DEPOSITION, CORROSION AND COLORATION OF
TUNGSTEN TRIOXIDE
ELECTROCHROMIC THIN FILMS

BY

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To my mother

and

Mei-Hwei, my beloved wife

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Abstract of Dissertation Presented to the Graduate School
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Electrochromism (reversible color change of a material, induced by an electric field) has been investigated in tungsten trioxide thin films. It is known that electrochromic device lifetime is generally limited by corrosion of WO_3 films in an acid electrolyte. Two mechanisms of corrosion were observed, viz., general dissolution and interfacial delamination. It was found that the dissolution of WO_3 films in acid could be attributed to high concentration of thermodynamically unstable species (WO_2 and W_2O_5) in the as-deposited films. These species were identified by X-ray photoelectron spectroscopy data and are consistent with Rutherford backscattering spectroscopy data which showed an oxygen deficiency ($O/W = 2.76$). The Pourbaix diagram for tungsten indicated that WO_3 was the thermodynamically stable specie for the present storage condition ($pH = 0.5$,

$E = 0.4 V_{SHE}$). A corrosion mechanism was proposed consisting of dissolution of WO_2 and W_2O_5 and precipitation of crystalline WO_3 and its hydrates. Interfacial delamination occurred when WO_3 and its hydrates precipitated back onto the original films.

The oxygen content in the WO_3 films was increased by oxygen back-filling during evaporation. Dissolution and interfacial delamination of the oxygen enriched films were reduced to negligible rates due to reduced concentration of WO_2 and W_2O_5 . However, the electrochromic properties were degraded by oxygen enrichment. For example, increased resistivity and decreased optical efficiency in the oxygen enriched films resulted in slower coloration speed. The resistivity increase and decreased optical efficiency were explained by postulating an increased density of inactive electron trapping sites. The porosity of the films could be increased by deposition at high background pressure, resulting in increased surface area and absorbed water. The bleaching speeds and self-erasure rates were increased since the rates of removal of protons were increased by the increases in porosity and absorbed water.

In another approach to increase the electrochromic device lifetime, the electrolyte was modified. Devices using a solution of $LiClO_4$ in propylene carbonate exhibited excellent lifetime. Switching speeds were increased by increased porosity, deposition of MgF_2 overlayers, and more conductive indium-tin-oxide layers. In addition, solid state electrochromic devices using a hydrated MgF_3 film were fabricated.

CHAPTER I INTRODUCTION

Electrochromism is broadly defined as the ability of a material or system to change color reversibly in response to an applied potential. A great variety of electrochromic materials or systems are known and can be conveniently classified into the following categories according to the physical mechanisms involved:

- reversible electrodeposition systems
- organic ion-insertion materials
- inorganic ion-insertion materials.

Viologens,¹ anthraquinones² and electroplating of very thin films of metals³ such as silver comprise the first class. Diphthalocyanines⁴ and tetrathiafulvalenes⁵ are included in the second class. Class three is comprised of transition metal oxides, among which WO_3 thin films* have received by far the most attention.⁶⁻³⁹ Other materials such as anodically deposited iridium oxide films of IrO_2 ,⁴⁰⁻⁴⁴ molybdenum oxide (MoO_3),⁴⁵⁻⁴⁷ vanadium pentoxide (V_2O_5),⁴⁸ and nickel oxide (NiO)⁴⁹ have also been shown to color electrochromically, and would be placed in this class. Besides coloring electrochromically, some of the transition metal oxides may also be colored by heating

* Although the vapor deposited tungsten trioxide films are substoichiometric as reported below, the term ' WO_3 thin films' will be used for simplicity unless otherwise noted.

(thermochromism),⁶ by exposure to ultra-violet light or X-ray (photochromism)⁷ or by electron beam irradiation (cathodochromism).⁵⁰⁻⁵²

The WO_3 electrochromic (EC) display device typically consists of a transparent electrode such as a SnO_2 coated glass substrate, a thin layer of transparent WO_3 , an electrolyte and a counter electrode (Pt or Au). When a small negative voltage (~ 1.0 V) is applied to the transparent electrode, the WO_3 film is colored blue in transmission.^{8,9} The induced optical change is proportional to the charge injected during the coloring pulse. If the voltage is removed, the WO_3 film remains colored. Reversing the polarity of the applied voltage will cause bleaching of the films. The electrochromic coloration of WO_3 in acidic aqueous solution involves the injection of electrons and protons into WO_3 films.⁹ The blue coloration in transmission is associated with the broad optical absorption band which gives an absorption minimum at wavelength of $0.4 \mu\text{m}$ and an absorption maximum at $0.95 \mu\text{m}$.^{8,9} The absorption band is generally explained by electron transfer between neighboring tungsten atoms, i.e., optical absorption by excitation of polaron hopping.¹⁰⁻¹²

The protons injected are for the purpose of charge compensation. Therefore, any monovalent cation can be used, e.g., Li^+ ,¹³⁻²¹ Na^+ ,²⁵⁻²⁸ or Ag^+ .²⁹

The electrochromic device exhibits many attractive features as displays, such as

- good color contrast especially under high level of ambient light;
- wide-angle viewability which is an advantage over most liquid crystal displays (LCD);

- low voltage operation (1.5 V down to approximately 0.5 V);
- low power, $\sim 9 \text{ mW/cm}^2$, somewhere between LCD and light-emitting diode (LED) displays;
- storage of the display without power dissipation;
- potentially low cost.

The response time has been reported to be approximately 50 ms with a modified device configuration in acid electrolyte,³⁰ and is comparable with LCD. However, there is a principal obstacle to the commercialization of EC displays, viz., short device lifetime. The general lifetime reported was about $\sim 10^5$ cycles at 0.5 Hz³¹ or less than two weeks for static condition. To understand the cause of degradation and to find a way to improve the lifetime was the major goal in the present research.

The degradation of EC devices was reported to result from corrosion of WO_3 thin films in the acid electrolyte.³²⁻³⁵ In Chapter II, the corrosion mechanism and the results of using oxygen backfilling during WO_3 evaporation to prevent corrosion will be discussed. The durability of the deposited films in sulfuric acid solution will be shown to be limited by two mechanisms-- a general uniform film dissolution and an interfacial delamination. Due to the deficiency of oxygen ($\text{O/W} = 2.76$), some of the configurations of tungsten atoms in as-deposited films may be thermodynamically unstable. A conversion process, viz., dissolution of these unstable species and precipitation of the stable crystalline WO_3 and its hydrates, leads to the general film dissolution and interfacial

delamination of WO_3 films. The delamination of films from the substrates occurs when the internal stresses induced by precipitation exceed the interfacial adhesion strength.

In order to improve the lifetime, two basic approaches were adopted in the present study. In one approach, oxygen backfilling during WO_3 evaporation was used to modify film structure and reduce the attack by the acid electrolyte. By this method, the O/W ratio was increased and the amount of degradation was reduced due to the increased concentration of the thermodynamically stable specie, WO_3 . The current injection and optical efficiency during coloration were lower, however, while the bleaching speed and self-erasure rate were faster for oxygen-enriched films. The mechanisms by which these modifications of EC properties were achieved are discussed.

The second approach to improve the device lifetime involved the use of non-aqueous electrolytes. Non-aqueous electrolytes have been shown to provide an inert environment where the corrosion of WO_3 was not observed.¹⁵ In Chapter III, trial devices using LiClO_4 dissolved in propylene carbonate (Li/PC) and solid MgF_2 thin film electrolytes are discussed. Previous investigators have reported that devices using Li/PC as an electrolyte exhibited slow response speed. In this study, an improvement in speed was achieved by nitrogen backfilling during WO_3 deposition and by the use of a MgF_2 overlayer. Layers of MgF_2 were also used as electrolyte to fabricate solid state display devices. These experiments indicated that the increased water content in MgF_2 films

resulting from air backfilling increased the coloration/bleaching (C/B) speed, while the operational area of the device was limited by the air backfilling during deposition of WO_3 films.

Preliminary data on cathodochromism (electron beam induced coloration) in WO_3 thin films are reported in Appendix A. The coloration density in WO_3 films was found to be increased by air backfilling, especially for higher energy electron beams. Results indicate that cathodochromism in amorphous WO_3 thin films may still be caused by polaron hopping absorption as in electrochromism.

CHAPTER II
CORROSION STUDIES AND MODIFICATION OF TUNGSTEN TRIOXIDE
THIN FILMS BY OXYGEN BACKFILLING

Introduction

Electrochromism (EC) has been investigated in tungstic oxide films for possible application in display devices. The devices typically used diluted sulfuric acid solutions as the electrolyte. With a modified device configuration (Figure 2.1), viz., a porous gold overlayer on the WO_3 films, it is possible to achieve a switching time of approximately 50 ms.³⁰ The time is comparable to that of liquid crystal displays (LCD). However, the lifetime of EC devices in such an electrolyte is normally short. The device lifetime was found to be limited by the degradation of WO_3 films in the acid electrolyte in the form of general dissolution and delamination.³²⁻³⁵ Short device lifetime is a principal obstacle to the commercialization of EC displays.

Degradation of WO_3 thin films has been studied and was correlated with corrosion,³²⁻³⁵ However, the mechanism(s) by which corrosion occurs and the thermodynamics of WO_3 corrosion have not been considered in detail. Faughnan and Crandall³⁵ studied evaporated WO_3 films in H_2SO_4 /water solution (pH = 0) and found the dissolution rate was approximately 300 Å per day. Cyclic coloring and bleaching of the films led to faster dissolution rates.

Figure 2.1. Schematic representation of the electrochromic cell with thin gold overlayer on WO_3 .

Randin³² replaced the water with glycerin as the solvent in the electrolyte and found the dissolution rate was lowered by an order of magnitude (approximately 20 Å per day). An increase in the dissolution rate was also observed under cycling condition. The film was eventually destroyed as a result of delamination from the substrate. To explain this behavior, Randin listed a number of possible mechanisms of degradation, e.g.:

- a) proton insertion process causing hydrogen embrittlement which undermined the internal strength of WO_3 ,
- b) anodic disintegration of the films,
- c) oxidative degradation occurring readily on semiconductor electrodes, such as $\text{WO}_3 + 6\text{h}^+ \rightarrow \text{W}^{6+}(\text{sol'n}) + 3/2 \text{O}_2$, where h^+ designates hole carriers.

However, no specific data and discussion supporting the above postulates were given. He also found WO_3 thin films were more stable in some non-aqueous solvents such as propylene carbonate, acetone and γ -butyrolactone. However, the response speed of the device using an electrolyte with such a solvent was too slow to be practical.

Reichman and Bard³³ reported that both the kinetic behavior and the stability of the films in acid electrolyte depend on the amount of water and the porosity of the films. From infrared absorption spectra, they found the water content was increased when the films were cyclically colored and bleached. On the basis of these observations, they speculated that during operation, uptake of water into the films caused expansion of the lattice, making it more porous and allowing even greater water penetration. The

result was higher water content in the films after cyclic coloration and bleaching. They also measured the dissolution rate of WO_3 film in acid by monitoring the decrease in current injected during cyclic coloration and correlated it with the increase in water content of WO_3 films. They concluded that the dissolution was due to the formation of WO_3 hydrates ($\text{WO}_3 \cdot \text{H}_2\text{O}$ or $\text{WO}_3 \cdot 2\text{H}_2\text{O}$) since these hydrates are more soluble than WO_3 . Hence, the higher the water content of the film, the more WO_3 dissolved. No model of dissolution was proposed, nor was saturation of the electrolyte discussed. In addition, no data were shown demonstrating the formation of hydrates. Reichman and Bard also observed slow dissolution in glycerin/ H_2SO_4 (10:1) as did Randin; they attributed this to the lack of water pickup during cycling.

Arnoldussen³⁴ studied the dissolution of the evaporated WO_3 films in deionized (DI) water and concluded the films dissolve to form metatungstate or pseudometatungstate ions. On the basis of previous study of vapors generated by subliming WO_3 ,³⁷ he postulated that as-deposited WO_3 films are composed chiefly of trimeric clusters weakly bound to one another through water-bridge or hydrogen bonds. The dissolution of the film was therefore postulated to occur by these trimeric clusters' being dissolved as 3-, 6-, or 12-mer ionized complexes directly from the dissolving surface. He also suggested cyclic conditions were just a natural extension of the dissolution process, i.e., voltage enhanced dissolution. Degradation in non-aqueous solvents was suggested

to result from formation of negative complexes with electrolyte anions or from tungstate formation due to H_2O incorporated into the films during manufacture. However, all of Arnoldussen's data dealt with electrolyte of $pH > 4$, and the corrosion reaction proposed was based on metatungstate ions; it has been shown that WO_2^{2+} is the dominant specie for dissolution of tungstic oxides in acid solution of $pH < 1$.³⁸ The O/W ratio in Arnoldussen's microstructure model is always ≥ 3 , since the oxygen is bound either in W_3O_9 or H_2O . It will be shown in this study that the O/W ratio was always < 3 . In addition, the idea of H_2O stabilized W_3O_9 rings is unreasonable, since the disintegration of the films would be expected if H_2O was removed. However, Zeller and Beyer³⁹ reported H_2O was removed at $170^\circ C$ without detectable change in the structure of WO_3 films. In fact, no structural change was observed until crystallization at $350^\circ C$,³² which is well above the H_2O removal temperature.

As is evident from reported studies, a variety of mechanisms have been proposed for degradation of WO_3 films. All of these investigators have speculated that water is a major cause of corrosion. The mechanisms proposed are normally not supported by strong and direct evidence, and are sometimes contradictory to existing data (e.g., Arnoldussen's H_2O model discussed above). However, it is generally recognized that WO_3 thinfilms in acidic electrolyte degrade in the form of general dissolution and delamination. In cycling conditions the dissolution was increased.

In the following, new mechanisms which can fully explain these phenomena without the shortcomings of the existing postulated mechanisms will be discussed.

There are several ways to counter corrosion problems, e.g.,

1. modify the electrolyte,
2. put protective coating on the WO_3 film,
3. modify the WO_3 thin film microstructure.

In the second half of the chapter, stability data will be reported for WO_3 films evaporated with oxygen backfilling (OB). The O/W ratio will be shown to be increased by backfilling. This led to reduced degradation. However, the coloration speed and optical efficiency were decreased while the bleaching and self-erasure rates were faster for the oxygen enriched films. The mechanisms by which these EC properties were modified are also discussed.

Experimental

Film Preparation

Thin films of WO_3 were prepared by evaporation of 99.9% pure WO_3 powder (Cerac, Inc.) from a resistivity-heated, alumina-coated tungsten spiral boat (Sylvania, Inc.). The substrate was normally tin oxide coated glass (NESA glass, Pittsburgh Plate and Glass Co.) with a resistance of $100 \Omega/\square$, but soda-silicate glass slides and pure graphite substrates (Ernest Fullan, Inc.) were used occasionally. Prior to deposition, the substrates were cleaned with Alconox/water solution, rinsed in deionized water for 10 minutes, etched in

Chromerge (a registered brand name of Monostat Labs representing a mixture of chromic acid and sulfuric acid, 1:10) and degreased in boiling methanol vapors for 5 minutes. The evaporation system was evacuated to a base pressure of 2×10^{-6} Torr and WO_3 was evaporated either at a residual pressure ($P_{res.}$) of 1×10^{-5} Torr. or with a partial pressure of oxygen (P_{O_2}) between 5×10^{-5} and 1×10^{-3} Torr. Oxygen (99% pure) partial pressure was manually controlled by a needle valve. The deposition rate was typically 10 Å/sec. The thickness of the films ranged from 2,000 Å to 4,000 Å. The source to substrate distance was 30 cm. No substrate heating was used during evaporation.

Chemical Characterization

Rutherford backscattering spectroscopy (RBS) was used to determine the oxygen to tungsten ratio (O/W) of the evaporated films. Briefly, a beam (300 nA, 300-600 μ C) of monochromatic (2 MeV) alpha ($^4He^+$) particles was focused (rectangular area 2 mm x 4 mm) onto a WO_3 films on a graphite substrates. Alpha particles were scattered through 155° by W and O atoms in the films losing an energy which depends on the masses of these atoms.⁵³ Analysis of the number of backscattered alpha particles versus their energy allowed the O/W ratio to be determined.

A typical RBS spectrum is shown in Figure 2.2, which is plotted as the backscattered yield (counts per second) versus the channel

Figure 2.2. Rutherford backscattering (RBS) data for a WO_3 film on graphite substrate using alpha particle of 2.0 MeV.

number. The channel number is related to the backscattered particle energy by a conversion constant (eV/channel number). The concentration of the elements in the films appears as square-top peaks in the spectrum. The ratio of the different elements in the films can be obtained by calculating the ratio of the area under the respective peaks and correcting for variations in their scattering cross sections. Since the width of the peak corresponds to the energy lost by alpha particles which traveled through the films, the thickness can be obtained by converting the peak width to depth using calculated stopping powers.⁴⁰ The shape of the peaks also provide information about the structure of the films (uniformity, interdiffusion, etc.).

Compositional information about light constituents such as alkali and water were obtained from secondary ion mass spectroscopy (SIMS).⁵⁴ The experimental system incorporated a UTI quadrupole mass filter (UTI 100C) with a 3M prefilter (Model 610), a 3M mini-beam ion gun, and a sample manipulator (Huntington PM-600XYZTRC). In this study, the vacuum system was pumped down to 1×10^{-9} Torr and was then backfilled to 5×10^{-5} Torr with argon. A primary ions energy of 4 KeV and beam current of 100 nA was used during the analysis.

X-ray photoelectron spectroscopy (XPS)⁵⁵ was used to obtain the information on the concentration of different oxidation states of tungsten ions in WO_3 thin films. The analysis was performed with a Krato XPS system (XSAM 800) using Mg K- α X-rays (1253.6 eV). The samples were maintained at room temperature and a pressure of 5×10^{-9} Torr.

Physical Characterization

The relative density of evaporated WO_3 films was changed by oxygen backfilling. A simple method using a quartz oscillator thickness monitor (Piezo Technology Inc. Model 990) was used to measure the areal mass change. The areal mass measured by the monitor was fixed for deposition at all pressure. The physical thickness of the deposited films was then measured by a profilometer (Sloan Dektek II). An arbitrary index was obtained when the physical thickness was divided by the thickness calculated from the areal mass by assuming the theoretical density of WO_3 . This index was used to compare the relative densities of the films. Thin films of WO_3 , with and without oxygen backfilling, were studied for surface damage (before and after corrosion) with a JOEL scanning electron microscope (Model JSM-35C).

X-ray diffraction spectra were obtained from as deposited and corroded films. Nickel-filtered $Cu-K\alpha$ radiation at 40 KV and 20 mA from a Phillips Electronics Instrument Model 690 spectrometer were used. A range of $10^\circ < 2\theta < 90^\circ$ was scanned at a speed of $2^\circ/\text{min.}$, with a counting time constant of 1.0 second. A Bicron model SR-BP941 scintillation detector was used.

Films of WO_3 deposited on glass substrates could be colored to blue by touching an indium wire to the film surface through an acid electrolyte ($3.6\text{ N H}_2\text{SO}_4$). The coloration occurs by the injection of electrons provided by the corrosion reaction: $\text{In} \rightarrow \text{In}^{3+} + 3e^-$, and protons being injected into the film from the electrolyte to

maintain charge neutrality. The coloration progressed uniformly outwards from the point of contact of the In wire with a circular color front. This phenomenon prompted Crandall and Faughnan⁵⁶ to propose a simple method for determining the electron diffusion coefficient. In this method, the radius of the color front was plotted as a function of the square root of the time. The electron diffusion coefficient (D_e) was obtained from the slope which is equal to $\sqrt{4D_e}$.

Resistivity was measured immediately after deposition without breaking the vacuum. The electrodes were parallel etched stripes of SnO_2 , 0.1 cm wide with a gap of 0.5 cm. The current upon application of 10 V was measured by an electrometer.

Corrosion Measurement

In the corrosion study, the WO_3 films deposited on graphite substrates were immersed horizontally in the unstirred acid electrolyte (3.6 N H_2SO_4 in water) contained in glass dishes at room temperature. The electrolyte was not deaerated during the experiment. The samples were removed at selected time intervals and examined by RBS to measure the WO_3 thickness. The average dissolution rate was obtained by dividing the change in thickness by time.

Electrochromic Properties Measurements

Optical absorption spectra were obtained from films deposited on glass slides both before and after coloration. The equipment

consisted of a quartz halogen lamp (Oriel Model 6140), a monochromator (Oriel Model 7240) and a silicon (for 400-1000 nm) or PbS (for 1000-2000 nm) detector. The range scanned was 300 to 1500 nm with measurements being taken in transmission.

The electrochromic (EC) properties (coloration/bleaching speed, optical efficiency and open circuit memory) were characterized in the electrochromic cell shown in Figure 2.3. EC properties are defined as follows

- Coloration time (t_c) is defined as the time needed to color a film to a contrast^c of 50% absorption;
- Bleaching time (t_b) is that time required to erase the film from 50% to 25% absorption;
- Optical efficiency is defined as optical density change per unit charge injected;
- Open circuit memory is defined as the time needed to bleach the film to half of the original contrast after the power was disconnected.

In the following discussion, the C/B speed will be used which is defined as the rate of coloration or bleaching to reach defined contrast, and is inversely proportional to C/B times. Electrical contact to the SnO_2 layer was made with indium solder outside the electrolyte. The active area was 1.5 cm^2 . The cell was made of Teflon[®] spacers and stainless steel holders for the glass plates. An optical path through the cell allowed electro-optical measurements.

The electrochemical data were taken using the circuit shown in Figure 2.4. A potentiostat (Princeton Applied Research Model 173)

Figure 2.3. Schematic representation of the electrochromic cell.

Figure 2.4. Circuit diagram showing the connection between EC cell, potentiostat and measuring devices. WE: working electrode, RE: reference electrode, CE: counter electrode.

was used as the power supply. Platinum wire and a calomel electrode were used as the counter electrode and reference electrode, respectively. Monochromatic light (700 nm) was used throughout the experiment.

Results

Corrosion Studies

The durability of vapor deposited WO_3 films in acid electrolyte was limited by two mechanisms - a general uniform film dissolution and an interfacial delamination. As prepared, WO_3 films exhibited featureless smooth surfaces with some isolated pinholes detected with SEM at magnification of x500 (Figure 2.5). After storage in the acid electrolyte, WO_3 films prepared without OB begin to degrade by general film dissolution, formation of crystallite-like particles, wrinkles spreading in a rosette-like pattern (Figure 2.6), and interfacial delamination of the films from the glass substrates (Figure 2.7 (A)). The dissolution rate was very high at ~ 16 A/hr (~ 350 A/day) as shown in Figure 2.8. However, the dissolution rate in the static condition (i.e., without electrochemical cycling) may have been enhanced by the graphite substrate, as will be discussed in the following section. The static dissolution rate is expected to be lower for films on glass substrates.

The peaks in the RBS spectra of WO_3 films also exhibited a significant change after corrosion (Figure 2.9). The original W

(A)

(B)

Figure 2.5. Scanning electron micrographs of as-deposited WO_3 films on glass substrates;
 (A) $P_{\text{O}_2} = 1 \times 10^{-5}$ Torr, $\times 500$,
 (B) $P_{\text{O}_2}^{\text{res.}} = 1 \times 10^{-3}$ Torr, $\times 3,000$.

(A)

(B)

Figure 2.6. Scanning electron micrographs of corroded surface₅ (3.6 N H₂SO₄, 4 days) of WO₃ films (P_{res} = 1 × 10⁻⁵ Torr) showing the forms of interfacial_{res} delamination; (A) wrinkles, (B) rosette pattern.

(A)

(B)

Figure 2.7. Scanning electron micrographs of WO_3 films after storage in 3.6 N H_2SO_4 ;
 (A) $P \cong 1 \times 10^{-5}$ Torr, 2 days, $\times 500$,
 (B) $P_{\text{res.}} = 1 \times 10^{-3}$ Torr, 8 days, $\times 3,000$.
 O_2

Figure 2.8. Dissolution rate of WO_3 films in 3.6 N H_2SO_4 solution versus the oxygen partial pressure during deposition.

Figure 2.9. Effect of corrosion on the RBS spectra for WO_3 films deposited without oxygen backfilling;
(a) as-deposited,
(b) after 5 hr. in 3.6 N H_2SO_4 ,
(c) after 20 hr. in 3.6 N H_2SO_4 .

peak was rectangular in shape indicating a uniformly thick film. After corrosion, the peak was triangular in shape which indicates a variable film thickness consistent with micropore formation by corrosion.

Modification of WO_3 Films by Oxygen Backfilling

Chemical and physical properties

The compositional changes caused by oxygen backfilling are shown in Figure 2.10 and 2.11. From RBS data, the average O/W ratio increased from 2.7 with no oxygen backfilling ($P_{res.} = 1 \times 10^{-5}$ Torr) to 2.9 at $P_{O_2} = 1 \times 10^{-3}$ Torr. Since the films were hydrated as shown later, the oxygen detected may have included that from the incorporated water. The actual number of oxygen atoms that were directly bonded between tungsten atoms might have been even lower. SIMS data indicated that the content of water in the films increased by about a factor of two between the two extreme cases (without oxygen backfilling and $P_{O_2} = 1 \times 10^{-3}$ Torr)*. The films prepared at the two extreme conditions were examined by XPS. The spectra of the W4f core levels for these films are shown in Figure 2.12. For comparison, the core level spectra for WO_3 on W representing a W^{6+} state and the positions of the reduced W states (W^{5+} , W^{4+}) are also shown. The multiplet split W4f peaks

*For simplicity in the following discussion, ' $WO_{2.7}$ ' (without OB) and ' $WO_{2.9}$ ' ($P_{O_2} = 1 \times 10^{-3}$ Torr) are used to denote WO_3 films prepared at these two extreme oxygen partial pressure conditions.

Figure 2.10. Oxygen to tungsten atomic ratio of WO_3 films from RBS data versus the oxygen partial pressure during deposition.

Figure 2.11. Relative signal intensity for H_2O from secondary ion mass spectroscopy (SIMS) versus the oxygen partial pressure during deposition of WO_3 thin films.

Figure 2.12. XPS W(4f) core level spectra for WO_3 films prepared at two extreme conditions, i.e., ' $\text{WO}_{2.7}$ ' and ' $\text{WO}_{2.9}$ '. For comparison, the spectra for WO_3 on W representing a W^{6+} state and the position of the reduced W states (W^{4+} , W^{5+}) are also shown.

of 'WO_{2.9}' spectra are located at the same energies and exhibit similar intensity as those peaks from W⁶⁺ in the reference spectra. The spectra of 'WO_{2.9}' therefore indicate that the tungsten existed mostly as W⁶⁺ in these films. On the other hand, the spectra of 'WO_{2.7}' exhibit a filled valley between and a shoulder on the low energy side of the multiplet split W4f peaks from W⁶⁺. This indicates that the concentration of subvalent W⁴⁺ and W⁵⁺ were high in 'WO_{2.7}' films. Therefore, the oxygen backfilling increased the oxygen content in the films as indicated by RBS data, and led to a concentration increase in W⁶⁺ states which was identified by XPS data.

The relative density of WO₃ films was found to decrease as a result of OB as shown in Figure 2.13. The unmodified films exhibited a relative density of 0.8 when compared to the normalized bulk density. For films prepared at $P_{O_2} = 1 \times 10^{-3}$ Torr, the relative density decreased to 0.5 and the porosity was expected to be substantially higher.

The surface topography of WO₃ films was modified by oxygen backfilling as shown by SEM photomicrographs taken at high magnification ($\times 3,000$, see Figure 2.5(B)) for films deposited at $P_{O_2} = 5 \times 10^{-4}$ Torr. The rough surface is consistent with the higher porosity in these films.

Figure 2.13. The relative density of WO_3 films versus the partial pressure of oxygen during deposition

Stability

Interfacial delamination was not observed for films prepared at higher partial pressures of oxygen, i.e., $>5 \times 10^{-4}$ Torr. However, a slightly corroded surface which was rougher than the original surface was observed at higher magnification ($\times 3,000$, see Figure 2.7(B)). The dissolution rates for these films were negligible as shown in Figure 2.8.

The X-ray diffraction pattern for the as-deposited films with or without OB showed a very broad diffused peak typical of an amorphous structure (Figure 2.14(A)). After 18 days storage in acid electrolytes, the X-ray diffraction patterns exhibited crystalline peaks on top of the diffuse scattering from the amorphous film. These data are interpreted to indicate a partial transformation into crystalline phases of WO_3 ,⁵⁷ $\text{WO}_3 \cdot \text{H}_2\text{O}$ ⁵⁸ and $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ ⁵⁹ (Figure 2.14(B) and 2.14(C)). The only observable difference between the spectra from the two extreme OB conditions is that there is a distinct peak 3.01 Å which is associated with $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ for films without OB (Figure 2.14(B)). This peak is absent from the spectra from films deposited at $P_{\text{O}_2} = 1 \times 10^{-3}$ Torr (Figure 2.14(C)). On the other hand, there is a peak at 5.37 Å in Figure 2.14(C) (associated with $\text{WO}_3 \cdot \text{H}_2\text{O}$) which is absent in Figure 2.14(B). This seems to indicate that the $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ phase was the dominant phase in the films without backfilling while $\text{WO}_3 \cdot \text{H}_2\text{O}$ dominated the films with OB.

Figure 2.14. X-ray diffraction spectra: (A) As deposited, showing amorphous pattern, and (B), (C) from WO₃ films after 18 days in H₂SO₄ solution where the amorphous background intensity was subtracted to emphasize the crystalline peaks. The spectra are from samples which were deposited with (B) residual pressure of 1×10^{-5} Torr, (C) oxygen partial pressure of 1×10^{-5} Torr. The symbols (○, +, ☆) show the origins of specific diffraction peaks. (☆: WO₃, ○: WO₃ · H₂O, +: WO₃ · 2H₂O).

Electrical and electrochromic properties

The coloration times, t_c , for films deposited at various pressure are shown in Figure 2.15. The t_c increased from 4.2 sec. for films prepared without OB to about 5.8 sec. for films prepared at $P_{O_2} = 1 \times 10^{-3}$ Torr. The increase in the coloration times may be due to a decrease in charge injection rate and/or a decrease in optical efficiency. Figure 2.16 shows injected current versus time (j vs. t) during coloration for films prepared at the two extreme OB conditions. The films exhibited similar behavior i.e., the current was almost independent of t at short time ($t < 0.2$ sec.), and followed a $t^{-1/2}$ dependence at long time ($t > 2.0$ sec.). However, the magnitude of the current was lower for films with OB. The charge injected versus time may be calculated from Figure 2.16 and is shown in Figure 2.17. Again it demonstrates the lower charge injection at a specified time for the high oxygen backfilled pressure. In Figure 2.18 the electron diffusion coefficients (D_e) which were measured by the color front growth rate technique are plotted versus the partial pressure of oxygen. The D_e was decreased by about a factor of three when the films were prepared at $P_{O_2} = 1 \times 10^{-3}$ Torr, as compared to the films without OB. The thermal activation energy (E_{th}) for electron conduction in the uncolored films was also found to have been changed by OB as shown in Figure 2.19. In this Figure, the temperature dependence of current is plotted versus T^{-1} for films prepared at the two extreme OB conditions. From the slope of the plot E_{th}

Figure 2.15. Time needed to color WO_3 films to obtain 50% absorption versus oxygen partial pressure during deposition. ($E = -0.6 V_{SCE}$, Film thickness: 3,000 Å).

Figure 2.16. Coloration current density versus time for WO_3 films prepared at two extreme conditions; solid circles: ' $\text{WO}_{2.7}$ ' and open circles: ' $\text{WO}_{2.9}$ '.

Figure 2.17. Injected charge versus time for WO_3 films prepared at two extreme conditions; solid circles: ' $\text{WO}_{2.7}$ ' and open circles: ' $\text{WO}_{2.9}$ '.

Figure.2.18. Electron diffusion coefficient in WO_3 films versus partial pressure of oxygen during deposition.

Figure 2.19. Temperature dependence of current in WO_3 films prepared at two extreme conditions: solid circles: ' $\text{WO}_{2.7}$ ' and open circles: ' $\text{WO}_{2.9}$ '.

can be calculated, i.e.,

$$I = I_0 \exp (-E_{th}/kT) \quad (2.1)$$

where I is the current measured, k is Boltzman's constant and I_0 is the pre-exponential constant. For films without OB, E_{th} was 0.52 eV but was increased to 0.67 eV for films prepared at $P_{O_2} = 1 \times 10^{-3}$ Torr. In Figure 2.20, the optical density change (ΔOD) is plotted as a function of the injected charge (Q) for the films deposited at various oxygen pressure. The optical efficiency is defined as the change in optical density per unit charge injected, and is the slope of the plot ΔOD versus Q . The optical efficiency was decreased by OB as shown in Figure 2.21. The absorption spectra for films prepared at the two extreme OB conditions for the same thickness (2 μm) and colored by the same injected charge ($\sim 6 \text{ mC/cm}^2$) are shown in Figure 2.22. For ease of calculation, the absorption intensity and the wavelength were converted into relative absorption coefficient and photon energy, respectively. The decrease in optical efficiency by OB is again apparent in these spectra since the relative absorption coefficient (normalized to unity for ' $WO_{2.7}$ ') at the absorption peak of ' $WO_{2.9}$ ' is only 65% of that of ' $WO_{2.7}$ '. The energies of the absorption maximum, E_{op} , and the widths of the absorption band were not changed significantly by OB, being 1.47 eV vs. 1.45 eV and 1.6 vs. 1.5 for ' $WO_{2.7}$ ' and ' $WO_{2.9}$ ', respectively.

The variation of bleaching time and color retention time (open circuit memory) with oxygen backfilling are shown in Figure

Figure 2.20. Optical density change as a function of injected charge for WO_3 films deposited with: (A) residual pressure of 1×10^{-5} Torr, (B), (C), (D) oxygen partial pressure of 5×10^{-5} Torr, 5×10^{-4} Torr and 1×10^{-3} Torr, respectively.

Figure 2.21. Optical efficiency of WO_3 films versus oxygen partial pressure during deposition.

Figure 2.22. Absorption spectra for WO_3 films prepared at two extreme conditions. '---' represents ' $\text{WO}_{2.7}$ ' and '—' represents ' $\text{WO}_{2.9}$ '. The films were of same thickness (2.0 μm) and colored with same injected charge (0.6 mC/cm^2).

2.23 and 2.24, respectively. The bleaching times were found to decrease from 4.7 sec. without OB to 1.6 sec. at $P_{O_2} = 1 \times 10^{-3}$ Torr. After coloration, the power supply was disconnected and the films would self-erase at different rates depending on the back-filling pressure. The time for self-erasure to half of the original OD decreased from 1,200 sec. for films prepared without OB to 460 sec. for films prepared at $P_{O_2} = 1 \times 10^{-3}$ Torr, as shown in Figure 2.24.

Discussion

The corrosion of WO_3 thin films in H_2SO_4 electrolyte proceeds in the form of general dissolution and interfacial delamination. Previously, it was speculated that the water in electrolyte and/or WO_3 films allowed or caused the corrosion. However, the mechanism proposed could not fully explain corrosion in the acid-organic solvent systems, nor was it compatible with data showing that WO_3 thin films are oxygen-deficient and stable up to 350 °C (crystallization temperature). A new corrosion model will be proposed below.

Corrosion of WO_3 Thin Films

General dissolution

The thermodynamic equilibrium between crystalline WO_3 and water predicts that WO_3 dissolves by hydrolysis to form tungstate ion;

Figure 2.23. Time needed to bleach the WO_3 films to 50% of the original optical density versus oxygen partial pressure during deposition.
(E: +0.6 V_{SCF} Thickness: 3,000 Å)

Figure 2.24. Time for self-erasure to half of the original OD of WO_3 films versus oxygen partial pressure during deposition.

$$\log (\text{WO}_4^{2-}) = -14.05 + 2\text{pH}. \quad (2.3)$$

The solubility at 25 °C is $10^{-4.9}$ moles/liter in neutral pure water and decreases exponentially with decreasing pH. In acid solution of pH ~ 0.5 such as used in the current studies, the solubility would be decreased to $\sim 10^{-13}$ moles/liter if this reaction is still valid at such a low pH. The equilibrium potential of WO_3 in this solution is 0.4 V with respect to the standard hydrogen evolution potential (SHE).⁶⁰ According to the Pourbaix diagram for W (Figure 2.25),⁶¹ the experimental condition for storage condition (pH = 0.5, E = 0.4 V_{SHE}) is located in the WO_3 stability region. That is, WO_3 is the thermodynamically stable specie under these storage condition. In contrast, the vapor deposited WO_3 thin films dissolved comparatively fast even in the small volume of low pH solution used in the present tests. To explain this discrepancy, a thorough understanding of structure and composition of the film and of the thermodynamics of corrosion is necessary.

Previous studies and present results have shown that thermally evaporated WO_3 films are

1. amorphous - X-ray diffraction pattern of these films exhibited broad diffuse peaks typical of amorphous structure;
2. oxygen deficient - XPS data also indicated that the tungsten atoms exhibited various oxidation states of W^{4+} , W^{5+} and W^{6+} due to the substoichiometry in these films;

FIG. Potentials-pH equilibrium diagram for the system tungsten-water, at 25°C

Figure 2.25. Pourbaix Diagram for tungsten from Atlas of Electrochemical Equilibria in Aqueous Solutions, by M. Pourbaix, Pergamon Press (1966). Reproduced with permission.

3. porous - the relative density is approximately 50% to 80% of that of crystalline WO_3 ;
4. hydrated - films were reported to contain as much as 0.5 H_2O per WO_3 .³⁵

The water might have been incorporated during WO_3 evaporation since the partial pressure of water is the primary contributor to the measured total residual pressure.³⁵ Water could also originate from absorption of moisture from air after deposition since the films were porous.

From the X-ray scattering experiments, Zeller and Beyeler³⁹ obtained the radial distribution function of these films and concluded that the amorphous WO_3 films consist of a disordered network of corner sharing W-O octahedra. The substoichiometry and the existence of the W^{4+} , W^{5+} and W^{6+} oxidation states in these films suggests that tungsten atoms may exist with a configuration not only as WO_3 but also as WO_2 and W_2O_5 . Therefore, it is logical to consider the evaporated WO_3 films as a random solution of WO_2 , W_2O_5 and WO_3 . These molecules are connected with each other through corner sharing O-bonds³⁹ and forming a network-like structure (Figure 2.26). The water incorporated during evaporation or after deposition is not expected to be important in structure formation, since no observable structural change was observed at 170 °C when most water was evolved.³⁹ Water may be bonded in the open space between tungstic oxide molecules by hydrogen bond or van der Waals forces.

The corrosion of these films in acid electrolyte can be explained by examining the Pourbaix diagram for tungsten. Both

Figure 2.26. Proposed microstructure of vapor deposited WO_3 films—a random network composed of WO_2 , W_2O_5 and WO_3 units linking each other through corner-sharing oxygen bonds. Note water molecules may occupy the empty space between tungstic oxide molecules.

WO_2 and W_2O_5 are not thermodynamically stable in the storage condition ($pH = 0.5$, $E = 0.4 V_{SHE}$). They should be converted to higher oxidation states, but the conversion processes and products are both unknown. However, Nazarenko et al.³⁸ have shown that for dissolution of tungstic oxide in acid ($pH < 1$), the cationic, WO_2^{2+} , form dominates. The anion forms, e.g., $WO_2(OH)_3^-$, WO_4^{2-} only dominate at higher pH (> 2). Di Paola et al.^{36,62} studied anodic WO_3 films on tungsten and proposed that the corrosion of these WO_3 films took place by hydration of WO_3 :

where $x = 1$ or 2 .

However, the free energy of hydration for forming both the mono- and di- hydrates was shown to be positive.⁶³ The hydration reaction was observed if electrochemically driven.^{36,62} Although the mechanisms for corrosion of WO_2 and W_2O_5 are unknown, it seems reasonable to postulate similar reactions. For example, the dissolution processes may be

$pH < 1$.

The solubility of WO_2^{2+} under these conditions is unknown, but the ions as postulated precipitate as WO_3 and its hydrates when the solubility limits are reached. The total reaction can then be

written as

where $x = 0, 1, \text{ or } 2$

and would result in the crystalline phases detected by X-ray diffraction after 18 days storage in acid.

Even though XPS data (Figure 2.20) indicated the existence of high concentration of subvalence states (W^{5+} , W^{4+}) in the evaporated WO_3 films, how much WO_2 and W_2O_5 does this represent? Gerard et al.⁶⁴ calculated the concentration of each valence states (W^{4+} , W^{5+} and W^{6+}) from XPS spectra of reactively sputtered WO_3 with varied O/W ratio as shown in Figure 2.27. The concentration of W^{6+} in a ' $\text{WO}_{2.9}$ ' films was 80% and decreased to only 40% for a ' $\text{WO}_{2.5}$ ' film. It is reasonable to expect that the same relation could be found in evaporated WO_3 films. For a film prepared without OB, the O/W ratio was about 2.7. Based on the data from Gerard et al.⁶⁴ the concentration of W^{6+} is expected to be $\leq 60\%$ with the remaining 40% tungsten atoms existing as W^{5+} or W^{4+} states. As discussed, the WO_3 films can be considered to be a random network consisting of WO_2 , W_2O_5 and WO_3 molecules linking each other through corner sharing O-bonds. Then every one out of three tungsten links in the network exists with a configuration of WO_2 or W_2O_5 . Since the oxygen detected may have included that from the incorporated water, the actual number of oxygen atoms that were directly bonded between

Figure 2.27. Concentration of W^{6+} , W^{5+} , W^{4+} and W^{0+} versus corresponding chemical shifts for the sputtered WO_3 films with different O/W ratio. From Gerard et al., J. Appl. Phys. 48, 4253 (1977). Reproduced with permission.

tungsten atoms might have been lower as discussed in the last section. Therefore, the concentration of WO_2 and W_2O_5 could be even higher than proposed here. In the acidic environment, these WO_2 and W_2O_5 links are selectively attacked and the whole network solid may be broken down into a distribution of random length of WO_3 chains. These broken WO_3 chains presumably can no longer stay in the bulk but drift into solution. These WO_3 chains may be the polymer ions in the solution observed by Arnoldussen.³⁴ As a result, the dissolution rate is quite high. Once the solubility limits in solution are reached, precipitation occurs on surfaces as crystalline WO_3 or hydrates, since the free energy of hydration may be negative starting with WO_2 and W_2O_5 .

Interfacial delamination

In addition to general dissolution, flaking by delamination at the interface were also observed and may be induced by:

1. the internal stresses caused by precipitation of these crystalline phases on the original sample;
2. gas evolution, e.g., $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$, accompanying the dissolution and re-precipitation processes;
3. surface contamination and defects which weaken the adhesion strength of the film to the substrate.

The first two mechanisms can be viewed as side effects of the general dissolution mechanism proposed. It is not uncommon to find some pinholes ($\sim 10 \mu\text{m}$) in the evaporated WO_3 films. In the corrosion processes, the dissolved ion concentration in these pinholes will

reach saturation limit much earlier than over the flat surface and lead to the rapid precipitation of crystallites of hydrated tungstic oxide. These crystallites serve as nucleation sites for further precipitation of crystalline phases, and eventually grow to a size larger than the volume of the pinhole. The induced stresses from the crystallites may be transmitted radially outward in the films and along the film-substrate interfaces since the pinholes go completely through the films. The rosette-shaped wrinkles in Figure 2.6(B) are typical result of this effect. The delaminated films can be easily broken into fragments by physical disturbance of the electrolyte (Figure 2.7(A)). Small bubbles were observed on the samples during corrosion and are assumed to be hydrogen gas evolved during the corrosion process. The gas evolution may also enhance the interfacial delamination.

Interfacial delamination was rare for films deposited on graphite substrates (semi-polished). The rough surfaces on these substrates may provide a mechanical interlocking through pore and valley. Gas bubbles were most often observed on films deposited on graphite substrates, since the rims of graphite substrates provided sites for cathodic reactions. However, gas evolution is not thought to be a major cause for film delamination. This is particularly true for films deposited on NESA glass substrates because little gas evolution was observed.

Corrosion during cyclic coloration and bleaching

The reported increase in the dissolution rate for cyclic coloration and bleaching condition⁶⁵ can be explained by mixed potential theory^{60,66} as shown in Figure 2.28. Since the WO_3 specie in the films should remain stable in this polarization range according to the Pourbaix diagram, only WO_2 and W_2O_5 species are involved in the dissolution process. Figure 2.28 schematically illustrates the current/voltage relations for the WO_2 - H_2SO_4 system, but the W_2O_5 - H_2SO_4 system is expected to be similar. The two reactions occurring are assumed to be WO_2 dissolution ($WO_2 \rightarrow WO_2^{2+} + 2e^-$) and hydrogen evolution ($2H^+ + 2e^- \rightarrow H_2$). The static corrosion potential and current for this particular system is represented by the intersection between the polarization curves for WO_2 dissolution and hydrogen evolution. This represents the storage conditions discussed above. During the bleaching pulse, the system is polarized anodically and the anodic current density (I_{BW} for WO_2 dissolution) is much higher than the cathodic current density (I_{BH} for hydrogen evolution). Thus more rapid dissolution of WO_2 (and W_2O_5) is expected during bleaching. However, the WO_2 dissolution current, I_{CW} , is much lower than hydrogen evolution current, I_{CH} , during the coloration pulse. As a result, WO_2 (W_2O_5) dissolution is less but gas may be evolved during coloration.

Figure 2.28. Combined activation polarization curves for WO_2 dissolution and hydrogen evolution show the effect of anodic and cathodic polarization on the dissolution of WO_2 . E_{corr} is the equilibrium potential (storage condition). η_B , I_{BW} and I_{BH} are the overpotential, dissolution current density of WO_2 , and reduction current of H_2 during bleaching pulse, respectively. While η_C , I_{CW} and I_{CH} are those for coloration pulse.

In addition, Faughnan and Crandall³⁵ observed an increase in dissolution rate when device were cycled at higher contrast. Higher contrast would require either operating at increased C/B voltage at the same frequency,³⁵ or an increased C/B time at the same voltage.³⁵ As discussed above, an increase in the dissolution rate can be expected when the bleaching voltage is increased. On the other hand, Randin³² reported shorter lifetimes when the devices were cycled at low frequencies (< 0.5 Hz). This low frequency effect is consistent with the contrast effect reported by Faughnan and Crandall if the higher contrast was obtained by prolonged C/B time at the same voltage. The causes of increased dissolution rates at low frequency can be attributed to a number of possibilites. For example, at higher frequency, the short bleaching pulse may allow a sharp concentration gradient of WO_2^{2+} to occur near the WO_3 film surface (due to limited diffusion). This limits subsequent dissolution of WO_2^{2+} and hence the kinetics of dissolution would be impeded.

Non-aqueous electrolyte

Attempts to use non-aqueous electrolytes have been reported by Randin³² and Reichman et al.³³ The results are summarized in Table 2.1. The WO_3 thin films dissolved not only in sulfuric acid, but also in formic acid and acetic acid, but remained stable in organic solvents such as acetone, γ -butyrolactone, and propylene carbonate. The WO_3 films dissolved when these organic solvents were combined with sulfuric acid, e.g., methanol plus H_2SO_4 or acetonitrile plus

Table 2.1

Stability of vapor deposited WO_3 films in various non-aqueous solvents or electrolytes.

Electrolyte (solvent)	Dissolution	Reference
Formic acid	Yes	Randin ³²
Acetic acid	Yes	
Acetone	No	
γ -butyrolactone	No	
Propylene carbonate	No	
H_2SO_4 /glycerin (1:10)	Yes	Randin, ³² Reichman and Bard ³³
H_2SO_4 /methanol*	Yes	Reichman and Bard ³³
H_2SO_4 /acetonitrile*	Yes	

* concentration unknown

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H_2SO_4 . The dissolution rates were not specified for these mixtures. Randin³² reported the dissolution rate in H_2SO_4 /glycerin (1:10) was an order of magnitude lower. These results indicate that in addition to the substoichiometry of the films, the pH of the electrolyte is also the culprit in corrosion. The water in the electrolyte can not be the main factor as most investigators claimed,³²⁻³⁵ since a) the corrosion does not occur until the organic solvents were combined with acid, b) the dissolution rate in H_2SO_4 /glycerin was decreased by only an order of magnitude while the water content in the electrolyte was reduced by many (~ 20) orders of magnitude lower. The water incorporated during evaporation is also unlikely to be the cause of corrosion in non-aqueous electrolyte as Arnoldussen claimed,³⁴ otherwise the corrosion should have been observed in acetone and propylene carbonate. The lowered dissolution rate of WO_3 film in H_2SO_4 /glycerin could be caused by lowered mobility of WO_2^{2+} ions because of the high viscosity³³ and/or by decreased proton concentration in the electrolyte because of the decreased dissociation constant.⁶⁷ However, no conclusion can be made as to which cause is dominant.

Modification of Stability of WO_3 Films by Oxygen Backfilling

Since the substoichiometry in the WO_3 films is responsible for the corrosion, an improved stability is expected at higher stoichiometry. By backfilling during WO_3 evaporation, the oxygen content of WO_3 films was increased. The XPS data also indicated the concentration of W^{6+} states in these films were increased relative to W^{5+} and W^{4+} . Since there are less dissolution-prone species available, the dissolution rate of oxygen enriched films in acid electrolyte should decrease. As shown in Figure 2.28, the dissolution did decrease and became negligible when the O/W ratio reached 2.9. Interfacial delamination was not observed as a result of the reduced corrosion rates (Figure 2.7b). However, the dissolution and precipitation of small amount of WO_2 and W_2O_5 still rearranged the surface portion of the films to give crystalline peaks of WO_3 and its hydrates in X-ray diffraction pattern from OB samples (Figure 2.14c). The bulk of the films remained intact when OB was used. As indicated by Figure 2.7b, only at higher magnification can the corrosion effect (the slightly roughened surface) be observed. The X-ray diffraction data also indicated that $\text{WO}_3 \cdot \text{H}_2\text{O}$ was the dominant phase in oxygen enriched films while $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ was in the films without OB. This difference may be another reason for lower dissolution in oxygen enriched films since $\text{WO}_3 \cdot \text{H}_2\text{O}$ dissolves less readily than $\text{WO}_3 \cdot 2\text{H}_2\text{O}$.⁶⁸ The cause for inducing different dominant phase by backfilling is unknown.

Modification of EC properties of WO₃ Films by Oxygen Backfilling

The performance of electrochromic display devices is generally determined by four electrochromic properties: 1. coloration speed 2. optical efficiency, 3. bleaching speed, and 4. coloration retention time (self-erasure rate). The effect of oxygen backfilling on the EC display performance will be discussed in this order.

Coloration speed

The rate controlling mechanism for coloration was proposed^{30 35} to be current limited by the WO₃ resistance at short time. The duration of WO₃ resistance control increases as the thickness of WO₃ was increased. In addition, the current was affected by the Schottky and Helmholtz double layer (HDL) barriers. At long time (>1 sec.) for thickness of <0.4 μm, the current control was dominated by the HDL. As shown in Figure 2.16, the coloration current for films prepared with or without oxygen backfilling showed a time independent behavior at the onset of coloration, and approached a $t^{-1/2}$ dependence at $t > 3$ sec. This $t^{-1/2}$ dependence is characteristic of HDL control.³⁰ In general, the charge injection process is not affected by OB. However, the magnitude of injected current was lowered for oxygen-enriched films. This can be explained by considering the Butler-Volmer equation:⁶⁰

$$J_p = J_0 \left[\exp \frac{(1-\beta) e \eta}{kT} - \exp \frac{-\beta e \eta}{kT} \right] \quad (2.10)$$

where J_p is the proton current density across the double layer, J_0 is the exchange current density, β is the barrier symmetry factor, k is Boltzman's constant, T is temperature, e is electronic charge and η is the overpotential (the potential drop across the HDL when $J_p \neq 0$). Since β is a property of the ionic solution,⁶⁰ it is not expected to be affected by changes in the film properties. The overpotential, η , can be expressed as

$$\eta = V_a - \frac{\Delta u(x)}{NF} - J_p R_f \quad (2.11)$$

where V_a is the applied potential, $\frac{\Delta u(x)}{NF}$ is the reduction in chemical potential due to the proton concentration (x) in the WO_3 , N is Avogadro's number, F is Faraday's constant and R_f is the film resistivity. As shown in Figure 2.18, the electron diffusion coefficient in WO_3 was found to be decreased by OB. The conductivity (resistivity) measured at room temperature was also found to be decreased (increased) by a factor of three (Figure 2.19). Since R_f is higher at the onset of the coloration ($x = 0$), η would be smaller for oxygen enriched films at the same applied bias V_a . The current injected would be lower as indicated by equation 2.13.

Resistance control was dominant at $t < 1-2$ sec. However, the effect on the magnitude of current injected persisted into the HDL control region, i.e., the decrease in current by OB was almost invariant with time even in the HDL controlling region (Figure 2.16). However, the optical efficiency, i.e., the change in optical density

per unit charge injected, was also decreased by OB as shown in Figure 2.21. This effect together with the lower current injection led to a slower coloration speed as shown in Figure 2.15. The mechanism of degraded optical efficiency is discussed in the following section.

Optical efficiency

An understanding of the electronic structure of WO_3 thin films is necessary before discussing the change in optical efficiency by oxygen backfilling. In the following, the mechanisms proposed for optical absorption and DC conduction are reviewed and compared with the present results.

Electronic structure for WO_3 thin films. Many models have been proposed to explain the optical transition in electrochromic WO_3 films. Optical absorption in these films is known to arise from a transition of an electron from one trapping site to an adjacent site. A trapping site is a position in the lattice where localization of an electron will result in a lowering of the total free energy of the system. The trapping sites are probably W sites as identified by electron spin resonance studies.⁶⁹ Faughnan and Crandall⁹ proposed an inter-valency charge transition model which can be expressed as shown below:

where A and B represent two neighboring sites of tungsten atom, and $h\nu$ is the photon energy. This model explains qualitatively the features of the optical absorption including the magnitude of oscillator

strength. However, the XPS data⁷⁰ have shown the presence of large concentration of W^{4+} and W^{5+} ($\sim 40\%$) even in the transparent WO_3 thin films and hence appear to disagree with this model.

An alternative model based on small-polaron theory has been proposed by Shirmer et al.¹⁰⁻¹² In a systematic study of the optical properties of amorphous and crystalline WO_3 films, they found a shift in the maximum absorption peak from ~ 900 nm to $\sim 1,200$ nm upon crystallization. This shift, plus the asymmetry of the high-energy side of the absorption maximum (Figure 2.22) in amorphous films has led Shirmer et al. to postulate a self-trapping term (i.e., a polaron formation) which would lower the energy of the site with the trapped electron relative to other W^{6+} sites. In a disordered system, the W^{6+} sites do not all have equivalent energy because of the existence of a range of W-O bond lengths and angles.⁷¹ The injected electrons will be trapped primarily at those sites of lower energy. Hence, optical transitions will occur with a range of energies. This explains the asymmetry in the optical-absorption peak. The shift to lower energy for crystalline films occurs because the disorder term disappear for crystalline films.

The optically excited polaron hopping between two neighboring sites can be described by a diagram showing the electron potential energy as a function of a single, one-dimensional lattice configuration coordinate (Figure 2.29). It has long been realized that

Figure 2.29. Configurational Coordinate model for the polaron hopping absorption in the WO_3 films.

optically induced transitions between two sites can be considered as Frank-Condon transitions,⁷² indicated by the vertical arrow in Figure 2.29. These processes take energy E_{op} which can be measured from the peak energy of the absorption band. The change of the lattice distortion accompanied by the electron transfer from site A to site B is represented by $\Delta q = q_A - q_B$. The energy E_{th} is the thermal energy of the small polaron hopping from site A to site B, which can be obtained from the measurement of conductivity change over a temperature variation as discussed below.

The DC conductivity of WO_3 amorphous films have been reported by several authors. Faughnan et al.⁷³ reported a $\log I - T^{-1/4}$ dependence at low coloration ($x < 0.3$ for H_xWO_3) between 10.2 and 300 °K, and concluded that the electron transport in this condition was best described by a variable-range-hopping model (electron hopping between trapping sites). Benci et al.^{74,75} in a similar study reported a $\log I - T^{-1/7}$ dependence for transparent film between 4.2 and 300 °K, although a $\log I - T^{-1}$ dependence could described the data at temperature near 300 °K. They concluded the conduction in transparent WO_3 films at $T < 300$ °K is in agreement with the hopping between two localized states (a donor state and a trap state). Gritsenko et al.⁷⁶ studied the DC conductivity of WO_3 films at a higher temperature range, 353 - 773 °K, and reported a $\log I - T^{-1}$ dependence and concluded that the overlapping of the potential of deep centers was responsible for the conductivity.

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The mechanism of electron transport between these centers was thermally assisted tunneling and the conductivity increased exponentially with temperature. Although the detailed nature of these "donor states"^{74,75} and "deep centers"⁷⁶ was not explained, they are expected to be associated with the active polaron states where a localized electron is allowed to contribute to conduction. The exact nature of active polarons will be discussed in a later section.

It seems, however, that the DC conduction mechanisms of electrons in WO_3 films vary with the temperature range investigated. The mechanism is associated with polaron hopping at low temperature ($T < 300$ °K), and with polaron tunneling at high temperature ($353 < T < 773$ °K). Hence, the thermal activation energy E_{th} obtained at high temperature will not have the same physical significance as that from low temperature measurement. One needs to be cautious in interpreting data to identify the controlling mechanism.

Effect of oxygen backfilling on EC characteristics and electronic structure of WO_3 films. As discussed, the optical efficiency (or the optical absorption per unit injected charge), the DC conductivity and the electron diffusion coefficient of WO_3 films were decreased by oxygen enrichment, while the thermal activation energy (between 300 - 450 °K) was increased. The decreased optical absorption for more oxygen enrichment was also reported by

Arnoldussen.³⁴ He observed that oxygen ion implantation of evaporated WO_3 films resulted in films which could no longer be colored. This is the extreme case. He attributed this phenomenon to the creation of electron traps by structural change as a result of oxygen implantation. However, no detailed discussion on the nature of electron traps or the mechanisms causing decreased optical absorption was given.

In the discussion of optical properties of the trapped or localized center as in WO_3 thin film, the Smakula's⁷⁷ equation is applicable

$$N'f = 8.7 \times 10^6 \frac{n}{(n^2 + 2)^2} (K_{\max} L) W_{1/2} \quad (2.13)$$

where N' is the number of absorption centers per cm^2 , n is the index of refraction of the film, $K_{\max}$ is the absorption coefficient at the band peak in cm^{-1} , L is the thickness of the film and $W_{1/2}$ is the full width at half maximum (FWHM) in eV. The index of refraction, n , does not vary significantly between films deposited from WO_2 or WO_3 powders (which were assumed to result in a different O/W ⁷⁸ ratio) or between amorphous films and single crystal WO_3 .⁹ The absorption spectra in Figure 2.22 are from film of the same thickness and injected charge. As reported earlier, the width of the absorption bands ($W_{1/2}$) are nearly the same (1.6 eV for films prepared without OB, ' $WO_{2.7}$ '; 1.5 eV for films prepared at $P_{O_2} = 1 \times 10^{-3}$ Torr, ' $WO_{2.9}$ '). Thus, equation 2.12 can be written as:

$$K_{\max} = \text{Constant } N' f \quad (2.14)$$

The analysis of degradation in optical efficiency therefore, can be initiated by either of the following two hypotheses:

1. The charge in $K_{\max}$ was caused by the change in f , while N' remained constant at constant charge injection (i.e., every electron injected resulted in the formation of a polaron). The decrease in the absorption coefficient was therefore caused by a decrease in the oscillator strength of the absorption center.
2. The change in $K_{\max}$ was caused by the change in N' , while f remained constant (i.e., the oscillator strength of absorption center remained unchanged by the backfilling). The decrease in absorption coefficient was caused by a decrease in the concentration of absorption centers, possibly by creation of electron traps by OB.

The first hypothesis was adopted by Yoshimura et al.⁷⁸ to explain the increase in optical efficiency of tungstic oxide films deposited from crystalline WO_2 powder. They observed the absorption coefficient $K_{\max}$ was increased for films deposited from WO_2 powder as compared with those from WO_3 powder (for the same film thickness, injected charge and nearly equal FWHM's of the absorption peak). By assuming every injected electron resulted in an absorption center (polaron) and the use of equation 2.13, they concluded that the oscillator strength, f , of films deposited from WO_2 powder was higher than that of films deposited from WO_3 powder. They also concluded that the increased oscillator strength was caused by an increase in the degree of extension of electron wave function for films from WO_2 powder. Using a configurational coordinate model, they suggested the change of lattice distortion Δq was decreased as a result of an increase in electron wave function extension and

predicted a decrease in both E_{op} and E_{th} for films deposited from WO_2 powder versus those from WO_3 powder. The predictions were consistent with experimental observations. Therefore, they concluded that the decrease in optical efficiency for films deposited from WO_3 powders was caused by a decrease in oscillator strength of the absorption centers. The decrease in f was caused by a change in the lattice configuration. Although they did not measure the O/W ratio in these films, they speculated that the change in lattice condition was introduced by the deficiency of oxygen in films deposited from WO_2 powder.

At first thought it would seem that the result in the present study, i.e., the decrease in optical efficiency in ' $WO_{2.9}$ ' films can be explained by a decrease in oscillator strength, ' f ', using the model of Yoshimura et al. The decrease in f was in turn caused by a decrease in the degree of electron wave function extension caused by oxygen enrichment. However, an increase in E_{op} was not observed. The increase in E_{op} might not have been measurable due to a number of factors that affect such measurements. For example, E_{op} was reported to increase in energy as the optical density was increased (as much as 0.15 eV).⁹ However, the optical density at constant charge injection decreased for ' $WO_{2.9}$ ' versus ' $WO_{2.7}$ '. Since data were taken at constant charge injection, the configurational coordinate model predicts a higher E_{op} for ' $WO_{2.9}$ ' films, but the lower optical

density may have resulted in the wavelength of absorption peaks being shifted lower and fortuitously coinciding with that of 'WO_{2.7}'.

On the other hand, the derivation of the model by Yoshimura et al. was based on a number of assumptions. One assumption was that the concentration of injected electrons was equal to that of absorption center. As will be shown later, there are a number of tungsten sites where electrons may become highly localized and are not able to cause optical absorption or contribute to electronic conduction. Therefore, the concentration of the electrons which can participate in optical absorption is expected to be lower than that measured by current integration.

A second assumption was that the DC conduction mechanism was assumed to be associated with polaron hopping even for the temperature range 300 - 500 K, where the measurements were performed. As discussed, the DC conduction mechanisms of electrons in WO₃ films varied with the temperature range investigated. The electronic conduction in the studies of Yoshimura et al. was expected to be controlled by thermally assisted tunneling as opposed to the hopping they assumed. In addition, the polaron hopping mechanism predicts that $E_{th} = 1/4 E_{op}^{10}$ while their measured relationship was $E_{op} \sim 2 E_{th}$ (i.e., E_{th} versus E_{op} were 0.75 eV and 0.55 eV versus 1.4 eV and 1.2 eV for films deposited from WO₃ and WO₂ powders, respectively). Therefore, the E_{th} Yoshimura et al. measured does not have the same

physical significance as the E_{th} in the model they proposed (i.e., the polaron hopping model). The prediction by their model of an increase in E_{op} which was not observed in this study further indicating that the model may be invalid and that a different approach is necessary.

The decrease in the absorption coefficient K_{max} of ' $WO_{2.9}$ ' films (for the same charge injection), therefore, could have been caused by a decrease in the concentration of optical absorption centers instead of a decrease in oscillator strength. However, the decrease in the concentration of absorption centers must be associated with an increase in the concentration of inactive electron traps as a result of OB.

The existence of inactive trapping sites have been indicated by a number of authors. Gritsenko et al.⁷⁶ reported that the calculated electrically active "deep center" concentration was two orders of magnitude lower than that of injected charge in WO_3 . They speculated that not all injected charge formed "deep center". However, no explanation for such behavior was given. In addition, most plots of optical density versus injected charge (e.g., Figure 2.20 and reported data³⁵) indicated that there is a threshold charge ($\sim 2 \text{ mC/cm}^2$) needed before coloration can be observed. The threshold charge strongly suggests the presence of inactive trapping sites. Thus, the decreased absorption center density could be explained by an active-inactive polaron site model. The electrons that are trapped at inactive sites will become highly localized, and the possibility for such electrons to re-escape and

contribute to absorption or electron conduction is very small compared to active polaron hopping. The energies of such inactive sites are expected to be lower than those of active sites. Electrons will preferentially occupy the lower energy states.

The origin of such inactive centers can be correlated with the increase in water concentration or the decrease in W^{4+} and W^{5+} by oxygen backfilling. Deneuville et al.⁶ have proposed that cation sites are important to coloration and that there are two types of sites in WO_3 films which protons can occupy. One type is optically inactive, i.e., the proton does not contribute to coloration. Protons incorporated during evaporation occupy these sites and the as-deposited films are transparent. The other site is optically active; coloration may occur when the protons in the optically inactive sites are redistributed into active sites by changes in the chemical potential of H within WO_3 . This in turn may be caused by changes in the chemical potential of H in the hydrated dielectric electrolyte as found for $WO_3/MgF_2/Au$ devices,⁷⁹ or from the absorption of photons as in ultra-violet irradiation.⁸⁰ The essentially invariant change in the H/W ratio in the films before and after coloration (reported by Deneuville et al. to be a 3% increase) was used to support this postulate of two sites. However, this model can not be used verbatim to explain electrochromism since electrically-induced coloration is accompanied with a large quantity of charge passed through the cell and an opposite amount of charge passed in bleaching. This charge is tens of mC/cm^2 for deep coloration, whereas in the

redistribution model, the only charge transported could be that to charge the double-layer capacitance, i.e., $\sim 20 \text{ mC/cm}^2$.⁶⁵ Should the charge be going into some other electrochemical side reaction, it is extremely unlikely that such a reaction would be completely reversible while having such a large capacity.

The idea of two types of cation sites is still acceptable, and supported by the observed aging effect in WO_3/Li^+ device reported by Knowles.¹⁴ The aging consisted of a gradual decrease in optical contrast obtained during a fixed time potentiostatic coloration pulse. It was reported⁶⁵ that some Li was present but did not make a contribution to coloration in the bleached state. This residual Li content increased with both the number of C/B cycles and the depth of coloration, and was dependent on the degree of hydration of the WO_3 films. The dependence of residual Li content on the degree of hydration of the films was postulated to result from the evaporated WO_3 film behaving as an ion-exchange material. The H^+ ion of an OH^- group within the film was postulated to exchange in a colored film for an Li^+ ion from either the electrolyte or from solid solution within the WO_3 . In the latter case, a film colored only by Li^+ insertion would then be bleached by extraction of the same total amount of charge comprised of both Li^+ and H^+ leaving a residual concentration of Li^+ . This would limit the rate of further injection and result in the observed aging effect. Knowles¹⁴ reported that a solution to this problem was ultra-violet illumination

of WO_3 films held in as-bleached state. As a result of UV illumination, the aged cell could be restored to close to its initial performance.

Therefore, it seems that the idea of active-inactive cation site can be related to the active-inactive polaron site model proposed here. The inactive cation incorporated during deposition might have introduced an extra lattice distortion on the local arrangement of W-O entities. The extra lattice distortion might cause an increase in the self-trapping energy for the trapped electron by Coulombic interaction.^{71,81} The electron trapped at such an inactive site would require much higher energy to escape and the possibility for such electron to contribute to conduction and optical absorption would be low. Since the water concentration was increased by OB, there were more inactive protons incorporated and hence an increase in inactive electron trapping sites.

On the other hand, the electrons that were localized around W sites (W^{4+} , W^{5+} states) in an as-deposited transparent film might cause a decrease in the self-trapping energy for the electrons trapped at neighboring W^{6+} sites (e.g., by Coulombic interactions). Therefore, the electrons localized at these neighboring sites might have a higher tendency to escape and behave as active polaron. For the W^{6+} sites that were not adjacent to a W^{4+} or W^{5+} , the electrons that were localized might self-trap in a deeper well and act as the inactive polaron. Therefore, when the concentration of W^{4+} and W^{5+} was decreased by OB, there were less active polarons formed upon

electron injection. As a result, the conductivity of the oxygen enriched films was lowered. The increased thermal activation energy in oxygen-enriched films might be caused by an increase in lattice distortion as shown in configurational coordinate model. The lattice distortion was increased by the decrease in active polaron density, since the average distance between polarons was increased and hence an increase in the lattice distortion would be required for polaron motion between the sites.

In conclusion, the decrease in optical efficiency in oxygen enriched films is best described as the result of an increase in the active trap density by OB. However, the oscillator strength of absorption center might have been decreased by oxygen enrichment; present data are not sufficient to preclude a decrease in oscillator strength but do show that the decreased optical efficiency is not a result of changing only the oscillator strength. While reasons for optical inactivity of selected sites are uncertain, it may be associated with the lower energy of the site and/or increased lattice distortion in the configurational coordinate model. Increased distortion in this model could result from the presence of W^{4+} , W^{5+} and protons:

Bleaching speed

The bleaching has been reported to be limited by proton diffusion in a space-charged region.³⁵ The current as a function of time is described by

$$I(t) = (p^3 k \epsilon_0 \mu_p)^{1/4} V_a^{1/2} (4t)^{-3/4} \quad (2.15)$$

where p is the volume charge density of protons (equal to proton charge per unit area multiplied by thickness of the film), k is the relative dielectric constant of WO_3 ($\epsilon_0 = 8.85 \times 10^{-12}$ Farads/m), μ_p is the proton mobility and V_a is the applied voltage. The time for complete erasure is

$$t_f = pL^4 / 4k\epsilon_0\mu_p V_a^2 \quad (2.16)$$

where L is the thickness of the film. If the thickness of the films, the applied voltage and the injected charge density are all kept constant, t_f is inversely proportional to the proton mobility, μ_p . There are two major factors which affect the diffusion of protons in the WO_3 thin films:

1. amorphous structure - crystallization of the films is known to decrease the proton diffusion coefficient by an order of magnitude;^{35,65}
2. water content - higher water₃₃ content in the films resulted in faster proton diffusion.

The microstructure of oxygen-enriched WO_3 films remained amorphous, but the water content was higher in these films as shown in Figure 2.11. Thus, proton mobility is expected to be higher. In addition,

the porosity in the oxygen enriched films was significantly increased (Figure 2.13). The increased surface area and decreased diffusion length caused by porosity will also facilitate the bleaching process. As shown in Figure 2.23, the bleaching time was reduced by a factor of three for the films prepared at $P_{O_2} = 1 \times 10^{-3}$ Torr as compared to the films without backfilling.

Self-erasure

The effect of increased proton mobility and reduced diffusion length is also reflected in the self-erasure rate of OB films. Hitchman⁸² has proposed that self-erasure is caused by the oxidation of the so-called 'hydrogen tungsten bronze' HWO_3 (which can also be viewed as a solid solution of protons in WO_3) back to WO_3 according to the reaction:

This is, however, a general description when the process is considered from a thermodynamically point of view, e.g., it could be written as

where the H^+ and the e^- are both removed from WO_3 films. In reality, the injected protons remained ionized and the colored WO_3 films contained a large concentration of proton.³⁵ A chemical potential is developed by the proton in the films resulting in a

back emf of 0.7 V for an OD of 1.0,⁸³ and this is the driving force for the self-erasure process. Therefore, similar to bleaching, self-erasure is controlled by concentration-dependent proton diffusion in WO_3 films. Since the proton mobility was increased and the diffusion path was reduced in the oxygen enriched films, the coloration retention time was decreased by approximately a factor of three (Figure 2.24). The magnitude of the reduction was the same for bleaching and self-erasure. This again indicates that proton transport was the controlling mechanism in both processes and was modified by the oxygen backfilling.

Summary

1. Vapor deposited WO_3 films have been confirmed to be amorphous, oxygen deficient ($\text{O/W} = 2.76$), and porous ($\sim 80\%$ of bulk density).
2. X-ray photoelectron spectroscopy data have confirmed that the tungsten atoms in the as-deposited films existed not only as W^{6+} , but also as W^{4+} and W^{5+} . The total concentration of subvalence states can be $\sim 40\%$ or higher.
3. The tungsten atoms in the as-deposited films are postulated to be present as WO_3 , W_2O_5 and WO_2 according to their valence states. The films structure can be visualized as a random network composed of WO_3 and lower valent oxide molecules linking with each other through corner sharing oxygen bond.
4. The Pourbaix diagram for W indicates that WO_3 is the thermodynamically stable specie for WO_3 films stored in the acid

electrolyte ($\text{pH} = 0.5$, $E = 0.4 \text{ V}_{\text{SHE}}$), while WO_2 and W_2O_5 are not. The conversion of WO_2 and W_2O_5 into WO_3 were observed as dissolution of WO_2 and W_2O_5 in acid to form crystalline WO_3 and its hydrates (i.e., $\text{WO}_3 \cdot \text{H}_2\text{O}$ and $\text{WO}_3 \cdot 2\text{H}_2\text{O}$). The reactions are uncertain, but appear to involve the formation of WO_2^{2+} ions in solution and saturation of these solution.

5. The dissolution of as seposited films was rapid ($\sim 16 \text{ A/hr.}$) due to the presence of these unstable species. In addition to the general dissolution, interfacial delamination between the film and substrate was observed. The precipitation of crystalline WO_3 and hydrates on the original film, particularly in the pinholes is postulated to cause delamination by introducing internal stresses which exceed interfacial adhesion strength between film and substrate. The hydrogen evolution accompanying the corrosion processes might also contribute to the delamination.
6. Corrosion was increased when films were cycled between colored and bleached states because the dissolution rates of WO_2 and W_2O_5 were greatly increased by anodic polarization during bleaching. The corrosion was still observed when the H_2O in the acid electrolyte was replaced by glycerin indicating pH rather than H_2O content of the electrolyte defined whether corrosion would occur.
7. The oxygen content in WO_3 films was increased by oxygen back-filling. The concentration of subvalence states (W^{4+} , W^{5+})

decreased with respect to W^{6+} states. The stability of the films in acid was improved because of decreased concentrations of dissolution-prone species in the films. The dissolution and delamination was negligible for films prepared at $P_{O_2} = 1 \times 10^{-3}$ Torr, ($O/W = 2.9$).

8. The coloration speed was slower for oxygen enriched films because of lower current injection and reduced optical efficiency. The current injection was found to be controlled by the same mechanisms as for films without backfilling (i.e., WO_3 resistivity and Helmholtz double layer). However, the magnitude of the current passed was lower because the effective potential across the HDL was decreased by the increased film resistivity from backfilling. The increased resistivity and decreased optical efficiency in the oxygen enriched films was explained by postulating an increased density of inactive electron trapping sites. This increased density of inactive trapping sites limited the formation of active polaron for optical absorption and DC conductivity. However, the possibility that a decreased oscillator strength resulted in a degraded optical efficiency could not be ruled out.
9. The porosity of the films was increased by deposition at high background pressure. Due to increased effective surface area, the films absorbed higher amounts of water after deposition as shown by secondary ion mass spectrometry. The bleaching speed

and self-erasure rates were increased since proton mobility was increased and the diffusion path was shortened by this porosity effect.

CHAPTER III DEVICE FABRICATION

Introduction

In Chapter II, the corrosion of EC display system based on $\text{WO}_3\text{-H}_2\text{SO}_4/\text{H}_2\text{O}$ was investigated. A solution to corrosion, viz., oxygen backfilling, was studied and shown to increase the device lifetime. However, the improvement was accompanied with degradation of EC properties.

In this chapter, modification of the electrolyte to increase the device lifetime is considered. Two types of ECD systems were investigated and fabricated. The first type involved the use of a liquid electrolyte consisting of LiClO_4 dissolved in propylene carbonate (Li/PC). Since the devices using this electrolyte were reported to exhibit slow switching speeds,¹⁵⁻¹⁷ two approaches were adopted to increase the speed, viz., nitrogen-backfilling and MgF_2 overlayer. The switching speed was found to be increased by depositing the WO_3 films at high partial pressure of nitrogen and by depositing a thick, dense MgF_2 overlayer. The second device configuration involved the use of a hydrated solid dielectric layer, i.e., a MgF_2 film deposited with air-backfilling. The results indicated that air backfilling during MgF_2 film deposition was effective in achieving fast switching, while air backfilling during deposition of WO_3

films limited the operational area of the device and may not be desirable. The mechanisms will be proposed to explain these results.

Experimental

Preparation

WO₃ films were prepared by thermal evaporation of pure WO₃ polycrystalline powder (Cerac, Inc., 99.9%) from a resistively heated source onto indium-tin-oxide (ITO) coated glass. The source used was an alumina coated tungsten basket (Sylvania CS-1010). The surface resistance of the ITO coated glasses ranged from 15 Ω / to 100 Ω / . However, during the experiment, the resistance of the ITO within the group of the samples to be analyzed was kept constant. The deposition rate was varied between 3 A/s and 30 A/s using a thickness monitor (Sloan DDC1000) and manually adjusting the power to the evaporator. Before evaporation, the chamber was evacuated to a base pressure of 6×10^{-6} Torr. The evaporation was accomplished either with a partial pressure of air or nitrogen controlled by a gas flow controller (Vacuum General) or directly without gas back-filling. Thin films of MgF₂ were prepared by thermal evaporation MgF₂ powder from Ta boat onto WO₃ coated ITO glass. Deposition rate was kept between 5-10 A/s. The pressure during the deposition was varied between 4×10^{-6} and 5×10^{-4} Torr of air or nitrogen. Thin gold films were prepared by DC sputter deposition from a small coating

system for SEM sample preparation, or by vapor deposition from an electron beam deposition system. The substrates were cleaned by rinsing with soapy water (Alconox with water) for 15 minutes followed by hand scrubbing with cotton wool. The substrates were then rinsed in deionized water for approximately 10 minutes, isopropyl alcohol (IPA) for one minute, and vapor degreased for 5 minutes in a IPA/Freon tank. The liquid electrolyte was prepared by dissolving LiClO_4 in propylene carbonate (PC) to make a 1 M solution. Neither LiClO_4 nor PC was processed to eliminate moisture before or after mixing.

Characterization

The relative density of the evaporated WO_3 films was changed by nitrogen backfilling and was measured by the same method reported in Chapter II, i.e. mass change versus surface step height. The surface topography of the films was examined by scanning electron microscopy (Cambridge XSEM-9). For Li/PC EC devices, the glass substrates deposited with WO_3 films or WO_3/MgF_2 films were assembled into an EC cell as shown in Figure 2.3. The coloration/bleaching (C/B) speeds were measured with the apparatus shown in Figure 3.1. A gold wire loop was used as the counter electrode. A constant potential, 2.75 V between SnO_2 and Au electrodes, was used to drive the cell (Heathkit IP-28). An Ar-Ne laser (633 nm) was used in the measurements. The operating area was 3.88 cm^2 . The solid

Figure 3.1. Electrochromic cell circuit diagram for the measurements of C/B speeds.

state devices were fabricated by successive deposition of WO_3 , MgF_2 and Au films as described above (Figure 3.2). The thickness of WO_3 , MgF_2 and Au was 4.0 KA, 1.5 KA and 0.2 KA, respectively. The C/B speed was measured in the reflection mode.

Liquid Electrolyte Device

Results

As shown on Table 3.1, the relative density of the WO_3 thin films increased as the deposition rate (DR) increased (for a fixed partial pressure of nitrogen), or increased with decreasing partial pressure of nitrogen (P_{N_2}) for the same DR. As shown in Figure 3.3, the films prepared at high background pressure ($P_{\text{N}_2} = 7 \times 10^{-4}$ Torr) exhibited a more rough surface topography than those prepared at low pressure. The films prepared without backfilling were featureless, even at a magnification of $\times 20,000$.

The effect of deposition rate, on the coloration time (t_c) for 2,000 Å thick WO_3 films to a contrast of 30% absorption are shown in Figure 3.4. The t_c remained nearly constant up to a DR of 10 A/s then increased drastically for a DR of 30 A/s. The data in the same figure also show that t_c decreased as the partial pressure increased from the residual pressure (1×10^{-5} Torr) to $P_{\text{N}_2} = 7 \times 10^{-4}$ Torr. This effect of backfilling pressure on t_c is again illustrated in Figure 3.5 for films deposited at the same DR (5 A/s) at three

Figure 3.2. Schematic representation of the ITO/
 $\text{WO}_3/\text{MgF}_2/\text{Au}$ EC device.

Table 3.1

Effect of nitrogen partial pressure and deposition rate
on the relative density of WO_3 film

D.R. P_{N_2} (Torr)				
	3 A/s	5 A/s	10 A/s	30A/s
1×10^{-5}	0.8	1.25*	1.33*	1.33*
2×10^{-4}	—	0.91	—	—
7×10^{-4}	0.67	0.67	0.67	0.73

* There are several possibilities for the relative densities of the WO_3 films to be greater than one; (1) Calibration errors, (2) The presence of lower oxides, e.g., WO_2 and W_2O_5 (bulk density of WO_2 is 12.1 g/cm³).

(A)

(B)

Figure 3.3. Scanning electron micrographs of WO_3 films showing the effect of nitrogen backfilling during deposition on the surface topography of the films;
 (A) $P_{\text{res.}} = 1 \times 10^{-3}$ Torr, $\times 20,000$,
 (B) $P_{\text{res.}} = 7 \times 10^{-4}$ Torr, $\times 20,000$.
 N_2

Figure 3.4. Effect of deposition rate variation on coloration time for films prepared at two extreme conditions. solid circles: residual pressure of 1×10^{-5} Torr and open circles: partial pressure of nitrogen at 7×10^{-4} Torr. The films were colored to a contrast of 30% absorption ($E = -2.75$ V on WO_3). Substrates used were high resistance ITO coated glasses ($75 \Omega/\square$).

Figure 3.5. Effect of variation of nitrogen partial pressure during deposition on coloration time for WO_3 films colored to different contrast: solid circles: 40% and open circles: 30% absorption ($E = 2.75$ V on WO_3). Substrates used were low resistance ITO glasses ($15 \Omega/\square$).

different partial pressures of nitrogen ($P_{N_2} = 2 \times 10^{-4}$, 7×10^{-4} , 2×10^{-3} Torr). The t_c generally decreased as the partial pressure of nitrogen was increased.

The effect of resistance in the ITO layer upon t_c is evident when comparing data in Figure 3.4 and 3.5. The average t_c for films prepared at 7×10^{-4} Torr and 5 A/s on an ITO glass substrate with a resistance of $75 \Omega/\square$ (Figure 3.4) was 9.8 sec. The average t_c for the films with the same deposition condition but on a more conductive ITO glass substrate ($15 \Omega/\square$) was only 6.0 sec. (Figure 3.5).

The effects of a MgF_2 overlayer is shown in Table 3.2. The WO_3 thin films were prepared under the same condition (7×10^{-4} Torr of nitrogen, 2,000 Å thick). Magnesium fluoride overlayers of 500 Å or 1,500 Å thickness were deposited at $P_{N_2} = 6 \times 10^{-5}$ Torr. Other films with thickness of 1,000 Å and 2,000 Å were deposited at a pressure of $P_{N_2} = 5 \times 10^{-4}$ Torr. The device were colored to a contrast of 30% absorption. Data in Table 3.2 show that the t_c was generally lower for MgF_2 films prepared at lower pressure and for larger thickness. The maximum decrease was from 12 sec. for WO_3 films without MgF_2 overlayer to 8.5 sec. for WO_3 with a 1,500 Å MgF_2 deposited at 6×10^{-5} Torr.

The bleaching time, t_b , also varied in the same manner with increased DR or P_{N_2} as shown in Figure 3.6. However, the change from 10 A/s to 30 A/s was similar compared to those for t_c .

Table 3.2

Effect of MgF_2 overlayer on the coloration
time of WO_3 -Li/PC devices

Thickness P_{N_2} (Torr)	0.5 KA	1.0 KA	1.5 KA	2.0 KA
6×10^{-5}	10.75 s	—	8.50 s	—
5×10^{-4}	—	10.00 s	—	9.50 s

Figure 3.6. Effect of deposition rate variation on bleaching time for films prepared at two extreme conditions as described in Figure 3.4. The films were bleached from 30% to 10% absorption ($E = +2.75$ V on WO_3). Substrates used were high resistance ITO coated glasses (75 $\Omega/\square$).

No corrosion of WO_3 films in Li/PC electrolyte was observed. The device was operable even after storage for one year.

Discussion

The charge transport mechanisms for Li^+ insertion in WO_3 thin films has been discussed by several authors. Mohapatra^{15,16} reported a diffusion coefficient of $6 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ for Li^+ in evaporated amorphous WO_3 films. However, he concluded that the rate limiting processes during coloration was charge transport across the interfacial barrier between WO_3 and the electrolyte, similar to HDL control in aqueous electrolyte. Green¹⁸ has reported diffusion studies for sputtered polycrystalline WO_3 thin films with a typical grain size of 250 Å. Diffusion was described as being relatively rapid along grain boundaries followed by slow diffusion within the grains. Evidence for this model is provided by the observed reduction in response time with reduction in average grain size in WO_3 films of equal thickness. The kinetic data were interpreted as corresponding to chemical diffusion coefficients within the grain of $6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and those in the grain boundaries of $2 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$. Ho et al.¹⁷ have also recently measured Li^+ diffusion using ac impedance techniques in evaporated and crystallized WO_3 films. The films were porous (66% of bulk density). The structure was either polycrystalline with a grain size ranging from a few tens to a few hundred angstroms, or consisted of

some large grains embedded in amorphous material. Under the small perturbation condition employed, the Li^+ chemical diffusion coefficient was found to increase with Li^+ content, from $2.4 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ at $x = 0.097$ to $2.1 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ at $x = 0.26$ (x refers to the ratio of H to W atom). No evidence for sequential grain boundary/grain diffusion was found since the data could be adequately fitted by a single diffusion coefficient. Ho et al. also proposed that both diffusion and interfacial kinetics are important for the injection of Li^+ into WO_3 films. He concluded that at long times, the interface is at equilibrium and the diffusion of Li^+ in a concentration gradient limits the rate of coloration. At time shorter than about 0.5 sec., however, charge transfer across the WO_3 /electrolyte limits the rate of injection. Thus it appears as if the controlling mechanisms for coloration processes in the WO_3/Li^+ EC cells are different for amorphous versus crystalline WO_3 films. Since the WO_3 films in this study were amorphous, the controlling mechanism for coloration at long times was expected to be interfacial barrier, i.e., Helmholtz double layer, control.

The bleaching process was generally postulated to be limited by the diffusion of Li^+ ions in the space charge regions by all the above authors.¹⁵⁻¹⁸

In the present study, the switching times decreased and the porosity increased as a result of lower deposition rates or higher

partial pressures of nitrogen. Therefore, it seems reasonable to correlate the decrease in switching times with the increase in porosity. However, the decrease in times was not generally consistent with the porosity change. For example, the relative densities were 0.8 both for films prepared at 3 A/s, 1×10^{-5} Torr and at 30 A/s, 7×10^{-4} Torr, but the average t_c was 11 sec. for the former and 26 sec. for the latter films. Hence, the porosity is not sufficient to explain the change in switching speed and detailed consideration of the DR and P_{N_2} on the nucleation, growth and structure of thin films is necessary to explain these phenomena.

It was expected that during film growth, the higher deposition rate could lead to an increased surface mobility of adatoms. Higher adatom surface mobility would lead to a reduced island density which would increase the agglomeration of the films.⁸⁴ The resultant films would have a larger grain size and smaller number of frozen-in structural defect, thus the film density would be higher.

For films deposited at lower pressure, the surface contamination by residual gas would be less and hence result in an increased nucleation density. The surface mobility of the adatoms at lower pressures was expected to be higher due to increased mean free path since there was less impingement of gas

molecules. In addition, there was less gas incorporation possible at such a low background pressures. Therefore, the resultant films were expected to exhibit higher density.

Therefore, both higher deposition rate and lower background pressure increase the film density but the mechanisms are not the same. Since low density may corresponded to a much rougher surface topography, the total effective areas of the films exposed to the electrolyte was increased. The amount of charge injection per unit time was expected to be increased by this increased surface area and result in the decreased coloration time (t_c) as shown in Figure 3.4 and 3.5. In addition, the diffusion path was shortened by porosity in the films deposited at high background pressure. Therefore, the bleaching times were decreased.

However, different combinations of these two parameters might have resulted in totally different film structures, but with the same relative density. These decrease in relative density might be caused by either an increase in the porosity or an increase in the entrapment of elements with lower mass (i.e., nitrogen gas molecules). The gas molecules entrapped are expected to be physically or chemically bonded to tungstic oxide molecules. The formation of effective pores was not possible if these entrapped gas molecules were finely dispersed and isolated. However, the gas molecules might agglomerate together and caused a pressure build-up

within the pores. Such pores became 'effective' when the pressure was high enough to penetrate the tungstic oxide matrix, release the gas and form interconnects between the pores. The surfaces of these pores would be exposed to the electrolyte during operation to increase the Li^+ injection and extraction, and hence are termed 'effective pores'. For films deposited at high DR and P_{N_2} , the film density was expected to be high because of high agglomeration rate of island at high DR. However, a certain amount of gas could have been trapped during film growth since the background pressure was high. The growth of the effective pores by gas entrapment was expected to be limited by the high agglomeration rate of islands. Therefore, the effective pore volume exposed to the electrolyte was limited. The porosity effect on the C/B speed was therefore limited. While the initial nuclei density was high for film deposited at low pressure and DR, the surface mobility of adatom was low due to low DR. The adsorption of residual gas was comparable with that of adatoms. During film growth, the pores could be well developed and interconnected. The total active surface area could be much higher than that from high DR and P_{N_2} . Therefore, the same pore volume but different type of structure led to variation in t_c 's.

The limitation of switching time by the resistance of the transparent conductive layer (ITO) on the glass substrate has been reported by several authors. Hamada et al.²⁵ proposed an

empirical formula to illustrate this effect:

$$t = Q \frac{R}{|V_{\text{appl}} - E_{\text{CD}}|} \quad (3.1)$$

where t is the response time, Q is the charge injected to achieve the required contrast, R is the series resistance which is the sum of the internal WO_3 resistance and any external resistance (dominated by the ITO layer), and E_{CD} is the difference between the equilibrium potential of WO_3 and that of counter electrode in a given electrolyte. The ITO resistance effect can be illustrated by examining the voltage drop due to resistance between the electrical contact and the active electrode area (i.e., IR drop). The value of the current per unit area for coloration of WO_3 was about 1.0 mA/cm^2 . The resistance of the electrical path from contact to electrode was approximately $750 \, \Omega$ (for $75 \, \Omega/\square$ from a contact 2 mm wide and 20 mm long). Therefore, the electrical current for coloration and bleaching caused a relative large IR voltage drop ($\sim 0.75 \text{ V}$). As the resistance of the ITO layer is reduced, the IR voltage drop will be decreased and a larger voltage will occur across the HDL. This will cause a more rapid charge injection. Therefore, higher conductive ITO glass provides higher charge injection and lead to faster coloration speed as illustrated in Figure 3.4 and 3.5.

Yoshimura et al.⁸⁵ reported that WO_3 is insulating for film thickness below 5,000 Å. For film thickness above 5,000 Å, WO_3

exhibits a semiconductor nature and the conductivity increases almost linearly with increasing film thickness. The reason for this behavior was explained⁸⁵ as the depletion layer formation on the surface of WO_3 films. The depletion layer was formed because of the discontinuity at the surface, which allowed surface states to be created. These states might trap the majority carriers causing recombination and low conductivity. For WO_3 , which is an n-type semiconductor, surface states trap electrons as shown schematically in Figure 3.7(A). However, it was reported that when a MgF_2 layer was deposited onto WO_3 , the conductivity increased dramatically.⁸⁵ The MgF_2 is an insulator and the resistivity is at least several orders of magnitude higher than that of WO_3 . It was suggested that deposition of MgF_2 removed the surface states as shown in Figure 3.7(B). This explains why the coloration speed was increased when a surface layer of MgF_2 was present (Table 3.2). Since there is a smaller voltage drop across the WO_3 films, the resistance limit at short times is reduced and the HDL controlled charge injection occurred much earlier. The data in Table 3.2 also indicate that this depletion layer removal effect is less pronounced if the deposited MgF_2 films are thin and porous. The porous MgF_2 films resulting from deposition at high background pressure or thin MgF_2 films may not be able to provide a continuous coverage to remove the surface states due to the discontinuity at the WO_3 surface, and hence the effect is less significant. In conclusion, the stability of WO_3 films in Li/PC

Figure 3.7. Energy band model of electrochromic device (A) before and (B) after the deposition of MgF_2 overlayer.

electrolyte is excellent. The C/B speed could be increased by a porous WO_3 film, by a MgF_2 overlayer and by more conductive ITO substrate.

Solid Electrolyte Device

Results

A qualitative study was conducted to determine the effect of air-backfilling on the WO_3 and MgF_2 films in the solid state devices. The results are shown in Table 3.3. The device made with WO_3 without backfilling and MgF_2 with or without backfilling were easily colored, even over larger areas ($\sim 36 \text{ mm}^2$). The C/B speed of these devices are shown on Table 3.4. With higher air-backfilling pressure during MgF_2 deposition, the t_c 's and t_b 's both decreased.

The devices made of WO_3 with air-backfilling ($P_{\text{air}} = 5 \times 10^{-4}$ Torr) and MgF_2 with or without backfilling can only be colored in a limited area ($\sim 2 \text{ mm}^2$). The memory is even poorer in the device made with MgF_2 with air-backfilling than that without backfilling; self-erasure to a completely bleached state occurred within several seconds. The cyclic lifetime of such device was limited. The device eventually failed to color when the Au film flaked off from the MgF_2 layer as a result of prolonged cycling (~ 100 cycles).

Table 3.3

Effect of air-backfilling during WO_3 and MgF_2 deposition on the electrochromic colorability of $\text{WO}_3/\text{MgF}_2/\text{Au}$ solid devices

WO_3 MgF_2	No air-backfilling	with air-backfilling
No air-backfilling	Colorable	Colorable in limited area
With air-backfilling	Colorable	Colorable in ex- tremely limited area, poor memory

Table 3.4

Effect of air-backfilling for MgF_2 on the C/B times of $\text{WO}_3/\text{MgF}_2/\text{Au}$ solid state devices.

<div>MgF_2</div> <div>Time (sec.)</div>	$P_{\text{res.}} = 1 \times 10^{-5} \text{ Torr}$	$P_{\text{air}} = 5 \times 10^{-4}$
t_c	4.00	1.75
t_b	6.75	2.50

Discussion

Device based on $\text{WO}_3/\text{MgF}_2/\text{Au}$ have been reported by various authors. Yoshimura et al.⁸⁶ reported that water in the ambient atmosphere or water near the MgF_2 film surface is dissociated at the counter electrode, generating protons which move through the MgF_2 films into the WO_3 films and thus contribute to coloration, i.e.,

During bleaching, the protons are ejected from the WO_3 films and H_2 gas is released from the semi-transparent Au electrode, i.e.,

Measurements of H_2 and O_2 evolution and weight change of the device during operation have supported these postulated mechanisms.

It is quite apparent that increasing the water content in both MgF_2 and WO_3 films could increase the switching speed of the device. However, it is difficult to increase water content simply by water backfilling. Therefore, air backfilling seemed to be a good substitute. Yoshimura et al.⁸⁵ have shown that the effect

of air backfilling can be ascribed to the water in air. The decrease in t_c and t_b by increasing partial pressure of air during MgF_2 deposition can be attributed to:

1. The porous structure resulted from deposition with a high background pressure could increase the adsorption of water during subsequent exposure to the atmosphere. The total water content in the films, therefore, would be the sum of the water incorporated during deposition and the water absorbed after deposition. It will be much higher than those without backfilling;
2. The porous structure of the MgF_2 films also facilitate the transport of the dissociated ions.

However, air-backfilling during WO_3 film deposition was unnecessary, especially from the viewpoint of device fabrication. It is believed that the porous structure and higher water content of the WO_3 films prevented the creation of uniform and dense MgF_2 films; dielectric breakdown occurred readily in the resulting thin film sandwich configuration. In addition, even a 1 μm particulate contamination was enough to make the device inoperable. Therefore, the operational area of the device was limited. The diffusion coefficient for proton in the WO_3 films prepared without backfilling was already sufficiently large ($\sim 10^{-8} \text{ cm}^2 \text{ s}^{-1}$)⁹ that the coloration was expected to be limited only by interfacial barrier.^{30,35} Hence, the modification of the interface between WO_3 and MgF_2 will be a more proper approach to try to achieve faster response. Yoshimura et al.⁸⁵ reported the water absorption at the WO_3/MgF_2 interface does increase the coloration speed.

The poor open-circuit coloration memory for the devices fabricated from WO_3 and MgF_2 both with air-backfilling again could have resulted from the high porosity and water content in these films. As mentioned in chapter II, self-erase resulted from protons diffusing to the WO_3 /electrolyte interface and reacting with oxygen. The high porosity and water content in MgF_2 films were expected to more rapidly provide the oxygen needed for self-erasure. Alternatively, the proton could also combined with OH^- to form water as described above. The porous structure can expedite the the removal of the reaction products from the interface region. Hence, the self-erasure was faster in these devices. In addition, gas evolution during operation would lead to a premature failure of the device either by loss of contact between the MgF_2 films and the counter-electrode or by exhaustion of the water in the MgF_2 films as reported by Yoshimura et al.⁸⁶

An ideal solid state EC display, therefore, should employ a configuration that is free from such side reactions. A reversible counter-electrode and a dielectric layer which has strong holding power for water would be the main requirements to satisfy these conditions. Devices based on this principle, such as $\text{ITO}/\text{WO}_3/\text{Ta}_2\text{O}_5/\text{IrO}_x/\text{ITO}$,⁸⁷ have been reported and exhibited fast response (50 ms for OD of 0.5) and long lifetime ($>10^7$ cycles).

Summary

1. In liquid WO_3 -Li/PC devices, the porosity of WO_3 films was increased by deposition at high partial pressure of nitrogen and low deposition rate. The coloration/bleaching speeds were slightly increased by the increased porosity possibly due to increased surface area for Li^+ injection during coloration, and shortened diffusion path for Li^+ extraction during bleaching.
2. The increase in the speeds was not generally consistent with the porosity change. It is possible that the pores introduced by high deposition rate and high P_{N_2} were not effective as those from low deposition rate and low P_{N_2} . Therefore, a variation in the switching speeds was observed even at the same relative density.
3. The coloration speed was found to be slightly increased when a dense, thick MgF_2 overlayer was deposited on the WO_3 film. Increased coloration speed was postulated to be caused by an decrease in the duration of WO_3 film resistivity control at the onset of coloration.
4. The resistance of the transparent indium tin oxide layer was found to limit the effective potential across the WO_3 /electrolyte interface. Therefore, a highly conductive ITO layer is desirable for a fast switching EC device.
5. In a solid $\text{WO}_3/\text{MgF}_2/\text{Au}$ device, the water content in the MgF_2 film was found to be increased by air backfilling during evaporation.

The coloration/bleaching speeds were increased because of increased proton mobility caused by increased water content in the MgF_2 film. The current injection was limited by the interfacial barriers between WO_3/MgF_2 rather than by the proton diffusion in MgF_2 films.

6. Air backfilling during WO_3 films deposition appeared to be undesirable for solid electrolyte devices, since the porosity and rough surface prohibited a uniform sandwich layered structure to be formed and led to local dielectric breakdown. The operational area of such devices was limited.
7. The lifetime of $\text{WO}_3/\text{MgF}_2/\text{Au}$ was limited (~100 cycles). The device failed as a result of the loss of contact between the Au electrode and the MgF_2 film. Exhaustion of water in MgF_2 film from gas evolution during operation may also have occurred.

CHAPTER IV SUMMARY

Conclusions

Electrochromic tungsten trioxide films have been studied in relation to their application to non-emissive display devices. Electrochromic display devices exhibit a number of attractive features such as no limitation on viewing angle, low power consumption, open-circuit memory, and good contrast at high ambient light. Therefore, they have varied applications not possible with other conventional display materials. However, there are some drawbacks. For example, the switching speeds are slow, lifetime is limited ($\sim 10^5$ cycles) and they color only to blue in transmission. Among these three, the lifetime problem is the principal obstacle to the commercialization of electrochromic displays. The lifetime of the device was found to be limited by the corrosion of WO_3 films in the H_2SO_4 electrolyte. The goal of the present research was to investigate the corrosion mechanisms and seek methods to improve the stability of the device.

The tungsten trioxide films for this study were prepared by vapor deposition. The as-deposited films were amorphous, oxygen deficient ($O/W = 2.7$), and porous (80% of the bulk density). Because of the oxygen deficiency, the tungsten atoms existed not only as W^{6+} but also as W^{4+} and W^{5+} as evident from the data of XPS. Calculations indicated the concentration of these subvalence states (W^{4+} ,

W⁵⁺) could be very high (approximately 40%). The tungsten atoms with 6+, 5+ and 4+ states may take the configuration of WO₃, W₂O₅ and WO₂, respectively. The microstructure of vapor deposited WO₃ films, therefore, may be considered as a random network of these molecules linking with each other through corner sharing oxygen bonds. The equilibrium potential of WO₃ thin film stored in a 3.6 N H₂SO₄ solution was 0.4 V_{SHE}. The Pourbaix diagram for tungsten indicated that WO₃ is the only stable specie for these conditions (pH = 0.5, E = 0.4 V_{SHE}). Specifically, WO₂ and W₂O₅ are not considered to be stable. The conversion of WO₂ and W₂O₅ occur by a dissolution and precipitation mechanism. It was postulated that WO₂ and W₂O₅ dissolved in the acid as WO₂²⁺ ions. These WO₂²⁺ ions then reacted with H₂O and formed crystalline WO₃ and its hydrates (WO₃·H₂O and WO₃·2H₂O), which precipitated within the cell. Since there are very large concentration of dissolution-prone species in the vapor deposited films, rapid dissolution in the acid (~ 16 A/hr) was observed.

The precipitation of crystalline WO₃ and its hydrates on the original films, particularly in the pinholes is postulated to cause delamination by introducing internal stresses which exceed interfacial adhesion strength between the film and its substrate. Gas evolution was observed and attributed to hydrogen gas formation during the dissolution-precipitation processes. This may have contributed to the force causing delamination. Interfacial delamination was not observed on the WO₃ films deposited on the graphite substrates which exhibited a rough surface, probably because the adhesion strength was increased by mechanical interlocking of the film and substrate through pores and valleys.

The corrosion process was enhanced when the WO_3 films was bleached after coloration because of the dissolution rate of WO_2 and W_2O_5 was increased in the bleaching condition. The WO_3 films were reported to be extremely stable in most organic solvents, but became soluble when the solvent was acidified. The corrosion of WO_3 thin films in H_2SO_4 /glycerin (1:10) electrolyte or other acidified electrolyte (H_2SO_4 /methanol or H_2SO_4 /acetonitrile) supported the postulate that the pH rather than water content defined whether corrosion would occur, since the order of magnitude of the reduction of the corrosion rate was not consistent with the reduction in the water content.

Knowing the causes of corrosion (the oxygen deficiency and the pH of the electrolyte) many solutions to the corrosion problem can be developed. Generally, there are two types of solutions, one involved the modification of the WO_3 films and the other the modification of the electrolyte. Both types of solutions were attempted during the study. Since the corrosion occurred because of oxygen deficiency in the WO_3 films, oxygen backfilling during WO_3 deposition was used to increase the oxygen content. Rutherford Backscattering Spectroscopy data indicated that the O/W was increased from 2.7 for films prepared without backfilling to 2.9 for films deposited at a $P_{O_2} = 1 \times 10^{-3}$ Torr. The increase in the O/W ratio was accompanied by an increase in the W^{6+} states relative to the W^{5+} and W^{4+} states as shown by XPS data. Since the concentration of unstable species (W^{4+} , W^{5+}) were reduced, the dissolution rate was decreased. Dissolution

was reduced to a negligible rate for films deposited at $P_{O_2} = 1 \times 10^{-3}$ Torr. Interfacial delamination was not observed for films prepared at $P_{O_2} > 1 \times 10^{-4}$ Torr because the corrosion process was reduced. However, the small concentration of subvalence states (W^{4+} , W^{5+}) still allowed some small scale corrosion process to occur and the films exhibited partial crystallization in X-ray diffraction data after long term storage. In addition, a slight roughened surface was observed at high magnification (x 3,000). Generally, the oxygen enriched films exhibited superior stability as compared to the unmodified films.

The electrochromic properties of these oxygen enriched films were altered too, however, the coloration speed was decreased because the magnitude of current injected and the optical efficiency were decreased. The current injection during coloration was found to be controlled by the same mechanisms as the films without backfilling (i.e., WO_3 resistivity and Helmholtz double layer). However, the magnitude of the current passed was lowered by backfilling due to an increased film resistivity. The increased resistivity and decreased optical efficiency in the oxygen enriched films resulted in slower coloration speeds and were explained by postulating an increased density of inactive electron trapping site. This increased density of inactive trapping sites limited the formation of active polaron for optical absorption and DC conductivity. However, the possibility that a decreased oscillator strength resulted in degraded optical efficiency could not be ruled out. The porosity of the films was

increased by deposition at high background pressure. Due to increased effective surface area, the film absorbed higher amounts of water after deposition as shown by secondary ion mass spectroscopy. The bleaching speed and self-erasure rates were increased since the rate of proton removal were increased by increase in porosity and absorbed waters. In summary, the compositional changes from OB (O/W ratio) resulted in a degraded coloration speed and optical efficiency while the structural change (porosity) led to an increase in bleaching speed and self-erasure rate. Of these four property changes, only increased bleaching speed is desirable from the viewpoint of device fabrication.

In a second approach to improve device lifetime, LiClO_4 /propylene carbonate (Li/PC) electrolyte and solid hydrated MgF_2 dielectric films were used in the place of the acid electrolyte. Since the switching speeds of these devices were slow, nitrogen and air back-filling during deposition was used to modify the structure and composition of WO_3 and MgF_2 films. In liquid WO_3 -Li/PC devices, the porosity of WO_3 films was increased by deposition at high partial pressures of nitrogen and low deposition rate. The coloration and bleaching speeds were slightly increased by the increased porosity, possibly due to the increased surface area for Li^+ injection during coloration, and shortened diffusion path for Li^+ extraction during bleaching. However, the increase in the speeds was not directly proportional to the relative density change. It was possible that the

pores were not equally effective in facilitating ion injection and extraction in different deposition conditions, e.g., high deposition rate and high partial pressure of nitrogen as compared to low deposition rate and low partial pressure of nitrogen. The resistivity of WO_3 thin films was high and was reported to be caused by the formation of a depletion layer by the presence of trapping states for electrons at the WO_3 surface. Deposition of a MgF_2 overlayer was expected to decrease the resistivity by decreasing the thickness of this depletion layer. The coloration speed of devices with a MgF_2 overlayer was slightly increased because the duration of the resistivity control was shortened. The resistance of the transparent indium tin oxide layer was found to limit the switching speed. Therefore, a highly conductive ITO layer will be desirable for a fast switching EC device. In general, the stability of WO_3 films in Li/PC electrolyte is excellent. The switching speed could be increased by a porous WO_3 film, a MgF_2 overlayer and more conductive ITO.

In the device using solid MgF_2 films as an electrolyte (i.e., $\text{WO}_3/\text{MgF}_2/\text{Au}$), air-backfilling during deposition of MgF_2 film was reported to increase the water content in these films. The switching speeds were increased because of the increased proton mobility in the MgF_2 films. Air-backfilling during WO_3 evaporation appeared to be undesirable, since the porosity and rough surface prohibited a uniform sandwich layered structure to be formed and led to local dielectric breakdown. The operational area of the device was limited. A different degradation mechanism was postulated

in this type of device, i.e., gas evolution during the operation resulted in loss of contact between Au and MgF_2 films. Exhaustion of water in the MgF_2 layer may also have occurred. The cycling lifetime was limited to ~ 100 cycles.

Future Development

1. Because of the nature of the vapor deposited WO_3 films (amorphous, porous and hygroscopic), the films are extremely unstable. In addition to corrosion in the acid, the films are also susceptible to the attack by the moisture in the air (see Appendix B). Future studies on crystalline WO_3 films with high ionic conductivity such as crystalline hexagonal WO_3 thin films⁸⁸ may provide a more reliable device.
2. Recently, the technology of devices using Li/PC has experienced vigorous development.¹⁹⁻²⁵ The reported long lifetime ($> 2 \times 10^7$ cycles and unlimited shelf lifetime), and fast switching speed (C/B times < 300 ms) look promising. However, the switching speed could be further increased by a reduced O/W ratio, by a MgF_2 overlayer and by increased porosity. A switching time in the millisecond range (comparable with LCD) is expected.
3. The ultimate goal is the development of a reliable solid state device. Devices using solid state protonic conductors (HUP Cr_2O_5 films, NAFION,⁴⁴ etc.) have reported long lifetimes and fast switching speeds. The stability of such devices, however,

is questionable since a fast switching speed would require a high water content in the electrolyte layer, and hence a corrosive environment may be created. Future studies with Li-electrolytes⁸⁹ may provide more stable devices.

APPENDIX A
PRELIMINARY STUDIES OF CATHODOCHROMISM IN TUNGSTEN
TRIOXIDE FILMS AND THE EFFECT OF AIR BACKFILLING

The coloration in vapor deposited WO_3 films can be induced not only by the electrochemical method described earlier but also by electron beam irradiation (cathodochromism)⁵⁰⁻⁵² or by high energy photon (e.g., ultra-violet or X-ray) irradiation (photochromism).⁷⁰ The area that is bombarded by the electron beam is colored deep blue and has a high contrast with the remaining unbombarded area. The coloration is normally limited by the size of the electron beam. The application of this phenomenon is limited by one's imagination. However, the mechanism for cathodochromism is unclear at this time due to the scarcity of studies. Lin and Lichtman⁵⁰ studied cathodochromism in WO_3 powder and oxidized W foil and suggested that the coloration was caused by the preferential removal of oxygen from the bombarded area by electron-beam-induced out-diffusion or by electron-beam-induced-desorption. They attributed the blue coloration to deficiency of oxygen atoms because polycrystalline WO_3 powder is yellow in color, while $WO_{2.9}$ powder is deep blue.⁹⁰ Morita et al.⁵¹ reported a similar study on vapor deposited WO_3 films and also observed the ejection of oxygen atoms from the bombarded area, and the blue coloration. Again they attributed the coloration to deficiency of the oxygen in the films. However, it is known that the vapor deposited WO_3 films are amorphous and

already oxygen deficient, i.e. $O/W = 2.7$. But the films are still transparent. Evidently, a different mechanism is needed to explain the cathodochromism in amorphous WO_3 thin films. In the following, the results of a preliminary study of cathodochromism in WO_3 thin films are presented and discussed.

Results and Discussion

The WO_3 films were prepared by thermal evaporation of pure WO_3 polycrystalline powder (Cerac Inc., 99.9%) from a resistively heated source onto indium tin oxide coated glass (ITO glass) at room temperature. Before evaporation, the chamber was evacuated to a base pressure of 6×10^{-6} Torr. The films were deposited at a residual pressure (during evaporation) of 1×10^{-5} Torr, or at a partial pressure of backfilled air of 5×10^{-4} Torr. The deposition rate was kept constant at 5 Å/s, while the thickness was either 4,000 or 8,000 Å. The deposited films were placed in a demountable electron beam writing system evacuated to 2×10^{-6} Torr by a diffusion pump with liquid nitrogen trapping backed by a mechanical pump. Electron dose was varied by changing the irradiation time. The electron beam was rastered over an area of 0.1 cm^2 . The sensitivity of the film colored by electron irradiation was characterized in terms of absorption of light at wavelength of 6,238 Å (He-Ne laser).

Results are shown in Figure A.1 and A.2 for 2.0 and 3.8 KV beam, respectively. Generally, there is no significant difference

Figure A.1. Coloration intensity versus electron dose for WO_3 films prepared at residual pressure of 1×10^{-5} Torr and partial pressure of air at 5×10^{-4} Torr. Solid circles refer to films of 8 KA while open circles to those of 4 KA. Electron accelerating voltage, ' V_{acc} ' was 2 KV.

Figure A.2. The coloration intensity versus electron dose for WO_3 films prepared at two extreme conditions and thickness as described at Figure A.1. $V_{\text{acc}} = 3.3 \text{ KV}$.

between films of the two thickness. However, increasing the accelerating voltage and air backfilling did increase the optical contrast in WO_3 films. For the same dose ($\sim 1.8 \times 10^{-2}$ C), the contrast increased from 15% absorption for films prepared without backfilling to 40% for films prepared at 5×10^{-4} Torr. For films prepared with air backfilling, the optical contrast was increased even further to 65% when the accelerating voltage was approximately doubled, while that in the films prepared without backfilling remained nearly constant.

Baba et al.⁵² have reported that the absorption spectra from electron beam induced coloration is similar to that of electrochromic coloration. The energy of the absorption peak was also identical, and the electron beam colored area can be electrochemically erased to a completely bleached state, indicating that the mechanism responsible for coloration may be same.

As shown in Chapter III, the air backfilling is known to increase the water content (or H content) in the WO_3 films. The result that the optical contrast was increased in the WO_3 films with air backfilling (higher H content) can be explained by the active-inactive-cation-sites discussed in Chapter II. Since there were more protons in the inactive site by backfilling the protons that were redistributed into active site upon electron beam irradiation and contribute to coloration would increase. When the electron accelerating voltage was increased, there was more

energy released during electron decelerating resulting in higher probability for protons to transfer into active sites and hence a denser coloration. However, the accelerating voltage effect is contingent upon the air backfilling effect as evident from the fact that the contrast remained the same when the accelerating voltage was almost doubled for the films prepared without backfilling. Deneuville, et al.⁷⁹ reported that WO_3 films prepared without backfilling contain less H when compared with the films prepared at 5×10^{-4} Torr (H/W = 0.6 and 1.2, respectively). Therefore, the coloration is solely controlled by the concentration of the protons in the films. These data strongly support the active-inactive-cation-sites model.

Increasing the thickness from 4,000 Å to 8,000 Å did not increase the contrast. It is possible the thickness range in this study was much higher than the electron penetration depth (~ 300 Å) at the operating voltage used (2.0 and 3.8 KeV). The optical contrast may be enhanced when a thinner film was used so the electrons scattered from the substrate can contribute to further coloration.

Judging from the features of the absorption spectra and the dependence of optical contrast on the proton concentration, the optical absorption mechanism may still be associated with the the polaron hopping mechanism as proposed for electrochromism. The electrons injected during the irradiation were expected to localize around tungsten atoms and eventually form the polaronic band. The

preferential removal of oxygen may still occur but is not expected to be the cause of coloration since the electron-beam-induced coloration can be removed by ensuing electrochemical bleaching. The fact that the electron beam colored area can be electrochemically erased is also strong evidence supporting the polaron hopping absorption mechanism in cathodochromism.

In conclusion, the mechanism that is responsible for cathodochromism in amorphous WO_3 thin films appears to be related more to polaron hopping absorption as opposed to the oxygen extraction model. The observed air backfilling and accelerating voltage effects support the active-inactive-cation-sites model proposed by Deneuville et al., and indicate that the position of cations in WO_3 films play an important role in both cathodochromism and electrochromism.

APPENDIX B
CORROSION OF TUNGSTEN TRIOXIDE FILMS DURING
STORAGE IN MOIST AIR

The WO_3 thin films are hygroscopic due to the high porosity in these films. The storage of these films before device fabrication constitutes a major problem. Hitchman⁸² reported that evaporated WO_3 films were crystallized after standing in air for 12 months. In our study, the conversion processes were expedited by moisture saturation of the atmosphere.

Films of WO_3 prepared with and without oxygen backfilling were stored in a sealed box containing a cup of water for moisture saturation. After three months, the box was opened, the surface topography was examined using a scanning electron microscope. Crystallite-like particles were distributed on the films. There was no significant difference between the films prepared with and without oxygen backfilling (Figure B.1). However, the surface damaged by moist air corrosion were different from those corroded by acid. The corrosion mechanisms in these conditions are expected to be different. In the air storage, the water condensed on the WO_3 films surface, especially in the pinholes, was the corrosive agent. As discussed earlier, the WO_3 is readily

(A)

(B)

Figure B.1. Scanning electron micrographs of corroded surface of WO_3 films after storage in moisture saturated air for three months;

(A) $P_{\text{res.}} = 1 \times 10^{-5}$ Torr, $\times 500$,

(B) $P_{\text{O}_2} = 1 \times 10^{-3}$ Torr, $\times 500$.

dissolved in neutral water,³⁶ and WO_2 and W_2O_5 exhibit even higher solubility:

The oxygen dissolved in water could also generate hydroxyl ions by

and render the condensed water more basic. This would lead to higher dissolution rates of tungstic oxides. When the saturation limit was reached, the crystalline WO_3 and its hydrates started to precipitate as shown in Figure B.1. The population of the crystallites on the surface was initially small and limited to the pinholes. Gradually they spread out and covered the surface. The mechanical strength of these films was therefore weakened. The proton diffusion coefficient was also reported^{35,65} to be lowered due to crystallization, the switching speed was therefore slowed. Eventually the films were useless for device fabrication.

In summary, because of the nature of the porous, hygroscopic and amorphous vapor deposited WO_3 films, they are extremely unstable. In addition to corrosion in the acid electrolyte, the films are also susceptible to the attack by air, or more specifically, by the moisture in air. Therefore, a strictly controlled atmosphere is

needed for the fabrication of electrochromic display devices where the moisture incorporated in the device (WO_3 films, electrolyte) will be reduced to a minimum.

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Sey-Shing Sun was born in Taipei, Republic of China, on July 9, 1955. He is the son of Yu-Ping and Ching-Der Sun. In June 1977, he received his B.S. in materials science and engineering from National Tsing Hua University, Hsinchu, Republic of China. After graduation, he served in the Chinese Army ROTC as a second Lieutenant for two years. In January 1980, he enrolled in the Graduate School of the University of Florida and is now completing the requirements for the degree of Doctor of Philosophy in materials science and engineering.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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