitted through the cell. Fig.3.3 shows the block diagram of the apparatus used in the electrochemical measurements. The incident light source was a tungsten halogen lamp (Wild, Switzerland) which has a steady output intensity spectrum.

The voltage applied was between -0.5 and -1.5 V with respect to the Ag/AgCl reference electrode. The transmittance of each experimental cell was measured before and while the voltage was applied. The output spectrum of the monochromator without the cell was used as the reference spectrum. Also the transmittance of a reference cell made of two highly conductive SnO$_2$:F (without WO$_3$ layer) films was measured.
before and while the voltage was applied.

White light was used to study the coloration time response of the cell during the voltage applied and to measure the transmittance as a function of the applied voltage.

As shown in Fig. 3.3, the potentiostat in conjunction with the universal programmer was used (dotted line) in measuring the I-V characteristic of the cell.
Fig.3.1 The diagram showing the construction of the pyrolytic spray deposition oven

A: Spray Tube (aerosol source)
B: Aerosol Path
C: Electric Heater with Molten Tin Bath
F: Substrate
A: Spray Tube
B: Aerosol Path
C: Electric Heater
F: Deposited Film
Fig. 3.2 The diagram of the cross-sectional geometry of the experimental cell
Fig. 3.3 The block diagram of electrochemical measurements

A: Tungsten Halogen Lamp
B: Filter
C: Chopper
D: Slit
E: Lens
ECC: Experimental Cell 1: working electrode,
    2: reference electrode, 3: counter electrode
F: Detector

Dotted lines were connected when measuring the I-V characteristic of the cells.
A: Tungsten Halogen Lamp

B: Filter

C: Chopper

D: Slit

E: Lens

ECC: Experimental Cell

1 working electrode, 2 reference electrode, 3 counter electrode

F: DETECTOR
CHAPTER 4

RESULTS AND DISCUSSION

4.1 PYROLYTICALLY SPRAY DEPOSITED SnO₂:F FILM

Fig. 4.1 shows the X-ray diffraction patterns of four types of SnO₂:F films deposited at substrate temperatures Tₛ = 300, 400, 450 and 500°C. It can be seen that the Tₛ dominates the film structure which shows amorphous, low polycrystalline, polycrystalline and highly polycrystalline structure respectively in the Tₛ range of 300°C to 500°C. SnO₂:F films are nonstoichiometric n-type semiconductors, their conductivity is due to the presence of a F donor level, Cl impurities, O vacancies and interstitial tin [45]. Table 4.1 lists the measured sheet resistance of several types of SnO₂:F films. Polycrystalline films ( Tₛ = 450, 500°C ) have a low sheet resistance of 20-50Ω/□ and amorphous film ( Tₛ = 300°C ) has a high sheet resistance of 10⁷Ω/□. The reaction SnCl₄ + 2H₂O → SnO₂ + 4HCl is only complete at substrate temperature equal to or greater than 500°C, below 500°C the pyrolytic hydrolysis process of SnCl₄ presumably results in the formation of SnO₂, SnO, Cl₂, H₂ and O₂ [46]. It seems
that films deposited at $T_s = 500^\circ C$ are slightly less conductive than films deposited at $T_s = 450^\circ C$. This may be due to a higher probability of $Na^+$ ions diffusing from the glass substrate into the $SnO_2:F$ film and thereby creating acceptor centers and forming larger $NaCl$ crystals in the films deposited at a higher substrate temperature during the deposition. The acceptor centers in the film can decrease the net carrier concentration and therefore decreasing the conductivity [45]. Further, the degree of crystallinity of $SnO_2:F$ films increases with the increase of $T_s$ up to $500^\circ C$, the X-ray diffraction peaks showed the same preferred orientation along the normal direction of the $(200)$ plane perpendicular to the surface of the film for all polycrystalline $SnO_2:F$ films. This observation is consistent with the results of Fantini et al. [47].

As shown in the Table 4.1, the thicknesses of all types of $SnO_2:F$ films deposited are greater than $5000\AA$, which are thick enough to eliminate the size effect on conductivity of the film at thickness about $4000\AA$ [45].

Fig. 4.2 presents the transmittance spectra of a $SnO_2:F$ film deposited at $T_s = 500^\circ C$ with a thickness of $5380\AA$. The average visible transmittance is greater than 80% which is highly desirable as the substrate for electrochromic coatings. The $F$ doping concentration may be used to control both conductivity and transmittance of $SnO_2:F$ films. Islam et al. [45] found that an increasing doping impurity
concentration results in an increased conductivity and decreased transmittance of SnO$_2$:F films. So by choosing a proper doping level and appropriate substrate temperature, high quality transparent conducting SnO$_2$:F films can be obtained and used as substrate films for electrochromic layers and as a counter electrode in ECCs.

4.2 PYROLYTICALLY SPRAY DEPOSITED WO$_3$ FILM

As shown in Fig.4.3, the angle positions of X-ray diffraction peaks of H$_2$WO$_4$ powder before and after being heated at a temperature of 450°C for 10 hours are completely different. According to eq. ( 3.7 ), this might imply that H$_2$WO$_4$ powder becomes WO$_3$ powder and water vapor during heating. By comparing the diffraction patterns of the heated H$_2$WO$_4$ powder and the WO$_3$ film deposited onto a glass from a tungsten chloride solution at a substrate temperature of 450°C ( Fig.4.3 ), it was found that the main peaks corresponding to the WO$_3$ crystal planes [001], [020] and [111] at the positions $2\theta = 23.2$, 23.8 and 28.3° respectively compare well in these two samples. In addition, some peaks at positions $2\theta = 21.7$, 38.8 and 56.2° in the diffraction pattern of the WO$_3$ film deposited onto a glass slide from a tungsten chloride solution may be assigned to the sub-oxides WO$_{3-x}$, ( 0<x<3 ) [10], [11]. However, the pyrolytically spray deposited
tungsten oxide films have a main composition of tungsten trioxide. This was also confirmed by XPS measurement by Craigen et al. [14].

X-ray diffraction also revealed that WO₃ films deposited onto glass slides at Tₛ = 350 and 400°C are amorphous and at Tₛ = 450°C are polycrystalline in nature; WO₃ films deposited onto SnO₂:F at Tₛ from 360 to 470°C are polycrystalline in nature. This is consistent with the prior report of pyrolytically spray deposited WO₃ films [14]. It was also found that the main peaks of the diffraction patterns of all pyrolytically spray deposited WO₃ films correspond to the WO₃ crystal planes [001], [020], [200] and [111] at the angle positions 2θ = 23.2, 23.8, 24.4 and 28.3° respectively. However, other peaks such as WO₃ [021], [221], [002], etc. and some peaks of other types of tungsten oxides were also observed in the diffraction patterns of some films. These observations show excellent agreement with those of evaporated and sputtered WO₃ films [9], [10].

4.2.1 Thickness and Resistivity of WO₃ Films

Table 4.2 lists the measured values of thicknesses of WO₃ films deposited using different deposition parameters. Thicknesses of films ranging from 380 to 4140±20% ㎛ are related to the deposition time and carrier gas N₂.
flowrate. But it is not a linear relationship with respect to these two parameters. It seems that the substrate temperature during deposition influences the crystallinity of the films, and also affects the thickness of the film. This may be due to the fact that a different degree of crystallinity of the WO$_3$ films may result in a different density of the films [11]. The uncertainty in the thickness measurements is about 20%. The thickness measurements by the mechanical "tally-step" technique compared well with those by the interference step technique within the uncertainty of about 20%.

The resistivity of WO$_3$ films was obtained by measuring the sheet resistance of films of tungsten chloride solution deposited onto glass slides. The following three WO$_3$ films were obtained by depositing the tungsten chloride solution the onto glass slides with a N$_2$ flowrate of 16.5 l./min for 10 minutes at various substrate temperatures:

<table>
<thead>
<tr>
<th>sample</th>
<th>$T_s$(°C)</th>
<th>thickness($\AA$)</th>
<th>sheet resistance($\Omega/\square$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WG1</td>
<td>300</td>
<td>2200</td>
<td>$&gt;10^9$</td>
</tr>
<tr>
<td>WG2</td>
<td>350</td>
<td>2300</td>
<td>$10^8$</td>
</tr>
<tr>
<td>WG3</td>
<td>450</td>
<td>2900</td>
<td>$10^4$</td>
</tr>
</tbody>
</table>

X-ray diffraction patterns revealed that WG1 and WG2 are amorphous and WG3 is polycrystalline in nature. From the sheet resistance and thickness as well as the dimensions of
above three films it is estimated that the amorphous film has a resistivity of about $2.3 \times 10^4 \, \Omega \text{cm}$ and the polycrystalline film has a resistivity of about $0.3 \, \Omega \text{cm}$. These values are a little lower than those of vacuum evaporated films reported by Miyake et al. [10]. Possibly this was due to the incomplete decomposition of $\text{WC}_6$ in our case.

The sheet resistance of the $\text{WO}_3$ films deposited onto $\text{SnO}_2:F$ were not determined since the $\text{SnO}_2:F$ film has a much lower resistivity than the $\text{WO}_3$ films and thus acts as a short.

4.2.2 Crystallinity of $\text{WO}_3$ Film

The carrier gas $\text{N}_2$ flowrate has a prominent effect on the crystallinity of $\text{WO}_3$ films. Fig.4.4 illustrates the difference in the X-ray diffraction patterns of three $\text{WO}_3$ films deposited onto highly polycrystalline ( $T_s = 500^\circ \text{C}$ ) $\text{SnO}_2:F$ at a substrate temperature of $400^\circ \text{C}$ for 7 minutes with $\text{N}_2$ flowrates of 7.5, 16.5 and 38 l./min respectively. Although all these three films were polycrystalline in nature, the film deposited with a $\text{N}_2$ flowrate of 16.5 l./min has a more randomly oriented crystallite structure since more diffraction peaks appeared. Further, as shown in the following table, the film deposited with a $\text{N}_2$ flowrate of 16.5 l./min has the largest crystallite size ( corresponding to the [001] plane ) in structure.
The nebulization rate was determined by measuring the initial and final volume of the tungsten chloride solution.

The speed of the aerosol droplets which is proportional to the carrier gas flowrate affects the deposition rate and hence the structure of the deposited films [48]. There may be an optimum value of nebulization rate for the crystallite size and orientation randomness of films within the range of the nebulization rate used. The dependence of crystallite size on the nebulization rate (related to deposition rate) shows a maximum value which is consistent with the prediction of Chopra for vapor-deposited polycrystalline films [48].

Fig. 4.5 shows the difference of the X-ray diffraction patterns between WO$_3$ films deposited onto four types of SnO$_2$:F substrates (shown in Fig. 4.1) at $T_s = 400^\circ$C with N$_2$ flowrate 16.5 l./min for 7 minutes. It was found that the higher crystallinity of the SnO$_2$:F substrate results in a higher crystallinity of the WO$_3$ film itself; films deposited onto the SnO$_2$:F at $T_s = 450^\circ$C show a more randomly oriented crystallite structure than those deposited at other

<table>
<thead>
<tr>
<th>Nz flow (l./min)</th>
<th>nebul. rate (ml./min)</th>
<th>cryst. size (Å)</th>
<th>thick. (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5</td>
<td>2.5</td>
<td>215</td>
<td>380</td>
</tr>
<tr>
<td>16.5</td>
<td>6.5</td>
<td>760</td>
<td>2230</td>
</tr>
<tr>
<td>38.0</td>
<td>10.5</td>
<td>639</td>
<td>3480</td>
</tr>
</tbody>
</table>

The nebulization rate was determined by measuring the initial and final volume of the tungsten chloride solution.
temperatures as can be seen in Fig. 4.5. The dependence of the crystallite size corresponding to the main peaks on the nature of substrate is shown as following:

\[
\begin{array}{c|ccc}
T_s \text{ of SnO}_2(\text{°C}) & \text{cryst. size(Å)±20% [001]} & \text{[020]} & \text{[200]} \\
\hline
300 & 392 & 220 & / \\
400 & 355 & 220 & 202 \\
450 & 760 & 760 & 760 \\
500 & 760 & 392 & 760 \\
\end{array}
\]

The nature and smoothness of the substrate surface can influence the atomic mobility and diffusion of surface atoms during the deposition and hence the crystalline structure of film deposited [47].

The substrate temperature is an important deposition parameter which influences the crystallinity of polycrystalline films. The average crystallite size corresponding to [001] plane vs substrate temperature of films deposited onto amorphous (\(T_s = 300\text{°C}\)) and highly polycrystalline (\(T_s = 500\text{°C}\)) \(\text{SnO}_2:F\) substrate is presented in Fig.4.6. Using the measurement uncertainty of \(\Delta(2\theta) = 0.05^\circ\) in measuring the half maximum broadening of the diffraction peaks, the average crystallite sizes calculated by eq. (3.5) and (3.6) were on the order of 200 to 760 Å. However, the crystallite size of some well crystallized films
may be larger than 760 Ω in the limiting case when $B_m$ approaches $B_s$. As shown in Fig. 4.6, the crystallite size of films deposited onto a amorphous substrate slightly decreases with the increase of $T_s$ from 400 to 470°C, and for highly polycrystalline substrates increases with the increase of $T_s$ from 360 to 420°C and then decreases with the increase of $T_s$ from 420 to 470°C. This dependence of crystallite size on the substrate temperature of $WO_3$ films is somewhat different from the observation reported for some films deposited by other methods, such as $SnO_2$ film [49]. Chopra [48] predicated theoretically that the crystallite size of most polycrystalline films would increase with substrate temperature during deposition or annealing. Maudes et al. [49] reported that the crystallite size of polycrystalline $SnO_2$ film increased with increasing substrate temperature. In contrast to Chopra, Achrya et al. [50] showed that the crystallite size of $MnO_2$ films decreases with annealing temperatures from 113 to 305°C and then increases with annealing temperatures from 305 to 413°C. The crystallite size of pyrolytically spray deposited $WO_3$ films has a maximum value at the substrate temperature of about 420°C as seen in Fig. 4.6. For large scale production of electrochromic coatings a lower substrate temperature is desirable to maintain low costs. Moreover, at high substrate temperatures, the Na$^+$ ions may diffuse from the glass substrate into the $SnO_2$:F film, thereby reducing the conductivity of $SnO_2$:F film. However, a high substrate conductivity is very
important for electrochromic windows.

Chopra [48] also expected that the crystallite size of polycrystalline films increases with thicknesses up to a certain value and then keeps constant with increasing film thickness [48]. As shown in Fig. 4.7, the (001) plane crystallite size of WO$_3$ films deposited onto highly polycrystalline (T$_s$ = 500°C) SnO$_2$:F substrate shows no trend with increasing film thickness up to about 1000Å but increases to a plateau at greater film thicknesses. Amorphous (T$_s$ = 300°C) SnO$_2$:F substrate also shows the same crystallite size distribution of WO$_3$ films with different film thicknesses although there are not sufficient experimental data available. This observation agrees with Chopra [48] in spite of the fact that substrate temperature and the nebulization rate were not kept constant during the deposition. The crystallite sizes corresponding to the main diffraction peaks of WO$_3$ films deposited onto polycrystalline (T$_s$ = 450°C) SnO$_2$:F substrate at T$_s$ = 420°C with N$_2$ flowrate 16.5 l./min seem to be independent of film thickness from 1200 to 4300Å except for a few scattered points of the (001) and (020) planes (Fig. 4.8). This may be because the thicknesses of this group of films are greater than crystallite size.

So far it is concluded that WO$_3$ film deposited onto polycrystalline (T$_s$ = 450°C) SnO$_2$:F film at substrate temperature 420°C with N$_2$ flowrate of 16.5 l./min shows the larger crystallite size and more randomly oriented crystallite size.
structure. The following discussion will therefore concentrate on films deposited under these conditions but with different deposition times, i.e. different thicknesses of the WO₃ films.

Preferential orientation of crystallites is an important phenomenon in polycrystalline thin films, especially the thickness effects on the orientation [48]. A preferentially oriented crystal face corresponds to the lowest surface free energy of the crystal. WO₃ films, which have a hexagonal close-packed (octahedron) crystal structure, are expected to show a [001] preferential orientation [51]. As shown in Fig.4.9 the diffraction peak intensities of the [001] and [020] planes are stronger than those of the [200] and [111] planes for WO₃ films deposited onto polycrystalline SnO₂:F at Tₑ = 450°C with a N₂ flowrate of 16.5 l./min. However, the intensities of the [001], [200] and [111] planes had the same distribution with a maximum value at thicknesses of about 2500Å and the intensity of the [020] plane increased rapidly with thicknesses greater than 2500Å. By taking the ratio of diffraction peak intensities of the [001] and [020] planes to other planes respectively (Fig.4.10 and Fig.4.11), it was found that the [001] plane showed a preferred orientation for film thicknesses of 1200 to 2500Å while the [020] plane was highly preferential oriented for film thicknesses 3000 to 4300Å. Further, films of thicknesses of approximately 2900Å showed a more randomly oriented crystallite structure although they still showed a slight
the [020] preferred orientation.

4.3 ELECTROCHROMIC BEHAVIOR OF WO₃ FILM

4.3.1 Visible and Near Infrared Transmittance

As shown in Fig.4.2, the visible average transmittance of a polycrystalline WO₃ film deposited onto highly polycrystalline (Tₛ = 500°C) SnO₂:F film at substrate temperature of 440°C with a thickness 440 nm is about 70%. The remaining 30% may be due to reflection [18] or absorption [16], or both. After applying a voltage (measured between WE and RE) to the ECC, it was observed that WO₃ films deposited onto highly conducting (Tₛ = 450, 500°C) SnO₂:F substrates showed a blue coloration. The degree of color depends on the voltage applied and with the increasing negative bias of the working electrode the transmittance reduced remarkably; WO₃ films deposited onto amorphous (Tₛ = 300°C) substrate showed no visible coloration and the transmittance changed little. This maybe due to the high resistivity of the substrate (see Table 4.1).

Fig.4.12 illustrates the thickness dependence on the transmittance change at three wavelengths (5500, 6330 and 9000 nm) for films deposited onto highly conducting (Tₛ = 450°C) SnO₂:F at a substrate temperature of 420°C with N₂.
flowrate of 16.5 l./min. The voltage applied was -0.5V. It was found that the crystallite orientation of the films has a strong influence on the transmittance change during the coloration. The visible (5500Å) transmittance change increased from about 10% to 65% and then decreased to 20%; and the near infrared (9000Å) transmittance change increased from about 50% to 90% and then decreased to 50%. The transmittance change was obtained by comparing the transmission spectra of before and during coloration for each experimental cell. Because the transmission spectra of every cells do not show interference effects, in Fig.4.12 the peaks at film thickness about 3000Å can not be due to interference effect. The variation in transmittance change corresponds to the crystallite orientation changing from [001] preferred orientation to a randomly oriented crystallite state (slight [020] preferred orientation) and then to the highly [020] preferred orientation state. It seems that the [001] crystallite preferred orientation has a stronger influence on the electrochromic behavior than the [020] crystallite preferred orientation of the WO₃ film. Joo et al. [52] measured the lithium diffusion coefficients in electrochemically grown KₓWO₃ single crystal along the a and c crystallographic direction. They reported that the lithium diffusion coefficient for the c crystallographic direction is 10⁻⁸ cm²/sec, which is one order of magnitude lower than that along the a crystallographic direction. The
lithium diffusion coefficient in K$_{0.26}$WO$_3$ single crystal along the b crystallographic direction has not been reported yet. However it may be higher than that along the c crystallographic direction because in a hexagonal close-packed (octahedron) structure the crystal face of the c crystallographic direction [001] corresponds to the lowest surface free energy, thereby the smallest atomic diffusion coefficient along this direction. The difference of influence on the transmittance change between the WO$_3$ films with [001] and [020] preferred crystallite orientation is consistent with the results reported by Joo et al. [52]. Referring to Fig.4.9, the unusual low points at thickness 2550Å in Fig.4.12 may be reasonable because this film showed an unusual high [001] preferred crystallite orientation structure. The infrared transmittance changed more than the visible transmittance because injected electrons in polycrystalline WO$_3$ film show near free electron behavior [4], [7], [15]. The transmittance change dependence on crystallite orientation of the films can be understood phenomenologically: polycrystalline films consist of crystallite domains, preferentially oriented crystallites have a smaller angle between grain boundaries. Then with the same voltage applied, films of randomly oriented crystallite with larger angle between grain boundaries could have more cations and electrons injecting into film through grain boundaries than films with preferentially oriented crystallites and thus results in higher reflection and thus a larger transmittance.
change.

Fig. 4.13 shows the dependence of the transmittance change on crystallite size for four films with thicknesses of 2550, 2600, 2780 and 3100 Å. The transmittance change increased rapidly with increasing crystallite size. The electrons injected into films with larger crystallite size show more likely free-electron behavior (less grain boundary scattering) which results in higher reflection and thus a larger transmittance change. Although there were only four experimental data points available in Fig. 4.13, the tendency of the relation between transmittance change and crystallite size supported the hypothesis of Svensson et al. [6], [7]. On the basis of spectroscopic ellipsometry studies and an analysis of the dynamical resistivity of colored polycrystalline WO$_3$ film and single crystal Na$_x$WO$_3$, Goldner et al. [53] estimated that the reflection of the single crystal Na$_x$WO$_3$ is twice as that of the polycrystalline WO$_3$ film in the visible and near infrared region. This may also imply that the higher crystallinity of polycrystalline WO$_3$ films results in higher reflection during coloration.

As expected, the transmittance of the reference cell (without WO$_3$ layer) did not change with applied voltage. Schirmer et al. [16] reported that the optical density of polycrystalline WO$_3$ film increases 50% only during electrochemical coloration, thus it was believed that the transmittance change of pyrolytically spray deposited
polycrystalline WO₃ film during the coloration was mainly
due to an increase in reflection, which was confirmed by us
in some preliminary measurements using a He-Ne laser.

4.3.2 I-V Characteristics of ECC

A typical cyclic voltammogram of a WO₃ electrochromic
cell is presented in Fig.4.14. The WO₃ film of this cell
was deposited onto highly conducting ( Tₛ = 450°C ) SnO₂:F
at a substrate temperature of 420°C with a N₂ flowrate of 16.5
l./min. This film has a thickness of 2780Å with randomly
oriented crystallites structure ( 760Å crystallite size
corresponding to main crystal planes ). The effective area of
this cell was 0.2cm X 0.25cm. As shown in Fig.4.14, the voltage
sweep starts from the spontaneous potential of -0.12V vs
Ag/AgCl, which was found to be the rest potential under open-
circuit condition. At the threshold potential of about -0.3V,
the cathodic current causes a coloration reaction of the WO₃
film, which was also reported by other authors [54]. At the
turning point ( -10.5V ), the cathodic current attains a peak
value of 4mA/cm². At the potential of -0.75V the anodic
current which is associated with the bleaching reaction begins
to appear, it increases to a peak value of 2.3A/cm² at the
potential of about -0.65V and then decreases dramatically until
bleaching is nearly complete at the potential of about -0.5V.

-49-
After one voltammogram cycle is completed, the cell returns to its initial state with a small residual anodic current of about 0.2mA/cm². The second cycle is almost the same as the first one.

The I-V characteristics of the cell are consistent with the white light transmittance of the cell as a function of the voltage applied as shown in Fig.4.15. The transmittance begins to drop at a potential of about -0.3V, which corresponds to the onset of coloration in Fig.4.14. The transmittance did not return to its initial value because the rather high scan rate (20mV/Sec.) results in incomplete bleaching.

Fig.4.16 presents the time response of the same experimental cell discussed above. The white light transmittance decreased 56% within 25 seconds after a bias of -0.5V applied and then reached a nearly steady transmission value of 20% in about 2 minutes. Due to the high ion mobility of the liquid electrolyte used, the bleaching time corresponding to 56% of the transmission was about 60 seconds under short circuit condition and 50 seconds with +0.5V applied. After +0.5 voltage applied for 5 minutes the cell returned to its initial clear state. Although the time response is much slower than that of amorphous WO₃ electrochromic display devices [55], it is acceptable for the purpose of "smart windows".
Table 4.1  SnO$_2$:F films deposited onto glass slides with a N$_2$ flowrate of 38.0 l./min

<table>
<thead>
<tr>
<th>$T_s$ (°C)</th>
<th>time (min)</th>
<th>thick. (Å)</th>
<th>sheet R (Ω/$\square$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>20</td>
<td>6050±20%</td>
<td>7X10$^4$</td>
</tr>
<tr>
<td>350</td>
<td>20</td>
<td>7850±20%</td>
<td>5X10$^3$</td>
</tr>
<tr>
<td>400</td>
<td>20</td>
<td>8500±20%</td>
<td>1X10$^2$</td>
</tr>
<tr>
<td>450</td>
<td>15</td>
<td>7700±20%</td>
<td>20</td>
</tr>
<tr>
<td>500</td>
<td>10</td>
<td>5380±20%</td>
<td>50</td>
</tr>
</tbody>
</table>
Table 4.2-1  WO3 films deposited onto amorphous SnO2:F
(T_s =300°C, R = 7X10^6Ω/□, thickness =
6050Å)

T_s(°) | N₂ flow.(l./min) | time(min) | thick.(Å)±20%
-------|------------------|-----------|------------------
400    | 7.5             | 7         | 580
400    | 16.5            | 7         | 1560
400    | 38.0            | 7         | 2310
420    | 7.5             | 10        | 610
440    | 7.5             | 10        | 730
460    | 7.5             | 10        | 800
470    | 7.5             | 10        | 850

-52-
Table 4.2-2  WO$_3$ films deposited onto low polycrystalline SnO$_2$:F  ( $T_s$ = 400º, $R$ = 100Ω/□, thickness = 8500Å)

$T_s$(ºC) | N$_2$ flow.(l./min) | time(min) | thick.Å±20%

| 400   | 7.5   | 7     | 610   |
| 400   | 16.5  | 7     | 1560  |
| 400   | 38.0  | 7     | 2890  |
| 360   | 7.5   | 10    | 630   |
| 380   | 7.5   | 10    | 870   |
| 400   | 7.5   | 10    | 1100  |
| 420   | 7.5   | 10    | 1150  |
| 440   | 7.5   | 10    | 1270  |
| 460   | 7.5   | 10    | 1380  |
| 470   | 7.5   | 10    | 1450  |
Table 4.2-3  
WO$_3$ films deposited onto highly polycrystalline SnO$_2$:F ( $T_s = 500^\circ$, $R = 50\Omega/\square$, thickness = 5380Å )

<table>
<thead>
<tr>
<th>$T_s (^\circC)$</th>
<th>$N_2$ flow (l./min)</th>
<th>time (min)</th>
<th>thick. (Å) ± 20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>7.5</td>
<td>7</td>
<td>380</td>
</tr>
<tr>
<td>400</td>
<td>16.5</td>
<td>7</td>
<td>2230</td>
</tr>
<tr>
<td>400</td>
<td>38.0</td>
<td>7</td>
<td>3480</td>
</tr>
<tr>
<td>360</td>
<td>7.5</td>
<td>10</td>
<td>410</td>
</tr>
<tr>
<td>380</td>
<td>7.5</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>7.5</td>
<td>10</td>
<td>400</td>
</tr>
<tr>
<td>420</td>
<td>7.5</td>
<td>10</td>
<td>370</td>
</tr>
<tr>
<td>440</td>
<td>7.5</td>
<td>10</td>
<td>440</td>
</tr>
<tr>
<td>460</td>
<td>7.5</td>
<td>10</td>
<td>360</td>
</tr>
<tr>
<td>470</td>
<td>7.5</td>
<td>10</td>
<td>520</td>
</tr>
</tbody>
</table>
Table 4.2-4  WO$_3$ films deposited onto polycrystalline SnO$_2$:F  
( $T_s = 450^\circ$C, $R = 20\Omega/\square$, thickness = 7700Å ) at a 
substrate temperature of 420°C with a N$_2$ flowrate 
of 16.5 l./min

<table>
<thead>
<tr>
<th>time ( min. )</th>
<th>thickness ( Å ) ± 20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1160</td>
</tr>
<tr>
<td>2</td>
<td>1473</td>
</tr>
<tr>
<td>3</td>
<td>1680</td>
</tr>
<tr>
<td>6</td>
<td>2310</td>
</tr>
<tr>
<td>8</td>
<td>2550</td>
</tr>
<tr>
<td>10</td>
<td>2600</td>
</tr>
<tr>
<td>10</td>
<td>2780</td>
</tr>
<tr>
<td>13</td>
<td>3100</td>
</tr>
<tr>
<td>15</td>
<td>3312</td>
</tr>
<tr>
<td>20</td>
<td>4140</td>
</tr>
</tbody>
</table>
Fig. 4.1 X-ray diffraction patterns of four types of SnO$_2$:F films deposited onto glass slides with a N$_2$ flowrate of 38.0 l./min

<table>
<thead>
<tr>
<th>type</th>
<th>substrate temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>300</td>
</tr>
<tr>
<td>B</td>
<td>400</td>
</tr>
<tr>
<td>C</td>
<td>450</td>
</tr>
<tr>
<td>D</td>
<td>500</td>
</tr>
</tbody>
</table>
Fig. 4.2  Normal transmittance spectra of a highly polycrystalline SnO$_2$:F film deposited onto glass with thickness 5380 Å and a WO$_3$ film deposited onto the above SnO$_2$:F film with a thickness of 440 Å

A: SnO$_2$:F film
B: WO$_3$ film on SnO$_2$:F
Fig. 4.3 X-ray diffraction patterns

A: WO$_3$ deposited onto a glass slide at $T_s = 450^\circ$C
   with a N$_2$ flowrate of 16.5 l./min for 7 minutes
B: H$_2$WO$_4$ powder heated at temperature 450°C for
   10 hours
C: H$_2$WO$_4$ powder untreated
Fig. 4.4 X-ray diffraction patterns of WO₃ films deposited onto highly polycrystalline (Tₛ = 500°C) SnO₂:F at a substrate temperature of 400°C for 7 minutes

A: N₂ flowrate 16.5 l./min
B: N₂ flowrate 7.5 l./min
C: N₂ flowrate 38.0 l./min
Fig. 4.5  X-ray diffraction patterns of WO$_3$ films deposited onto four types of SnO$_2$:F substrates (as shown in Fig. 4.1) at $T_s$ 400°C with N$_2$ flowrate 16.5 l./min

<table>
<thead>
<tr>
<th>sample</th>
<th>$T_s$ of SnO$_2$:F (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>300</td>
</tr>
<tr>
<td>B</td>
<td>400</td>
</tr>
<tr>
<td>C</td>
<td>450</td>
</tr>
<tr>
<td>D</td>
<td>500</td>
</tr>
</tbody>
</table>
Fig. 4.6 Dependence of crystallite size (corresponding to the [001] plane) on the substrate temperature of WO$_3$ films.

- A: deposited onto amorphous ($T_s = 300^\circ C$) SnO$_2$:F
- B: deposited onto highly polycrystalline ($T_s = 500^\circ C$) SnO$_2$:F
Fig. 4.7 Dependence of the crystallite size (corresponding to the [001] plane) on the thickness of WO₃ films deposited at substrate temperatures ranging from 360 to 470°C

○ A: highly polycrystalline (Tₛ = 500°C) SnO₂:F substrate
○ B: amorphous (Tₛ = 300°C) SnO₂:F substrate
Fig. 4.8 Dependence of the crystallite size on the thickness of WO₃ films deposited onto polycrystalline (Tₛ = 450°C) SnO₂:F at a substrate temperature of 420°C with N₂ flowrate 16.5 l./min

○ [001]

○ [200]

▲ [111]

For [020] plane the crystallite sizes of all films are about 760Å. The error bars for some points close to each other are not shown, and are similar to the error bars indicated.
Fig. 4.9  Diffraction peak intensity distribution with thickness of the same WO₃ films as in Fig. 4.8

- A: [001]
- B: [002]
- C: [111]
- D: [020] The actual intensity is 8 larger than shown.
Fig. 4.10 Dependence of the intensity ratio on the thickness of the same WO$_3$ films as in Fig. 4.9

- A: [001]/[111]
- B: [001]/[002]
- C: [001]/[020]
Fig. 4.11  Dependence of intensity ratio on thickness of the same WO$_3$ films as in Fig. 4.10

- A: [020]/[111]
- B: [020]/[002]
- C: [020]/[001]
Fig. 4.12. Transmittance change at three different wavelengths vs thickness of the same WO$_3$ films as in Fig. 4.11

- A: 9000Å
- B: 6330Å
- C: 5500Å
Fig. 4.13  Transmittance change vs crystallite size corresponding to the [001] plane of four WO$_3$ films deposited onto polycrystalline SnO$_2$:F ( $T_s = 450^\circ$C ) at substrate temperature of 420$^\circ$C and N$_2$ flowrate 16.5 l./min. The film thicknesses were 2550, 2600, 2780 and 3100Å.
Fig. 4.14 Current–voltage characteristics of a typical experimental ECC

CE: polycrystalline (T_s = 450°C) SnO_2:F film onto glass
WE: WO_3 film of thickness 2780Å on the EC film
RE: Ag/AgCl
scan rate: 20mV/Sec
Fig. 4.15  Dependence of white light transmittance on applied voltage of the same cell as in Fig. 14.
scan rate : 20 mV/Sec
Fig.4.16 Time response of the same cell as in Fig.4.16
Pyrolytically spray deposited WO$_3$ films on SnO$_2$:F film substrates were investigated.

X-ray diffraction patterns revealed that SnO$_2$:F films deposited onto glass slides at a substrate temperature of 300°C are amorphous and at substrate temperatures higher than 350°C they are polycrystalline. The degree of the crystallinity of the films is proportional to the substrate temperature during deposition. The amorphous SnO$_2$:F films are highly resistive with sheet resistances on the order of $10^4$ ohms per square ($\Omega/\square$) and the polycrystalline SnO$_2$:F films are highly conducting with sheet resistance of 20 to 25 $\Omega/\square$. Both amorphous and polycrystalline SnO$_2$:F films are transparent in the visible light region with an average transmittance of about 80% for polycrystalline films. In order to get highly conducting transparent SnO$_2$:F films for substrates of WO$_3$ films, pyrolytically spray deposited SnO$_2$:F films on glass slides at a substrate temperature of 450°C with a N$_2$ flowrate of 16.5 l./min for 10 minutes may be the best choice.

WO$_3$ films were deposited with different deposition
parameters such as the crystalline nature of the substrate, the substrate temperature and the carrier gas flowrate as well as the deposition time. X-ray diffraction studies showed that films of the tungsten chloride solution spray deposited onto the SnO$_2$:F films at substrate temperatures ranging from 360 to 470°C are polycrystalline with average crystallite sizes ranging from 200 to 800Å and mainly tungsten trioxide in composition.

WO$_3$ films deposited onto polycrystalline (T$_s$ = 450°C) SnO$_2$:F revealed the largest crystallite size among the four types of SnO$_2$:F substrate films (amorphous T$_s$ = 300°C; low polycrystalline T$_s$ = 400°C; polycrystalline T$_s$ = 450°C; highly polycrystalline T$_s$ = 500°C) used with other parameters kept constant. This may be due to the nature and smoothness of the substrate surface which influences the atomic mobility and diffusion of tungsten atoms and hence the crystal structure of the WO$_3$ films. WO$_3$ films deposited with a N$_2$ flowrate of 16.5 l./min have the largest crystallite size and a more randomly oriented crystallite orientation among the three value of N$_2$ flowrate (7.5, 16.5 and 38.0 l./min) used while other parameters were kept constant. This is most likely due to the proper speed of aerosol droplets thereby the proper deposition rate, which affects on the crystal structure of the films. Fixing other parameters except the substrate temperature, WO$_3$ films deposited onto amorphous SnO$_2$:F substrate showed an almost constant average crystallite size with an increase in
substrate temperature from 400 to 470°C; WO₃ films deposited onto highly polycrystalline SnO₂:F substrates showed a maximum average crystallite size at a substrate temperature of 420°C, with an increase in substrate temperature from 360 to 470°C during deposition.

X-ray analysis revealed that the thickness of the films did not affect the crystallite size when the film was thicker than 1200Å but the thickness of the films affected the preferential orientation of crystallites. For films deposited onto polycrystalline SnO₂:F substrates, the [001] plane was preferentially oriented for thicknesses from 1200 to 2500Å and the [020] plane was preferentially oriented in thicknesses ranging from 3100 to 4200Å. Thicknesses on the order of 2900Å films showed a slightly [020] preferred orientation but had a more randomly oriented crystallite structure than films with other thicknesses.

The electrochromic performance showed that films which have a larger crystallite size and more randomly oriented crystallite structure showed most remarkable coloration and a near infrared transmittance change of 90%; which most likely results from an increase in reflection. Injected electrons in the film with larger crystallite size show more likely free-electron behavior and in addition less grain boundary scattering, which results in a larger reflection. Films which are more randomly oriented have larger angles of grain boundaries such that more cations and electrons are injected.
into the films, which also results in an increased reflection.

The [001] plane preferential orientation of the WO$_3$ film has a larger influence on the electrochromic behavior than the [020] preferential orientation. This is probably due to the [001] plane corresponding to the lowest surface free energy crystal plane for hexagonal closed-packed (octahedron) crystal thereby the hydrogen diffusion coefficient is the smallest along the $\overline{c}$ crystallographic direction.

Pyrolytically spray deposited tungsten oxide onto polycrystalline (T$_s$ = 450°C) SnO$_2$:F at a substrate temperature of 420°C and a N$_2$ flowrate of 16.5 l./min with film thickness about 3000Å, revealed the optimum electrochromic behavior which is desirable for the preparation of "smart windows".
Bibliography


-78-

