MULTIPLE THERMAL SWITCHING EFFECT ON THE STABILITY OF VANADIUM DIOXIDE FILMS

BY

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A thesis submitted in partial fulfilment for the award of Master of Science Degree of Kenyatta University

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DECLARATION

This thesis is my original work and has not been presented for the award of a degree in any university.

All sources of information have specially been acknowledged by means of references.

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This thesis has been submitted with our approval as university supervisors.

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Dedication

To my love Vernard, son Ngaruiya, daughter Njoki, parents, brothers and sisters.
Abstract

The study aimed at establishing the effect of multiple thermal switching on the stability of vanadium dioxide films. The films were produced in an atmosphere of a mixture of argon and oxygen. On optimization of oxygen flow rate, films which were approximately 80 nm thick and showed metal to semiconductor phase transition were obtained. Electron diffraction pattern showed the films to be polycrystalline. The sheet resistance was found to change by three orders of magnitude upon heating the films from room temperature to temperatures above transition temperature. The spectral normal transmittance over the wavelength range of 300 to 2500 nm showed a monotonic increase in transmittance at 30°C to 69% and a decrease in the infrared to about 16% on running the spectrum at 100°C. The refractive index, $n$ and the extinction coefficient, $k$, for the as-deposited films were 2.85 and 1.47 for the semiconducting state respectively. Values of 2.62 and 1.37 were obtained for the films in the metallic state for $n$ and $k$ respectively. Upon multiply switching the films the sheet resistance was found to increase by a small magnitude at both semiconducting and metallic states. The magnitude of change of sheet resistance decreased by a small magnitude but retained the same order. From the temperature dependent transmittance the transition temperature was found to decrease and tend to stabilise at 61°C from 69°C for the as-deposited. The hysteresis loop width was found also to decrease from 15°C to 10°C upon cycling. The spectral normal transmittance showed no appreciable change upon cycling. After one thousand thermal cycles $n$ increased to 3.08 and $k$ decreased to 1.08 at semiconducting state. In the metallic phase both $n$ and $k$ decreased to 2.46 and 0.64 respectively, after cycling.
Table of Contents

Content
Title
Declaration
Acknowledgements
Dedication
Abstract
Table of Contents

Chapter One
Introduction
1.1 General Introduction
1.2 Introduction
1.3 Literature Review
1.4 Objectives
1.5 Rationale

Chapter Two
Theory
2.1 Introduction
2.2 Ambient Radiation
2.3 Thin Films
2.3.1 Thin Film Production
2.3.1.1 Sputtering Technology
2.3.1.2 Sputtering Yield
2.3.1.3 Thin Film Growth
2.3.2 Thin Film Optics
2.3.2.1 Single Layer Film
2.3.2.2 General Theory of Ellipsometry
2.4 Material of Study
2.4.1 Vanadium Dioxide
Chapter Three
Experimental Procedures

3.1 Introduction
3.2 Thin Film Production
3.3 Measurement of Substrate Temperature and Cooling Systems
3.4 Measurements
3.4.1 Electrical Measurements
3.4.2 Optical Measurements
3.4.2.1 Spectral Measurements
3.4.2.2 Determination of Optical Constants
3.4.3 Thickness Measurements
3.4.4 Structural Characterization

Chapter Four
Results and Discussions

4.1 Introduction
4.2 Structural Analysis
4.3 Film Thickness
4.4 Electrical Properties
4.5.1 Optical Properties
4.5.2 Optical Constants

Chapter Five
Conclusion and Suggestions

5.1 Conclusion
5.2 Suggestions for Further Work

References

Appendix

(I) Fortran Program to compute the refractive index (n) and the extinction coefficient (k) from the ellipsometric parameters
(II) Vertical magnifications for the metric chart paper
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Conductivity versus reciprocal temperature for several transition metal compounds (Adler, 1972)</td>
</tr>
<tr>
<td>1.2</td>
<td>Variation of sheet resistance ratio with oxygen flow rate for rf sputtered vanadium dioxide films (Kivaisi and Samiji, 1999)</td>
</tr>
<tr>
<td>1.3</td>
<td>Temperature dependence of electrical conductivity for different vanadium dioxide phases.</td>
</tr>
<tr>
<td>2.1</td>
<td>Spectra for black body radiation, at two temperatures, solar radiation that has passed through the earth's atmosphere, and relative sensitivity of the human eye (Granqvist, 1991).</td>
</tr>
<tr>
<td>2.2</td>
<td>Schematic diagram of DC diode sputtering process chamber</td>
</tr>
<tr>
<td>2.3</td>
<td>Typical variation of mean free path with pressure</td>
</tr>
<tr>
<td>2.4</td>
<td>Stages of structure evolution in polycrystalline thin films. 1: nucleation; 2: crystal (grain) growth; 3: coalescence; 4: filling the channels; 5: growth of continuous film. Crystals before coalescence are marked by broken line; dark circles mark adatom, bright circles impurity species.</td>
</tr>
<tr>
<td>2.5</td>
<td>Symbols used for deriving Fresnel relations for an interface between two media</td>
</tr>
<tr>
<td>2.6</td>
<td>Geometry for the interfaces in a thin film (2). f denotes light incident from the back.</td>
</tr>
<tr>
<td>2.7</td>
<td>Tetragonal rutile type structure of VO₂ in the metallic phase (M). (Shin et al., 1990)</td>
</tr>
<tr>
<td>2.8</td>
<td>Crystal field splitting of V⁴⁺ (3d¹) energy levels as calculated by Sommers et al., (1975)</td>
</tr>
<tr>
<td>2.9</td>
<td>Schematic energy diagram of the bands around the Fermi level for VO₂ (Shin et al., 1990)</td>
</tr>
<tr>
<td>3.1</td>
<td>Across section of the vacuum chamber for the Balzers BAE 250 sputtering unit.</td>
</tr>
<tr>
<td>3.2</td>
<td>Measurement of temperature inside the vacuum chamber</td>
</tr>
<tr>
<td>3.3</td>
<td>The calibration curve for thermocouple (K-type)</td>
</tr>
<tr>
<td>3.4</td>
<td>Connection diagram for water cooled vacuum chamber</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>3.5</td>
<td>Magnetron cooling system</td>
</tr>
<tr>
<td>3.6</td>
<td>Circuit diagram showing a two point probe</td>
</tr>
<tr>
<td>3.7</td>
<td>Spectrophotometer set-up</td>
</tr>
<tr>
<td>3.8</td>
<td>Schematic arrangement of the conventional reflection ellipsometer</td>
</tr>
<tr>
<td>4.1</td>
<td>Electron diffraction pattern of thin film vanadium dioxide on carbon</td>
</tr>
<tr>
<td></td>
<td>backed copper grids prepared at 400°C</td>
</tr>
<tr>
<td>4.2</td>
<td>Step height traces at 1 x 10^5 magnification for a VO₂ film prepared</td>
</tr>
<tr>
<td></td>
<td>by DC reactive magnetron sputtering on glass slide at 400°C</td>
</tr>
<tr>
<td>4.3</td>
<td>Variation of sheet resistance with temperature for DC reactively sputtered</td>
</tr>
<tr>
<td></td>
<td>VO₂ films on glass at 400°C</td>
</tr>
<tr>
<td>4.4</td>
<td>Sheet resistance variation with temperature for DC reactively sputtered VO₂</td>
</tr>
<tr>
<td></td>
<td>film before and after ten, hundred and thousand thermal cycles</td>
</tr>
<tr>
<td>4.5</td>
<td>Temperature correction curve for the thermocouple thermometer</td>
</tr>
<tr>
<td>4.6</td>
<td>Temperature dependent transmittance curve for the as-deposited DC reactively</td>
</tr>
<tr>
<td></td>
<td>sputtered VO₂ film on glass at 400°C</td>
</tr>
<tr>
<td>4.7</td>
<td>Temperature dependent transmittance for DC reactively sputtered VO₂ film</td>
</tr>
<tr>
<td></td>
<td>before and after thermal cycling</td>
</tr>
<tr>
<td>4.8</td>
<td>Variation of transition temperature with the number of thermal cycles</td>
</tr>
<tr>
<td>4.9</td>
<td>Variation of the hysteresis loop width with the number of thermal cycles</td>
</tr>
<tr>
<td>4.10</td>
<td>Spectral normal transmittance of the as-deposited DC reactively sputtered</td>
</tr>
<tr>
<td></td>
<td>VO₂ film on glass below (T &lt; T_c) and above (T &gt; T_c) the transition</td>
</tr>
<tr>
<td>4.11</td>
<td>Spectral normal transmittance for the VO₂ film before and after ten,</td>
</tr>
<tr>
<td></td>
<td>hundred and thousand below(T &lt; T_c) and above (T &gt; T_c) the transition</td>
</tr>
<tr>
<td></td>
<td>temperature</td>
</tr>
</tbody>
</table>
List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Determination of optical constants by ellipsometric method</td>
<td>63</td>
</tr>
<tr>
<td>4.2</td>
<td>Comparison of n and k for VO₂ film</td>
<td>64</td>
</tr>
</tbody>
</table>
CHAPTER ONE
INTRODUCTION

1.1 General Introduction

This thesis presents results of investigations on the stability of vanadium dioxide films. The films were deposited on glass for studies on 'smart window' applications. They were subjected to multiple thermal cycling about the transition temperature. The deposition of the films was by planar reactive magnetron sputtering. Characterization of the films was by determination of electrical, optical and structural properties. These characterizations were done for the as-deposited films and after the films were recycled for ten, hundred and thousand times about the transition temperature.

The thesis is organized as follows. Chapter one gives the general introduction with a definition of 'smart windows'. The need for the 'smart windows' is reviewed and what has currently been achieved. In the same chapter the gap to be filled has been identified. The chapter ends with the objectives set to be achieved and the rationale of the work. Chapter two examines the theory of the subject matter and the chapter's content is introduced at its beginning. The experimental procedures constitute chapter three. Chapter four gives the results and discussions, while conclusions and suggestions are made in chapter five.
1.2 Introduction

Space conditioning of residential and commercial buildings accounts for substantial fractions of the annual energy consumption in many countries. This is about 5% for United States and 7% for Sweden (Granqvist, 1988). Current architecture and car designs have created great demand for 'smart' windows. These windows can change color and hence transmit different amounts of infrared radiation depending on ambient temperature conditions. Property requirements for energy efficient windows vary with climates. For a warm climate we require a window that has a substantial transmittance in the visible region but highly reflecting in the near infrared region while in a cold climate a window with improved thermal insulation without deteriorating solar transmittance is required. In a temperate climate there is need for preventing excessive solar heating, whereas at other times one wants to let in solar radiation as much as possible to provide free heating. Thus one wants to have a window which enables a dynamic throughput of radiant energy commonly referred to as a smart window. Window properties have therefore a significant effect on our visual and thermal comfort as well as on energy consumption at a global level.

An energy efficient window is a device capable of providing good lighting during the day and good thermal comfort both during day and night at a minimum amount of paid energy. Thermal comfort requires that overheating and excessive cooling be avoided i.e. the radiative inflow and heat transport due to radiation, conduction and convection be controlled. The fact that the fundamental function of a window is to transmit visible light
makes radiative inflow significant. This significance is from the fact that radiative properties can be modified by thin coatings and surface treatment of the glass.

Two types of windows have been studied. There are those that have static properties. For these the optical performance remain the same irrespective of the external conditions and include thin noble metal coatings and heavily doped oxide wide band-gap semiconductor coatings (Kivaisi, 1996). There are also those that have dynamic properties (Babulanam et al., 1986). Their optical properties vary with changes in their environment and are referred to as chromogenic materials.

Chromogenic materials are categorized into three groups. First there are the photochromic materials, which change reversibly upon irradiation with light. Strong photochromic effect can be produced by metal halides, for example with small quantities of silver and copper as light absorbing substances (Hoffman, 1990). Some eyeglasses fall in this category. Secondly there are the electrochromic materials which are characterized by their optical properties being able to change under the action of an electric field. The change is caused by injection or extraction of mobile ions from an ion storage layer to the electrochromic layer. The electrochromic layer consists of several sub-layers and in addition to these, there is outer application of the field and an ion conductor. These layers should be as transparent as possible in order not to interfere with the features of the coating. Lastly, there are the thermochromic materials, which form a subject of this work, whose electrical and optical properties are able to reversibly change upon temperature. Such materials have been studied for buildings and vehicles to get an automatic control of the solar transmission.
Thermochromism occurs in many organic and inorganic liquids and solids. Transition metal oxides and sulphides that are of particular interest include vanadium oxides, nickel sulphide, nitric oxide, ferrous sulphide, titanium oxide and ferrous oxide. Of all the different types of transition metal oxides, VO\(_2\) has been studied the most because its transition temperature lies near room temperature and hence appropriate for technical applications. Crystalline VO\(_2\) exhibits a change in electrical resistivity in the order of 10\(^3\) - 10\(^5\) at 68°C with a thermal hysteresis width of 2 to 5°C upon heating and cooling down. These features make VO\(_2\) films suitable for application in thermal sensing and switching.

Thin surface films play a significant role in many processes in engineering, chemical, semiconductor and material sciences. Thin films are widely used in optical devices as mirror coatings, interference filters, absorption filters, antireflective coatings and protective coatings to prevent abrasion and degradation of optical properties. Other applications include thin conducting or insulating films in electronics industry, temperature control of objects in outer space and as optical and thermal detectors.

Thin films of VO\(_2\) have been prepared by several methods. These include: metal-organic chemical vapor deposition (Takahashi and Kanamori, 1989), evaporation (Case, 1990), sputtering (Chain, 1986) and sol-gel dip coating (Speck et al., 1988; Yin et al., 1996). The choice of deposition technique depends on several selection criteria such as what material is to be deposited, permissible cost of coating, rate of deposition, deposit-
substrate adherence, limitations imposed by substrate, global abundance of material and availability of apparatus.

Major techniques of making surface coatings and thin films fall in three broad categories namely: sputtering, evaporation, and chemical vapor deposition (CVD). Evaporation involves a vacuum chamber with an evaporation source, for example a resistive wire, and a substrate onto which thin film is to be formed. The material to be evaporated in the vapor source is heated until the atoms vaporize out in to the chamber. The atoms of the evaporant then condense on the substrate surface and form the thin film. The chemical vapor deposition takes place inside a ‘reactor’. The object onto which the thin film is to be grown is placed inside the reactor in a stream of gas, which contains the raw materials - the reactants, of the coating. The gas flows around the object and the reactants adsorb on the surfaces where chemical reactions, surface diffusion and lattice incorporation take place. Afterwards byproducts desorb and form the thin film on the object. Sputtering, the method used in this work, has a vacuum chamber containing the raw material of the thin film and a substrate where the film is to be grown. In the chamber, a low pressure, inert gas is present and this gas is used to set up a glow discharge. Energetic ions of the gas then bombard the target and knock out the target atoms. The atoms move to the substrate where they condense and form the thin film.

1.3 Literature review

Thin-film coatings are characterized by the presence of materials with one of exceedingly small dimension and with interfaces that are of prime importance in determining the
structure’s overall properties. The large surface-to-volume ratio characteristic of thin films permits great differences in their microstructure composition and resultant properties compared with bulk materials.

A thermochromic smart window should incorporate a material, which diminishes the radiative influx as the temperature rises so that automatic temperature stabilization is accomplished. The hypothetical performance of the smart window involves two things. First at low temperatures the coated glass transmits solar radiation quite well. Secondly on increase of temperature beyond the transition temperature, $T_c$, the glass switches to metallic phase and reflects the infrared solar radiation thus lowering the flux of radiation through the window. More than 40 transition metal oxides and rare-earth metal based compounds exhibit a metal-semiconductor phase transition observed as a sharp and reversible change from semiconducting to metallic conduction at a well defined temperature, $T_c$ (Sobhan et al., 1994). From the work of Adler (1972), figure 1.1, it is apparent that unlike other materials that exhibit transition, the transition temperature is closest to the range useful for solar energy control in buildings. The dark vertical band in figure 1 is at the temperature range of interest ($\sim$20°C to 30°C). The optical properties of VO$_2$ change appreciably in the visible region having low reflectivity in the metallic phase. In the infrared region between 2 and 12µm wavelengths, VO$_2$ exhibits a decrease in transmission and an increase in reflectivity upon irradiation with light. In the visible wavelengths, where absorption is relatively high in both phases this contrast in optical behavior is not as pronounced.
Crystalline VO$_2$ is characterized by a transition temperature $T_c = 68^\circ$C. The metal has its plasma wavelength in the near infrared. The infrared solar radiation is therefore reflected off at temperature higher than 68°C. It is transmitted at temperatures lower than 68°C. This transition temperature is too high for normal window applications. It is imperative therefore to suppress it to vicinity of normal comfort level temperatures of about 20 to 30°C.

Figure 1.1 Conductivity vs. reciprocal temperature for several transition metal compounds (Adler, 1972)

The transition temperature, $T_c$, can be depressed by several techniques (Babulanam et al., 1987), such as replacement of some vanadium atoms by tungsten (W) (Kivaisi et al., 1994), molybdenum (Greenberg, 1983), niobium (MacChesney and Gaggenheim, 1969) and rhenium (Grangvist, 1991). The other technique is by replacement of oxygen atoms.
by fluorine (Chamberland, 1971). Alternatively $T_c$ can be reduced by introducing stress (Case, 1989) either by use of a suitable substrate or by applying an over-layer (Duchene et al., 1972). Alloying with a small amount of tungsten appears to be the most efficient way in reducing $\tau_c$ and W amount has recently been reported for sputter-deposited $V_{1-x}W_xO_2$ films (Jin et al., 1997).

A high luminous transmittance is imperative for the windscreen and other car windows: it is also often desired for windows in buildings. Further, a low reflectance may be desired both for architectural and automotive windows especially in hot climates. These requirements lead to considerations of antireflection coatings, which can be produced by large area sputter technology. Research has shown improvement on increasing transmittance and reducing reflectance by utilizing changes in the real coefficient of the index of refraction (Babulanam et al., 1986). Vanadium dioxide films lender themselves well to these properties and improvements. From these and the fact that they can cut on energy expenses if properly utilized, as earlier mentioned, leads to further need for their study.

A major problem with thin films is that the resulting properties are quite often process dependent. In other words, even if a coating is prepared from a material whose behavior is well known, the coating may have different optical properties. The increasing use of reactive preparation processes further underlines the problem. In particular it has been difficult to form thin films of a VO$_2$ single phase due to the complex V-O system. The desired VO$_2$ phase is just one of the nine of vanadium–oxygen phases. The others are
Because of the existence of this large number of distinct vanadium-oxygen phases with different crystalline structures, the stabilization of pure VO$_2$ films is very sensitive to the deposition conditions. The substrate temperature and the oxygen partial pressure can strongly influence the stoichiometry of the deposited film. Figure 1.2 (Kivaisi and Samiji, 1999) shows the variation of sheet resistance ratio with oxygen flow rate for radio frequency (rf) sputtered vanadium dioxide films. From the figure it is apparent that the sheet resistance of VO$_2$ films investigated in this study was very sensitive to the variation of the oxygen flow rate.

Figure 1.2 Variation of sheet resistance ratio with oxygen flow rate for rf sputtered vanadium dioxide films (Kivaisi and Samiji, 1999)

Figure 1.3 shows the temperature-dependent electrical conductivity for different vanadium oxide crystals as compiled from literature (Babulanam et al., 1986). The transition
temperatures of the various vanadium oxides are displayed and they can be used to identify a certain vanadium oxide phase from the others.

Figure 1.3 Temperature dependence of electrical conductivity for different vanadium oxide phases. Arrows denote the direction of change for hysteresis transitions (Babulanam et al., 1986).

With regard to deposition conditions, VO\textsubscript{2} thin films have been formed by variety of techniques, which require substrate temperatures in the region of 400-500°C. Deposition of VO\textsubscript{2} films at 400°C has been reported for DC planar reactive magnetron sputtering (Kusano et al., 1988). Low temperature lead to decreased crystallite size and the V-O system becomes less favorably reactive to the formation of VO\textsubscript{2}, resulting in the degradation of phase properties. Extrinsic stress in film layers (due to differential thermal expansion) is higher at elevated temperatures (≥ 500°C), often resulting in poor adhesion. For example, both reactively evaporated and thermally oxidized VO\textsubscript{2} thin films deposited near 500°C onto ZnS or ZnSe are known to delaminate. A substrate temperature of 400°C is therefore best for VO\textsubscript{2} deposition.
The magnitude of the resistivity change and the narrowness of the hysteresis are very sensitive to the stoichiometry and the crystalline structure of the VO$_2$ films, these parameters are therefore good indicators of its quality. Resistivity ratios between $10^3$ and $10^4$ have been obtained for VO$_2$ films deposited onto sapphire substrates by DC planar diode reactive magnetron sputtering (Fuls et al., 1967), rf planar diode reactive sputtering (Griffiths and Eastwood, 1974), reactive ion beam sputtering (Chain, 1986), ion assisted reactive evaporation and annealing (Case, 1984) and reactive evaporation (Nyberg and Burhman, 1987). The deposition of thin films of VO$_2$ with high transition resistivity ratios ($\rho_S/\rho_m$), requires deposition procedures that yield films with a minimum density of band-gap states in the semiconductor phase and a low resistivity in the metallic phase (Kusano et al., 1988). $\rho_S$ denotes resistivity in the semiconducting state and $\rho_m$ resistivity in metallic state. Polycrystalline films are usually fabricated in most deposition cases. A polycrystalline film is characterized by reduced sharpness in the changes in electrical and optical properties upon switching, as well as a large thermal hysteresis resulting in unexpected different temperature responses between the heating and cooling. On the other hand, it has been known that a single crystal VO$_2$ exhibits much sharper changes in electrical and optical properties with little thermal hysteresis (Goodenough, 1971). Sharp changes in electrical and optical properties upon switching imply higher sensitivity and control efficiency, and a little hysteresis means a better temperature response between heating and cooling cycles. It is therefore very important to fabricate high quality VO$_2$ films with electrical and optical properties near those of the single crystal. Our literature search shows that no report exists on systematic study on multiple thermal switching effect...
on VO₂ films. DC planar reactive magnetron was the preferred method because of its wide area coating capabilities. The method is suitable for depositing thermal control coatings commercially (Boyle et al., 1968). The complexity of the V-O phase diagram also provides an excellent vehicle for investigating the reactive sputtering process. Reactive deposition is a cheaper alternative to rf magnetron sputtering of compounds because DC power supplies are cheaper and target materials cheaper. Furthermore the method gives a comparatively thin coating which is desirable for a window (Babulanam et al., 1986).

1.5 Objectives

The aim of this work was to produce thin films of VO₂ by DC planar reactive magnetron sputtering, with good optical, electrical and structural properties and to determine the effect of multiple thermal switching about the transition temperature on them. The objectives of the research are therefore summarized as follows:

(i) Prepare vanadium dioxide films by DC planar reactive magnetron sputtering.

(ii) Characterize the electrical and optical properties of the films at the transition temperature before and after thermal cycling.

(iii) Determine the optical constants (n and k) of the films by ellipsometry.

(iv) Perform structural analysis before and after thermal cycling.
1.6 Rationale

Accurate knowledge of the properties of thin surface films is necessary for their effective and efficient utilization. The quality of the deposited films is very sensitive to the deposition technique as well as deposition parameters such as deposition rate, oxygen partial pressure, substrate temperature and annealing, and hence play a crucial role to produce films of adequate stoichiometry. Correlation of film structure and properties with deposition conditions provide important guidance for optimization of materials to meet a given application. The demand for smart windows and the existing thin film technology to modify the surface of window glass has led to an intense research in materials that can realize the energy efficient window. Vanadium dioxide has been found to be among the most promising materials for use in energy efficient windows. Its stability about the transition temperature upon multiple switching needs to be established if it shall have to be used successfully.
CHAPTER TWO
THEORY

2.1 Introduction
This chapter gives an overview of the basic theory of the interaction of radiation with matter. The concept of ambient radiation, which forms the basis of studies in this area is discussed here. Thin film production and in particular sputtering technology, which was used to fabricate the thin films are also discussed. The growth of films and the thin film optics, which gives the necessary theory for the exploitation of the spectral selectivity using materials in thin film form, are briefly mentioned. We have also given the general theory of ellipsometry, which give rise to the determination of a material's optical constants. The theory on vanadium dioxide, the main material in this project, concludes the chapter.

2.2 Ambient Radiation
Spectral selective surfaces are characterized by an appreciable variation in optical properties. These properties are functions of wavelength. The concept of spectral selectivity derives its practical meaning from the radiative properties of our natural surroundings. This radiation can be understood by starting from an ideal black body whose emitted spectrum referred to as the Planck’s spectrum is uniquely defined as in equation (1). Planck’s law is a consequence of the quantum nature of the electromagnetic radiation.
\[ q_\lambda = \frac{c_1 \lambda^{-5}}{e^{c_2/\lambda T} - 1} \]  

where \( q_\lambda \) is the monochromatic emission at wavelength \( \lambda \) and of units Wm\(^{-2}\). \( T \) is the absolute temperature and \( c_1 \) and \( c_2 \) are constants.

To obtain the thermal radiation of a material the Planck spectrum is multiplied by a ratio called the emittance, \( e_\lambda \).

Fig. 2.1 shows Planck spectra for two temperatures close to room temperature. The spectra are bell shaped, a consequence of Planck's law and they are confined to the \( 2 < \lambda < 50 \) \( \mu \)m range, where \( \lambda \) is the wavelength. Due to Wien's displacement law in equation (2), the peaks of the two spectra lie at different wavelengths.
\[ \lambda_{\text{max}} = \frac{2898}{T} \]  

where \( \lambda_{\text{max}} \) is the peak value for the expression of \( q_\lambda \) and \( T \) is the absolute temperature. The constant has units \( \mu \text{mK} \).

Solar radiation is emitted at \( 0.3 < \lambda < 3 \mu \text{m} \) interval and is peaked at approximately \( 0.5 \mu \text{m} \). Atmospheric absorption modulates the solar radiation at ground level and is also of importance for thermal radiation given off towards the sky. During clear weather, most of the solar radiation at \( 0.3 < \lambda < 1 \mu \text{m} \) and the thermal radiation at \( 8 < \lambda < 13 \mu \text{m} \) are transmitted through the full atmospheric envelope. The luminous radiation is determined by the sensitivity of the light-adapted human eye. The luminous spectrum extends from over \( 0.4 < \lambda < 0.7 \mu \text{m} \), with a peak at approximately \( 0.55 \mu \text{m} \). Thus only part of the solar radiation is useful for vision. The higher the temperature of the black body, the shorter the wavelength for the peak of the curve. Thus the spectrum of black body radiation do not overlap by appreciable amount. From the foregoing discussion of the physical laws of physics governing the selective surfaces, it follows that a material or surface can be found or synthesized that can differentiate in their absorption, reflection or transmission characteristics of radiation.

Thus the radiative properties comprise of the absorptance \( A \), reflectance \( R \), transmittance \( T \) and emittance \( E \), each signifying a certain fraction of incident, or maximum emitted, radiative power. Energy conservation dictates that at each wavelength, \( \lambda \), one has

\[ A(\lambda) + R(\lambda) + T(\lambda) = 1 \]  

and from Kirchoff's law for thermodynamic equilibrium
Pertinent wavelength-averaged radiative properties can be defined by integrating over the eye's sensitivity curve, which gives the luminous (lum) performance, a typical solar (sol) spectrum, which gives the thermal (therm) radiative performance. Quantitative data can be obtained from the general relation (Grangvist, 1991)

\[ \chi_r(\theta) = \frac{\int d\lambda \phi_r(\lambda) \chi(\lambda, \theta)}{\int d\lambda \phi_r(\lambda)} \]

where \( \chi \) is A, R, T or E; \( \theta \) is the angle from the normal for the incident or emitted radiation; and \( \gamma \) denotes lum, sol or therm. In principle angle averaged properties can be specified by integration over \( \theta \).

2.3 Thin Films

2.3.1 Thin Film Production

2.3.1.1 Sputtering Technology

Sputtering is the process whereby atoms or molecules of a material are ejected from a target by the bombardment by high energy particles. More significantly, reactive sputtering, the process discussed here, is the method to deposit films which have a different composition from the target by adding a gas to the sputtering system to produce a material by reaction of the gas and the target material. Material is ejected from the target in such a way as to obtain usable quantities of material, which can be coated directly onto substrates. The reaction may be controlled to dope the film with the desired percentage of the gas or enough gas may be supplied to ensure complete reaction of the sputtered metal. To obtain sputtering as a useful coating process a number of criteria
must be met. Firstly, ions of sufficient energy must be created and directed towards the surface of a target to eject atoms off the material (fig. 2.2). Secondly, ejected atoms must be able to move freely towards the object to be coated with little impedance to their movement. This is why sputter coating is a vacuum process; low pressures are required (i) to maintain high ion energies and (ii) to prevent too many atom gas collisions after ejection from the target. The concept of mean free path (MFP) therefore becomes useful. Fig 2.3 shows how the MFP varies with pressure and it can be seen that in order to obtain relatively unimpeded travel through a gas it is necessary to operate at pressures of 1 Pa ($10^{-2}$ mbar or better). All cathodic processes require a plasma or glow discharge in order to work. The plasma may be generated by direct current (DC) or radio frequency (rf) power.

To overcome the problem of low ionization at low pressures a magnetron source design is used at the diode sputtering target. The magnetron uses the principle of applying a specially shaped magnetic field such that electron traps are created so that $E \times B$ drift currents close in on themselves. The situation is such that primary and secondary electrons are trapped in a localized region close to the cathode (target) into an endless ‘racetrack’. In this manner their chance of experiencing ionization is vastly increased and so the ionization efficiency is increased too.
Fig 2.2 Schematic diagram of DC diode sputtering process chamber

Fig 2.3 Typical variation of mean free path with pressure
2.3.1.2 Sputtering yield

When ions impinge on a surface different types of processes occur: (i) ion scattering in the target with the ion being likely to be neutralized in the process, (ii) secondary electron ejection, (iii) ion implantation, with the ion being permanently buried in the target, (iv) radiation damage in the target with structural rearrangements varying from simple vacancies and interstitial to more severe lattice defects, and (v) sputtering in which the ion impact sets up a series of collisions between target atoms ultimately leading to the ejection of one of these. All these processes take place when a glow discharge is set up but of course the sputtering is the most interesting. To be able to quantify it, we define the sputtering yield as the number of atoms ejected from the target by one incident ion. The sputtering yield increases with increasing energy and mass of the ions. There exists a sputtering threshold between 5-25eV for most metals, where the lower limit is set by the sublimation energy. The yield increases very rapidly for energies above threshold, followed by a region of linear proportionality and then approaches saturation. At very high energies the yield decreases because of the increasing penetration depth since all atoms colliding with the ions are not able to reach the surface to escape. The yield is also dependent on the angle of incidence of the ion. It is found to increase with increasing angle and to reach a maximum. The pressure of the gas present in the vacuum chamber affects the yield. As the pressure is increased, the number of ions produced is increased but their energies are decreased, since the yield increases proportionally with the number of ions but decreases with decreasing ion energy linearly or less than linearly with a net increase in the total number of ejected atoms results. Due to collisions between the ejected atoms and the gas at higher pressures the ions will hit the target at higher oblique
angles which helps to increase the yield. There is an upper limit though, since further increasing the pressure will lead to so many collisions that the atoms are prevented from reacting with the substrate. The effect of target temperature on the yield is rather negligible. It is only at very high temperatures that there is a rapid increase due to accompanying thermal evaporation.

2.3.1.3 Thin film growth

The structure of a thin film has a big influence on many physical properties of the film and it is generally dependent on the substrate and film materials. There are three different ways a film can grow on a surface. These are the island growth mode, the layer mode and the layer plus island growth mode. The most common of these is the island growth mode. It consists of several stages of film growth. First small clusters are nucleated on the substrate surface and grow into islands and a network of the condensed phase occurs. Finally the channels in the network are filled in and a continuous film is grown as illustrated in figure 2.4. Island growth takes place when cohesive forces of the atoms of the growing film are stronger than the adhesive forces between the atoms and the substrate. On the other hand, if the adhesive forces are stronger than the cohesive forces of the atoms making the film, the film formed is a monolayer on the surface. This layer is then covered by progressively loose layers. An intermediate case is the layer plus island growth mode, where after a couple of mono-layers have been formed, the atoms are loosely bound to the substrate that island takes over. The substrate temperature has a critical influence on the structure of the film. At low substrate temperatures, i.e. \(< 0.3T_m\) where \(T_m\) is the melting temperature, the films have a columnar structure separated by
voids. The diffusion mobility is low and the structure is mainly determined by shadowing effects, i.e. the upper tips of the columns are more likely to collect the impinging atoms than the lower valleys. The as-deposited films have great hardness but a low lateral strength. At higher temperatures surface diffusion determines the structure which consists of dense columnar grains. When the temperature is beyond $0.8T_m$ the film structure consists of isotropic grains. The deposited atoms can diffuse through the bulk of the coating, which gives films deposited at high temperatures bulk like properties. At high temperatures sputtered atoms have a high energy which make them mobile and they can easily diffuse on the surface. Thus the films become dense and have few defects.

Fig. 2.4 Stages of structure evolution in polycrystalline thin films. 1:nucleation; 2:crystal (grain) growth; 3:coalescence; 4:filling the channels; 5:growth of continuous film. Crystals before coalescence are marked by broken line; dark circles mark adatom, bright circles impurity species.
2.3.2 Thin Film Optics

2.3.2.1 Single layer film

The incidence of electromagnetic (EM) wave upon the interface between two media of different optical properties leads to the splitting of the EM wave into two waves: a transmitted wave that proceeds into the second medium and a reflected wave propagating back into the first medium. An EM field is represented by two vectors: the electric vector, $\vec{E}$ and the magnetic induction vector, $\vec{B}$. The description of the effect of the EM field on material objects makes it necessary to introduce another set of vectors namely; the electric current density $\vec{j} = \sigma \vec{E}$, the electric displacement $\vec{D} = \varepsilon \vec{E}$ and the magnetic vector $\vec{H} = \vec{B}/\mu$, where $\sigma$, $\varepsilon$, and $\mu$ are the electrical conductivity, the electric permittivity and the magnetic permeability respectively. The space and time derivatives of the five quantities above are related by Maxwell’s equations, which are valid at every point in whose neighborhood the physical properties are continuous. The EM propagation in a homogeneous material is thus completely described by Maxwell’s equations (Heaven’s, 1955) as follows:

$$\nabla \times \vec{E} = -\frac{1}{c} \frac{\partial \vec{B}}{\partial t}$$

(6)

$$\nabla \times \vec{H} = \vec{j} + \frac{1}{c} \frac{\partial \vec{D}}{\partial t}$$

(7)

$$\nabla \cdot \vec{D} = \rho$$

(8)

$$\nabla \cdot \vec{B} = 0$$

(9)
The study of the optical properties of a given material normally incorporates its transmission (T) and reflection (R) behavior. In some cases, as in determination of optical constants, the incident radiation intensity and the state of polarization are considered too. The T and R properties of a material are related to the magnetic and dielectric permeabilities. The latter are characteristics of the specific material.

The problem of determining the light transmitted and reflected at a boundary separating two optically different media is resolved by applying boundary conditions to the solutions of Maxwell's equations (Lorrain and Corson, 1970). The reflectance and transmittance of a thin film on a substrate can be used to derive the complex dielectric function of the film. This function is the fundamental material property that describes the optical behavior of the film. The dielectric function or the permeability, $\varepsilon = \varepsilon_1 - i\varepsilon_2$, is related to the complex refractive index by the following equations:

$$N = n - ik$$  \hspace{1cm} (10)

$$\varepsilon = N^2$$  \hspace{1cm} (11)

resulting in

$$\varepsilon_1 = n^2 - k^2$$  \hspace{1cm} (12)

$$\varepsilon_2 = 2nk$$  \hspace{1cm} (13)

Either set of $(\varepsilon_1, \varepsilon_2)$ and $(n, k)$ are called optical constants. The constants are properties dependent on the wavelength of the material. $\varepsilon_1$ is related to the polarizability and $\varepsilon_2$ is the true optical absorption. $n$ is the refractive index and $k$ is the extinction index, or the absorption coefficient. In order to determine the above quantities, we review the theory of
the optical properties of thin films on a substrate following Heavens (1955) and Born and Wolf (1980).

For the infrared, visible and ultraviolet spectral regions, the electromagnetic radiation is considered to be propagating as plane waves. Consider plane waves incident upon a specimen composed of one or more homogeneous phases, separated by specular surfaces. The amount and degree of transmission, reflection and refraction are direct measures of the material parameters.

Let us consider first an interface between two media denoted by i and j. The amplitude ratios for transmitted and reflected light are denoted by \( t_{ij} \) and \( r_{ij} \), respectively. The dielectric permeabilities of the two media are \( \varepsilon_i \) and \( \varepsilon_j \), respectively. The light is incident from medium 'i' with an angle \( \theta_i \) which is shown in fig. 2.5

![Fig. 2.5 Symbols used for deriving Fresnel relations for an interface between two media.](image)

The amplitude ratios are given by the well known Fresnel relations:
\begin{align*}
    r_{s}^{y} &= \frac{(\varepsilon_{r})^{\frac{1}{2}} \cos \theta_i - (\varepsilon_{r} - \varepsilon_{i} \sin^2 \theta_i)^{\frac{1}{2}}}{(\varepsilon_{r})^{\frac{1}{2}} \cos \theta_i + (\varepsilon_{r} - \varepsilon_{i} \sin^2 \theta_i)^{\frac{1}{2}}} \\
    r_{p}^{y} &= \frac{(\varepsilon_{r})^{\frac{1}{2}} (\varepsilon_{r} - \varepsilon_{i} \sin^2 \theta_i)^{\frac{1}{2}} - \varepsilon_{j} \cos \theta_i}{(\varepsilon_{r})^{\frac{1}{2}} (\varepsilon_{r} - \varepsilon_{i} \sin^2 \theta_i)^{\frac{1}{2}} + \varepsilon_{j} \cos \theta_i} \\
    t_{s}^{y} &= \frac{2(\varepsilon_{r})^{\frac{1}{2}} \cos \theta_i}{(\varepsilon_{r})^{\frac{1}{2}} \cos \theta_i + (\varepsilon_{r} - \varepsilon_{i} \sin^2 \theta_i)^{\frac{1}{2}}} \\
    t_{p}^{y} &= \frac{2(\varepsilon_{r} \varepsilon_{j})^{\frac{1}{2}} \cos \theta_i}{(\varepsilon_{r})^{\frac{1}{2}} (\varepsilon_{r} - \varepsilon_{i} \sin^2 \theta_i)^{\frac{1}{2}} + \varepsilon_{j} \cos \theta_i}
\end{align*}

where 's' and 'p' denote s-polarized (electric vector is perpendicular to plane of incidence) and p-polarized (electric vector is parallel to plane of incidence) light, respectively.

If we consider a thin homogeneous film on a transparent substrate, the above equations can be used to describe the amplitude reflection and transmission at each interface. The full reflection and transmission of the film must be calculated including phase factors. The phase change \( \delta \) of the beam when traversing the film of thickness \( d \) is given by

\[ \delta = \frac{2 \pi d (\varepsilon - \sin^2 \theta_i)^{\frac{1}{2}}}{\lambda} \]
Figure 2.6 Geometry for the interfaces in a thin film (2). 'f' and 'b' denote light incident from the front and back respectively. Symbol s denotes s-polarized.

If we neglect the backside of the substrate, we get the following expressions for the reflectance and transmittance of a thin film with geometry in fig 2.6.

\[
R_{2s}^f = \frac{r_{12}^{12s} + r_{32}^{23s} e^{2i\delta}}{1 + r_{12}^{12s} r_{32}^{23s} e^{2i\delta}} \quad (19)
\]

\[
R_{2p}^f = \left| R_{2s}^f \right|^2, \quad R_{2p}^f = \left| R_{2p}^f \right|^2 \quad (20)
\]

\[
t_{2s,p}^f = \frac{i_{12}^{12s,p} i_{23}^{23s,p} e^{2i\delta}}{1 + r_{12}^{12s,p} r_{32}^{23s,p} e^{2i\delta}} \quad (21)
\]

\[
T_{2s,p}^f = \left| t_{2s,p}^f \right|^2, \quad T_{2p}^f = \left| t_{2p}^f \right|^2 \quad (22)
\]

Relations of the same form are obtained by interchanging indices 1,3 for light incident from the back side i.e. from the substrate. The intensities are proportional to \( |r_2|^2 \) and \( |t_2|^2 \), and are denoted by capital letters, \( R_2 \) and \( T_2 \). If the substrate is metallic, the transmittance is zero, and the only quantity of importance is the reflectance.
If we include the back side of a transparent substrate, a more complicated situation exists, and multiple reflections in the substrate must be taken into account. The reflections are incoherent for large substrate thickness and are included through addition of the intensities of the multiply reflected beams. The final expressions for the reflectance and the transmittance are (Born and Wolf, 1980)

\[
R_s = \frac{R_s^f + T_s^f T_s^b R_s^b}{1 - R_s^b R_s^3} \\
T_s = \frac{T_s^f T_s^b}{1 - R_s^b R_s^3}
\]

where $R_{3s,p}$ and $T_{3s,p}$ are the reflectance and transmittance expressions pertaining to the backside of the substrates. Analogous expressions are obtained for the p-components.

### 2.3.2.2 General Theory on Ellipsometry

Ellipsometry is an optical technique for the observation and characterization of processes occurring within thin films or interfaces between two media. It is based on the polarization transformation that occurs when a beam of polarized light is reflected from or transmitted through the interface or film. The transformation consists of two parts: (i) a phase change, and (ii) an amplitude change and is determined by the optical properties of the material, which are related to the fundamental material parameters such as the dielectric function. These changes are different for incident radiation with its electric vector oscillating in the plane of incidence (p-state polarization) as compared to that for
radiation with its electric vector oscillating perpendicular to the plane of incidence (s-state polarization). An ellipsometer measures the result of these two changes, which are typically presented at two angles, $\varphi$ and $\Delta$. The parameters $\varphi$ and $\Delta$, often referred to as the ellipsometric angles, can be used in Ditchburn relations viz.

$$\varepsilon_1 = \sin^2 \phi_1 [1 + \tan^2 \phi_1 (\cos^2 2\varphi - \sin^2 2\varphi - \sin^2 \Delta)] / (1 + \sin 2\varphi \cos \Delta)^2 \quad (26)$$

$$\varepsilon_2 = (\sin^2 \phi_1 \tan^2 \phi_1 \sin 4\varphi \sin \Delta) / (1 + \sin 2\varphi \cos \Delta)^2 \quad (27)$$

to obtain dielectric functions $\varepsilon_1$ and $\varepsilon_2$, where $\phi_1$ is the chosen angle of incidence of laser beam falling on the sample to be analyzed. From Drude's relations a simultaneous equation

$$n^2 = \frac{1}{2} \left[ \varepsilon_1 + \left( \varepsilon_1^2 + \varepsilon_2^2 \right)^{1/2} \right] \quad (28)$$

$$k^2 = \frac{1}{2} \left[ -\varepsilon_1 + \left( \varepsilon_1^2 + \varepsilon_2^2 \right)^{1/2} \right] \quad (29)$$

is solved and positive roots taken since $n$ and $k$ are real.

2.4 Material of Study: Vanadium dioxide

Vanadium dioxide has an induced first order phase transition where it transforms from a semiconducting to a metallic state. This transition takes place at 68°C for crystalline VO$_2$ and includes large changes in optical, electrical and magnetic properties. It has been shown that the metal-insulator transition of VO$_2$ can be explained by changes in the 3d-band structure, considering the crystal structure change. In the metallic phase at higher temperatures, VO$_2$ has a tetragonal rutile structure, as shown in fig 2.7 (M). The five
fold-degenerate d levels of the V$^{4+}(3d^1)$ ion are first split into doubly degenerate $e_g$ levels and triply degenerate $e_{2g}$ levels in the octahedral crystal field, figure 2.8. The $e_g$ orbitals are strongly hybridized with the O 2$p\sigma$ orbitals and have a large bandwidth. The $t_{2g}$ levels are further split into the $d_{||}$ and $\pi^*$ levels, by the orthorhombic component of the tetragonal crystal field. Thus the $d_{||}$ and $\pi^*$ bands are situated at the lowest energies around the Fermi level. Since the $\pi^*$ orbitals are more hybridized with the O 2$p\pi$ orbitals than the $d_{||}$ orbitals, the $\pi^*$ bands have higher energies and a wider bandwidth.

![Diagram](image)

**Fig 2.7** Tetragonal rutile type crystal structure of VO$_2$ in the metallic phase (M). In the insulating phase (I), the VO$_2$ lattice is distorted to the monoclinic crystal structure with the pairing of vanadium ions (Shin et al., 1990)
On the other hand the $d_{\parallel}$ orbitals are rather nonbonding. Thus the $d_{\parallel}$ and $\pi^*$ bands overlap at the Fermi level as shown in fig 2.9.

![Energy level diagram](image)

**Fig. 2.8 Crystal field splitting of $V^{4+}(3d^1)$ energy levels as calculated by Sommers et al., (1975)**

In the insulating phase, however, VO$_2$ has a monoclinic structure, where the pairing of the vanadium atoms along the C$_2$ axis occurs as shown in figure 2.7(I). Because of the change in the V-O hybridization, the energy of the more hybridized $\pi^*$ band rises above the Fermi level and becomes empty. Furthermore, the $d_{\parallel}$ band is split into two states by the pairing of the vanadium ions along the C$_2$ axis. The Ultra-Photonic Spectra (UPS) in the insulating phase show that the occupied 3d band consists of only a single band ascribable to the lower $d_{\parallel}$ band, figure 2.9, in agreement with Goodenough’s suggestion (Shin et al., 1990).
Figure 2.9 Schematic energy diagram of the 3d bands around the Fermi level for VO$_2$. The energy of 0.2eV is obtained by UPS spectra. The energies of 0.5 and 1.1eV are obtained by ultraviolet reflectance spectra. 0.65eV is a value from the infrared absorption spectra (Shin et al., 1990)
CHAPTER THREE
EXPERIMENTAL PROCEDURES

3.1 Introduction
This chapter gives the procedures used to achieve the objectives of this project. In it we discuss the method of production of vanadium dioxide thin film. This incorporates a description of the coating unit used, substrate cleaning and the setting of various parameters. Measurement of substrate temperature and the accompanying cooling systems are also illustrated. Electrical, optical and structural characterizations are described. Film thickness measurement is also described.

3.2 Thin Film Production
VO₂ films were produced in a BALZERS BAE 250 coating unit by DC planar reactive magnetron sputtering of a vanadium target. A vanadium metal disc of 51 mm in diameter with 99.7% purity was used as the target. The sputtering atmosphere was a mixture of argon and oxygen. The unit is equipped with diffusion and turbo-molecular pumps, which can attain pressure of up to 1.0 x 10⁻⁶ mbar. The system also accommodates a substrate heating and holder facilities, radio frequency (rf)/direct current (DC) power sources, quartz crystal thickness monitor, gas regulating valves for reactive sputtering and allowance for mounting two magnetrons. Other facilities include a cooling system, power control unit (PCU), window for plasma viewing and shutters to cover targets during pre-
sputtering, all as depicted in fig 3.1. The chamber was first covered to the inside with an aluminium foil to avoid coating it too. Ordinary glass slides were used as substrates and measured 38 mm x 26 mm x 1 mm. Before use they were cleaned in several steps. First the glass slides were soaked in warm soap solution for 10-15 minutes and then degreased to remove gross contaminants. The glass slides were then rinsed with distilled water, stack in a rack and then hang in a beaker which is placed in an Ultra-sonic Frequency Sweep (US) cleaner for 20 minutes, a step intended to remove remaining particles not rinsed off by distilled water. After the US the glass slides were then rinsed in ethanol and suspended in ethanol vapor to dry for about 20 minutes. The slides were then stored inside a dessicator with silica gel that absorbed humidity. Caution was exercised in handling the substrates prior to coating in order to avoid undue contamination. Handling was therefore done with a pair of tweezers.

The chamber was loaded with the substrate 15 cm above the target and then pumped down to $3.0 \times 10^{-6}$ mbar in about 2 hours. Thickness was determined using the talystep profilometry because the quartz crystal thickness monitor could not be used for it can only handle temperatures of up to 150°C. The sputtering gas, argon, was introduced at the commencement of heating at a rate of 65.0 ml/min, which made the pressure to rise to $3.0 \times 10^{2}$ mbar. Pre-sputtering or ‘conditioning’ of the target was done for 10 to 15 minutes to clean the target. During this phase, oxides and other surface contaminants such as grease were removed from the surface and deposited on the shutter placed between the target and substrate. This conditioning was necessary every time the target was in contact with a contaminating atmosphere.
Fig 3.1 Across section of the vacuum chamber for the Balzers BAE 250 sputtering unit.
The reactive gas, oxygen, was then let in and after its flow stabilized, the shutter was opened to allow deposition to take place. Pressure with oxygen and argon rose to $3.2 \times 10^{-3}$ mbar.

$\text{VO}_2$ is stoichiometric and hence oxygen flow rate was varied in order to obtain a film with the best electrical and optical switching. In the mean time, the substrate temperature ($\approx 400^\circ C$), DC power of 150 W and the argon flow rate (65 ml/min) were all kept constant. After the timed deposition the chamber was then cooled for one hour before breaking the vacuum and unloading the sample. After initial characterizations, which are given in chapter four, the films were then mounted on a heater for the purpose of thermal cycling. A thermal cycle involved heating the films for two minutes from about 30°C to 100°C which was well beyond the transition temperature. The heater was then switched off to allow cooling of the film back to 30°C. This cooling took 8 minutes and temperature was being monitored through a thermocouple in contact with the film. Characterization was then done after ten, hundred and a thousand times of thermal cycling.

### 3.3 Measurement of Substrate Temperature and cooling system

It is not possible to deposit stoichiometric $\text{VO}_2$ onto a room temperature substrate and therefore the substrate had to be heated to its final temperature of about 400°C. A thermocouple was used to monitor the substrate temperature with time (Figure 3.2). The power controlling unit (PCU101) for the system has digits starting from position 1 to 9, calibration was therefore necessary in order to know the maximum temperature attained at
each position. In this case position 8 was found to be equivalent to the required temperature of 400°C (Figure 3.4) which was a prerequisite for optimal deposition. During heating, the pressure inside the chamber increased slowly as a result of the chamber degassing but eventually came down to the initial value. Heating was done for about 45 minutes after which the temperature stabilized as depicted in figure 3.3.

*Figure 3.2 Measurement of temperature inside the vacuum chamber.*
Cooling of the deposition chamber was done by connecting the chamber to the water supply and return lines via hose couplings as shown in figure 3.4.

Since target heating is so important, the suitability of the target in dissipating this heat is equally important. It is therefore bonded to a water-cooled holder as in fig 3.5.
3.4 MEASUREMENTS

3.4.1 Electrical measurements

The sheet resistances of the films were measured using the two-point probe. The films were fixed onto the probe by four copper pins, which pressed the films firmly on the surface of the probe. The probe was then placed on a hot plate, which had a heat jacket to avoid draughts. The power of the heater was regulated so as to maintain the temperature below 120°C. The temperatures of the films were obtained by placing the 71517B Platinum Resistance Thermometer (PRT) surface probe on the films through an opening made on the probe. The terminals of the probe were connected to the SI SYSTEM MULTIMETER for temperature readings. Two terminals of the probe were connected to the SI 7061 SYSTEM VOLTOMETER for sheet resistance measurements. The sheet resistance measurements were recorded for both increasing and decreasing temperatures. This procedure was followed before and after each set of ten, hundred and a thousand thermal cycles.
3.4.2 Optical Measurements

Optical properties of a material are predominantly determined by composition and microstructure, making optical measurements ideally suited for determining the characteristics of coating structures. Optical methods are particularly attractive because they are non-destructive, capable of in-situ monitoring, yield information in real time and have excellent spectral resolution. Spectrophotometric methods are useful for the determination of the spectral variation of near-normal reflectance and transmittance of coatings, while ellipsometric measurements yield complex refractive indices of thin structures, which can be correlated with structural variations such as layer thickness and dopant densities.

3.4.2.1 Spectral measurements

The optical characterization was carried out by taking (i) spectral transmittance in the range of wavelengths $300 \leq \lambda \leq 2500\text{nm}$ and (ii) the transmission profiles data as a function of temperature at a fixed wavelength ($\lambda = 2500\text{nm}$). These were obtained by use of Perkin Elmer
Lamda 9 Spectrophotometer interfaced to a PC 386 computer as shown in the schematic diagram in fig 3.7. Transmittance measurements were carried out at room temperature (26°C) by running the spectrum over the 300 to 2500nm wavelengths range. To be able to measure transmittance at different temperatures, especially below and above the transition temperature, a heating device was constructed. The heating device consisted of a heater cell, a rectangular cavity of dimensions 1cm x 2cm entrance and exit apertures, made by Formica sheet, that was mounted in the sample compartment of the spectrophotometer. The temperature was measured with a thermocouple in thermal contact with the film and recorded using a Fluke 52 K/J thermometer. These measurements were repeated for the films after each set of thermal cycles.

*Figure 3.7 Spectrophotometer set up*
3.4.2.2 Determination of optical constants

The refractive index $n$ and the absorption coefficient $k$ of the films were determined by ellipsometric method. A conventional reflection ellipsometer (wavelength of 632.8 nm) was used to determine the polarization angles $\Delta$ and $\psi$ at an angle of incident $\phi$, from which $n$ and $k$ were calculated. To accomplish these a number of steps were followed. Initially the ellipsometer basic components were aligned into a straight line, i.e. the line of sight of the laser beam and the spectrometer base scale was recorded. The secondary arm was unlocked and rotated counterclockwise through an angle $(180 - 2\phi)$ where $\phi$ is the chosen angle of incidence. This set the angle between the secondary arm and the laser beam to $2\phi$ and the secondary arm was locked. Reference azimuths for analyzer, $\alpha$ and polarizer, $\pi$, were first determined. The polarizer and compensator were demounted and analyzer rotated until the beam coming out through it as viewed with a white screen was completely extinguished. This analyzer scale reading was recorded. The polarizer was mounted in the place of analyzer and rotated to give the polarizer scale reading at complete extinction of the beam. Polarizer and analyzer were later remounted at their respective positions and either the analyzer or the polarizer rotated through $90^\circ$ from recorded scale readings at extinctions, a procedure, which gave the crossed position. After fine-tuning by use of the detector and amplifier to achieve total extinction the recorded final readings of the analyzer and the polarizer at their crossed positions were defined as the reference azimuths, $\alpha$ and $\pi$, respectively. All through caution was taken not to distort the alignment of the laser beam, the reflecting prism, and the detector aperture.
Next, the Soleil-Babinet compensator was reinstalled in order to align it. This involved, initially, aligning the compensator so that the reflections from the crystal elements fell back upon the source. The knurled-thumb screw was raised to set the indexing head to 0° position. By locking the knurled lock nut the compensator was rotated until extinction resulted and rocked at this position so that its position with respect to the detent positions of the indexing head was fixed. This procedure oriented the crystallographic axes of the quartz elements to 0° and 90° with respect to the incident light polarization vector. The knurled thumb was raised and the indexing head rotated either positive or negative 45°, which made some leakage through the analyzer to be detected. This leakage was completely stopped by adjusting the micrometer head. This procedure gave two positions of extinction within the range of the micrometer drive.

Figure 3.8 Schematic arrangement of the conventional reflection ellipsometer

All components were then locked and adjustments were only made to the micrometer head and indexing head detects. To calibrate the compensator the micrometer was set to the lower limit and then adjusted until the minimum leakage through the analyzer was
obtained. This value was recorded and the micrometer was turned to the second value of extinction. This corresponded to the full order of retardation at the operating wavelength (632.8nm). The VO$_2$ film was placed on the spectrometer table so as to reflect the laser beam through the compensator and analyzer apertures and on to the detector aperture. This set the angle of incidence of the laser beam on the sample at $\phi$. The analyzer and polarizer were approximately set at their reference azimuths respectively. The compensator was set so as to introduce quarter wave retardation by turning the micrometer to a value given by first extinction reading plus quarter of the difference in value readings between the first and second extinctions of the full order retardation. Both the analyzer and the polarizer were rotated counter-clockwise to the next immediate positions of extinction of the laser beam as viewed on a white screen. The exact positions of the analyzer and polarizer extinctions were determined. The final scale readings of the analyzer and polarizer were defined as $A_+$ and $P_+$, respectively. The ellipsometric parameters $\Delta$ and $\psi$ were calculated using the relation

$$\Delta = (A_+ - \alpha) - 90^\circ$$

$$\psi = P_+ - \pi$$

The ellipsometric parameters were then used in the computer program appendix (1) to determine $n$ and $k$.

### 3.4.3 Thickness measurements

A "Taylor Hobson Talystep", a mechanical step gauge, phonograph-cartridge-like stylus-type instrument with a 5 Angstrom ideal resolution limit was used to determine the film physical thickness by tracing over the step-heights at the edges of the films. The steps had
been created on the film by shadow casting or masking the substrates during deposition. The stylus uses a fine pick-up head, suspended normal to the film surface, to scan horizontally over the film surface under investigation. Vertical displacements of the head were monitored, magnified and relayed to a tracer by an electronic amplifier. Periodical calibration checks comprising “pick-up balance”, “phase adjustment”, and “pick-up sensitivity” were done on the instrument. The pick-up balance was to maintain the pick-up head normal to the surface under investigation. Synchrony between the pick-up head and tracer pen was ensured by the phase adjustments. A calibration standard for pick-up sensitivity checks was factory provided along with the instrument. Mechanical vibrations resulting from the movement of the people and machinery impair the displacements of the pick-up head and consequently of the tracer pen. The response of the tracer pen to the amplifier signals may also be interfered with by effects of temperature fluctuations and electrical signals (from other electrical/electronic equipment) on the amplifier. Care was taken to minimize mechanical vibrations and other effects during measurements. Measurements were done on a properly leveled horizontal table. The pick-up head scans horizontally over the sample surfaces and unambiguous traces were thus obtained. Setting of the stylus force to bear on the sample surfaces was done with the pick-up head at the center of the stylus displacements. Care was thus taken to position the samples with the step-heights at the center of the horizontal displacements of the stylus. Traces of the thickness profiles of the films were made. Calculations of the heights of the steps were done using a Table of Vertical Magnifications [Appendix (2)]. The heights so calculated corresponded to the thickness of the films at the points of the steps.
3.5 Structural Characterization

An electron microscope, LEO 910, was used to analyze the diffraction pattern of VO$_2$ films backed by carbon-covered copper grids. The carbon covered copper grids measured 3mm in diameter. An aluminum foil tape was used to mount the carbon films on one section of the glass substrate, so that deposition could take place on it. The other section of the glass substrate was used to analyze the films for electrical and optical properties to ensure that the film had the right sheet resistance and transmittance.
CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

This chapter presents the results obtained and their discussion. The results are for the as-deposited VO₂ films prepared at an oxygen flow rate of 2.41 ml/min, argon flow rate of 65 ml/min and substrate temperature of 400°C. Results of the films after they were temperature recycled for ten, hundred and thousand times are also presented. Specifically we report on diffraction pattern obtained from the as-deposited VO₂ films backed by carbon films on copper grids. We present the thickness trace-out. An analysis of the sheet resistance for the as-deposited and multiply switched films has been done. Transmittance measurements include temperature dependent transmittance and the spectral normal transmittance in the 300 ≤ λ ≤ 2500 nm range for the as-deposited and thermally recycled films as well. Lastly we present the optical constants.

In general, the surfaces of the as-deposited vanadium dioxide films were smooth and uniform and showed excellent adherence to the glass substrates. The films appeared golden brown to the eye in transmitted light characteristic of the conventional "bronze" form of thin film VO₂. The films were quite stable in ambient atmosphere, experiencing no spectral degradation over a period of six months.
4.2. Structural Analysis

Films backed by carbon-covered copper grids were investigated by electron microscopy using LEO 910 instrument operating in diffraction mode. Figure 4.1 shows electron diffraction patterns for the as-deposited VO₂ film. The diffraction pattern are clear rings characteristic of polycrystalline films (Begishev et al. 1977) and also indicate a monoclinic atomic arrangement expected of VO₂ at temperatures below the transition (Jiang et al., 1991). The bright intensity at the center of the pattern was as a result of direct beam of electrons whereas the scattered beams account for the rings. Close inspection of the rings in the pattern reveal spots, which according to Heavens (1955) are from individual crystallites. We could not obtain the diffractograms at temperatures beyond transition temperature because of limitations in heating the sample, within the microscope, to attain the metallic state. Though standard diffractograms were not available the results generally compared well with what is in the literature. The results indicate that polycrystalline films were realized, a step prerequisite for further analysis and treatment as observed in the literature.

4.3 Film Thickness

Step heights were created and measured as described in procedure 3.3.3. Samples of the thin film profile traces as obtained by the "Taylor Hobson Talystep" instrument are as displayed in figure 4.2. Computations of the physical thickness from the step height traces were effected with the aid of the Table of Vertical Magnifications (Appendix 2). The physical thickness was found to be approximately 80nm.
Figure 4.1 Electron diffraction pattern of thin film vanadium dioxide on carbon backed copper grids prepared at 400°C
Figure 4.2 Step height traces at $1 \times 10^5$ magnification for a $\text{VO}_2$ film prepared by DC reactive sputtering on glass slide at 400°C
4.4 Electrical properties

The sheet resistance of the films was measured as described in section 3.3.1. Figure 4.3 shows the variation of sheet resistance in logarithmic scale against temperature in °C for the as-deposited film. The sheet resistance was found to change by three orders of magnitude when the samples were heated from room temperature to temperatures above the transition temperature. A blurred transition was observed specifically for the heating curve but a more abrupt transition for cooling was evident. The observed electrical behavior is in keeping with what is expected of VO₂ film and agrees with observations by other researchers (Kivaisi and Samiji, 1999; Annakarin, 1998).

![Graph showing variation of sheet resistance with temperature](image)

*Figure 4.3 Variation of sheet resistance with temperature for DC reactively sputtered VO₂ films on glass at 400°C*
The electrical switching behavior of thin film VO$_2$ is highly sensitive to the stoichiometry, continuity and structure of the film. The magnitude, sensitivity and temperature of the resistivity change between the switched and un-switched states are all significant. In un-oriented films, as in this case, the influences of grain boundary phases and lattice mismatch can significantly lower the measured electrical properties (De Natale et al. 1989). Therefore in comparison with oriented films the resistivity change is of the order of $10^3$ for un-oriented to (2 to 4) x$10^4$ in oriented. De Natale et al. (1989) attributed this to a combination of overall film density and the enhancement in stoichiometry offered by substrate lattice matching. They observed that the lack of registry at grain boundaries results in a discontinuous propagation of the transformation, requiring additional thermal energy to cross the boundaries. This leads to a broadened transformation width. Case (1984) points out that transition temperature is also a function of intrinsic stress brought about by low energy ion bombardment of pre-deposited thin films. He also hypothesized that hysteresis loop width is correlated to grain size and may also be somewhat dependent on intrinsic stress.

The smeared out transition makes it therefore very difficult to pinpoint the transition temperature from electrical characterization of the films. In the high resistivity polycrystalline samples, a discontinuity of the optical properties may be accompanied by the absence of a jump in resistivity at the phase transition. This may not mean that there is no such a jump in the bulk of the material. The reason is that the equivalent resistance of the sample, is dominated by the series connected and temperature independent large resistance of the crystallite boundaries. Baleisis et al. (1979) accounts for the blurring in
terms of disperseness of the structure of the VO₂ films. They observe that, even in single crystal films the phase transition is initiated in separate nuclei, which in all likelihood, is due to the elastic stresses and mechanical flaws in the film. The principal flaws encountered in polycrystalline films are inter-granular barriers, which would be in large concentrations in this case. The temperature of each nucleating center will differ radically and the existence of both metallic and semi-conductor phases in the vicinity cannot be ruled out at this point. This is, in their opinion, the basic reason for the temperature induced smearing out of the phase transitions in such samples and we concur with them. It was therefore not possible to use the electrical characterization results to determine the transition temperature.

Figure 4.4 shows the variation of sheet resistance in logarithmic scale against temperature before and after ten, one hundred and one thousand times of thermal cycling. The results show a slight increase in sheet resistance at semiconducting state and metallic state as the number of cycles increase reflecting a vertical shift but retaining the switching effect. There is a partial overlap between the curves of the as-deposited and the one of after ten cycles. Another overlap is evident between the curves of after one hundred cycles and the one of thousand cycles. From these observations, it can be concluded that the sheet resistance only slowly changes upon multiply switching the films. The order of change remains also relatively the same upon recycling the films about the transition temperature. Grain structure, stoichiometry and the crystallographic phase contribute to the resistivity ratio.
Figure 4.4 Sheet resistance variation with temperature for DC reactively sputtered VO$_2$ film before and after ten, hundred and thousand thermal cycles.

The results of sheet resistance variation with temperature therefore point towards a stabilized film, which implies good grain structure, stoichiometry and a stable crystallographic phase. This is therefore a desirable quality of the films because their deterioration in sheet resistance would not make them promising for use in dynamic windows.
4.5 Optical properties

As described in section 3.3.2, the measurement of temperature dependent transmittance required use of a thermocouple. To eliminate the cooling effect caused by the part of junction not in contact with the film, we had to correct the readings obtained by the thermocouple thermometer. To do this, we noted that the Platinum Resistance thermometer probe had a flat surface, which made a good contact with the film. Figure 4.5 shows the temperature correction curve with the best line fitted. From the equation of the best line fit the correct value of temperature was given by
\[ P = \frac{(T - 1.3881)}{0.8092}, \]
where \( T \) was the thermocouple thermometer reading.

Figure 4.5 Temperature correction curve for the thermocouple thermometer
Measurements of the temperature dependent transmittance at $\lambda = 2500$ nm of the as-deposited film are plotted out in figure 4.6. The results show that the film exhibits thermochromism i.e. the transmittance has a sharp contrast between the semiconducting state at $32^\circ$C and the metallic state at $80^\circ$C, changing from 69 $\%$ to 16 $\%$ respectively. These results are in agreement with work by Babulanam et al. (1986), Annakarin (1998) and Kivaisi et al. (1999). A transition temperature of $69^\circ$C was observed. Here we define transition temperature as the midpoint of the heating curve i.e. transmittance at semiconducting state and transmittance at the metallic phase divided by two. A hysteresis loop width of $15^\circ$C was obtained, where we define the hysteresis as the width at half-maximum.

![Temperature dependent transmittance curve for the as-deposited DC reactively sputtered VO$_2$ film on glass at 400 $^\circ$C](image)

*Fig 4.6 Temperature dependent transmittance curve for the as-deposited DC reactively sputtered VO$_2$ film on glass at 400 $^\circ$C*

It is important to note that there is no much smearing out of the transition for the optical
transmission as observed with the electrical properties. De Natale et al. (1989) observe that while the resistance change in the films is strongly dependent upon the nature of the grain boundary structures and percolation effects, the optical transmission is controlled by the number of individual grains that have transformed. The optical transmission is therefore fairly insensitive to the presence of local non-stoichiometric grain boundary structures, although the switching response as a function of temperature is strongly dependent on the microstructure. To achieve rapid optical switching over a narrow temperature range, the micro-structural orientation in the films must be favorable to rapid interface propagation.

![Graph](image)

Figure 4.7 Temperature dependent transmittance for DC reactively sputtered VO₂ films before and after thermal cycling.
Figure 4.7 shows the temperature dependent transmittance before and after ten, one hundred and a thousand times of films' thermal cycling about the transition temperature. The curves clearly show a progressively reduced transition temperature—from 69 to 66 to 63 and to 61°C and a reduced hysteresis loop width from 15 to 13 to 10 and increasing to 11°C before and after ten, hundred and thousand times of thermal cycling. A plot of transition temperature against number of cycles, figure 4.8, clearly points towards a stabilized transition temperature of approximately 61°C. A further plot of hysteresis loop width against number of cycles, figure 4.9, indicates very little variation with increasing cycles.

![Graph showing transition temperature over number of thermal cycles](image)

*Figure 4.8 Variation of transition temperature with the number of cycles*
As of the reduced transition temperature Begishev (1978) observes that the reduction in the degree of structural order is caused due to the increase of the number of destroyed V-V pairs. The proposed mechanism is, in a sense, analogous to that of the influence of the Niobium(Nb), Molybdenum(Mo), Tungsten(W) and Fluorine(F) impurities on the phase transition in VO$_2$. The action of these impurities amounts to a reduction of the V-V pairs and the formation of V$^{3+}$ ions. Borek et al. (1993) notes that the transition temperature of VO$_2$ may shift due to the presence of intrinsic stress, thermal expansion mismatch, doping and presence of a second phase. Case (1990) attributes the low transition temperature to be a reduction in extrinsic stress. We pick on Borek's (1993) factors namely intrinsic stress and thermal expansion and also agree with Case (1990) to account for our observed reduced temperature. Doping and presence of a second phase were not likely in our case since there was no explicit doping and the optical and electrical
behavior confirmed the films to be VO$_2$. The overall results from temperature dependent transmittance indicate a need for heat-treatment of vanadium dioxide films. The thermal cycling has emerged as a way of lowering and stabilizing both the transition temperature and the hysteresis loop width. The importance of a lowered and stable transition temperature cannot be over emphasized in window applications. While on the other hand a small and stable hysteresis loop width implies better and predictable temperature response: which is desirable for windows.

Spectral normal transmittance of the as-deposited film was as shown in figure 4.10 for the visible through to infrared. Transmittance measurements were done at 30°C and at 80°C corresponding to $T<T_c$ and $T>T_c$, respectively. It was found that transmittance as a function of wavelength, $T(\lambda)$, depends strongly on temperature in the infrared. At temperature lower than the transition temperature $T(\lambda)$ shows a monotonic increase with increasing wavelength and reaches 69 % at $\lambda=2500$. At temperature greater than the transition temperature, $T(\lambda)$ displays a peak at $\lambda=700$ nm and decreases to 16 % at 2500 nm. The property that $T(\lambda)$ falls off markedly above a certain critical temperature is the desired one for a thermochromic 'smart window'. The cutoff of the short wave visible gives the films a light amber color. We note that our films with a thickness of 80 nm were not very effective at rejecting the solar infrared. The rejection of infrared is thickness dependent, being effective with increasing thickness at a disadvantage of decreasing luminous transmittance. The remedy here lies with the use of anti-reflecting coating (AR)(Jorgenson and Lee, 1985).
Figure 4.10 Spectral normal transmittance of as-deposited DC reactively sputtered $\text{VO}_2$ film on glass below ($T < T_c$) and above ($T > T_c$) the transition temperature

Thermal cycling does not seem to alter the results of transmittance by very appreciable values. The curves (figure 4.11) obtained after ten, one hundred and one thousand times of thermal cycling show same trends with a slight decrease in transmittance after a thousand cycles. These results clearly indicate stabilized films because as earlier mentioned it’s the behavior of these films above and below the transition temperature that indicate their suitability as materials for smart window applications.
Figure 4.11 Spectral normal transmittance for the VO₂ film before and after ten, hundred, and a thousand times of thermal cycling for temperature below \((T < T_c)\) and above \((T > T_c)\) the transition temperature.

4.6 Optical Constants

Table 4.1 illustrates the various values of \(n\) and \(k\) obtained for the films in various states. The refractive index, \(n\) and extinction coefficient, \(k\), were measured at an angle of incidence of 56.36° for both semi-conducting and metallic state for the as-deposited and the thermally recycled VO₂ films. The analyzer and polarizer reference azimuths, \(\alpha\) and \(\pi\), were 198.9° and 19.3° respectively. In table 4.1 \(A_+\) and \(P_+\) are the final readings of the analyzer and polarizer, respectively upon rotating them counterclockwise from their reference azimuths as explained in section 3.3.2.2. From equations 30 and 31 the ellipsometric parameters delta \((\Delta)\) and psi \((\Psi)\) were found and from equations 28 and 29,
the refractive index, n, and the extinction coefficient, k, were computed using an 'nk' program, appendix 1.

Table 4.1 Determination of optical constants by ellipsometric method. The values of n and k were obtained for an incident angle of 56.36°. \( \tau_c \) is the transition temperature

<table>
<thead>
<tr>
<th>State of VO_2 film</th>
<th>( \Delta )</th>
<th>n</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td>Semi-conducting (Temperature &lt; ( \tau_c ))</td>
<td>24.6°</td>
<td>2.85</td>
<td>1.47</td>
</tr>
<tr>
<td>Fresh film (as-deposited: ( T_c=69°C ))</td>
<td>313.5°</td>
<td>315.8°</td>
<td>296.5°</td>
</tr>
<tr>
<td>After 1000 cycles (( T_c=61°C ))</td>
<td>307.0°</td>
<td>314.5°</td>
<td>295.2°</td>
</tr>
<tr>
<td>Metallic (Temperature &gt; ( \tau_c ))</td>
<td>27.6°</td>
<td>2.62</td>
<td>1.37</td>
</tr>
<tr>
<td>Fresh films (as-deposited)</td>
<td>316.5°</td>
<td>314.6°</td>
<td>295.3°</td>
</tr>
<tr>
<td>After 1000 cycles</td>
<td>310.3°</td>
<td>308.5°</td>
<td>289.2°</td>
</tr>
</tbody>
</table>

We report a refractive index of 2.85 in semiconducting state, which reduces to 2.62 in metallic state for the as-deposited films. The extinction coefficient, k, decreases from 1.47 in semiconducting state to 1.37 in metallic state for the as-deposited films. After one thousand cycles, the refractive index increases to 3.08 in semiconducting state and reduces to 2.46 in metallic state. For the same number of cycles, k decreases from 1.08 in semiconducting state to 0.64 in metallic state. Table 4.2 compares the results of this work with other researchers for as-deposited VO_2 films. Swan et al. (1985) reported an n of 2.82 and a k of 0.317 whereas Balberg et al. (1975) obtained 2.81 and 0.53 for n and k respectively for films in the semi-conducting state. Kivaisi et al. (1999) reported an n of 2.67 and a k of 0.04 at semi-conducting state for RF sputtered VO_2 films. As in this work there seems to be some consistency for the value of n but a considerable disparity in the value of k. This is also evident from the values obtained for the metallic state.
### Table 4.2 Comparison of n and k for VO\textsubscript{2} film for 632.8 nm wavelength

<table>
<thead>
<tr>
<th>Source</th>
<th>Semi-conducting state</th>
<th>Metallic state</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>k</td>
</tr>
<tr>
<td>Balberg et al., (1975)</td>
<td>2.81</td>
<td>0.53</td>
</tr>
<tr>
<td>Bersneva et al., (1977)</td>
<td>2.80</td>
<td>0.4</td>
</tr>
<tr>
<td>Swan et al., (1985)</td>
<td>2.82</td>
<td>0.317</td>
</tr>
<tr>
<td>Kivaisi et al., (1999)</td>
<td>2.67</td>
<td>0.04</td>
</tr>
<tr>
<td>This work</td>
<td>2.85</td>
<td>1.47</td>
</tr>
</tbody>
</table>

Literature reveals that the ellipsometric method is best suited for completely opaque films, whereas in this case, the DC reactively sputtered films show some degree of transparency (fig4.10); a factor that could have contributed to many workers obtaining different results. The differences could also be accounted for in terms of method of film preparation and the inherent film properties. Machaggah et al., (1989) obtained a big discrepancy with chromium film results for values of n and k and attributed this to the different methods used in preparing surface samples.
CHAPTER FIVE

CONCLUSION AND SUGGESTIONS

5.1 CONCLUSION

We have presented data of up to one thousand cycles about the transition temperature in an effort to investigate the stability of vanadium dioxide films on glass being one of the promising thermochromic window materials. DC reactive magnetron sputtering was successfully utilized in film fabrication because of its large area capability required for window coating and the fact that the sputtering deposition provides an excellent vehicle for investigating the reactive processes. Furthermore, the method is suitable for fabrication processes where compositional control, step coverage, film uniformity and ease of automation are required. DC magnetron reactive sputtering is a cheaper alternative to rf magnetron sputtering of compounds because DC power supplies and target materials are cheaper.

We fabricated VO$_2$ films of approximately 80nm in thickness, as obtained with a Taylor Hobson Talystep. The as-deposited films were found to have a transition temperature of 69°C and a hysteresis loop width of 15°C, as determined from their temperature dependent transmittance.

The crystallinity of these films was of prime importance because as pointed in the literature single crystals would get destroyed after a few cycles. This would have made
studies about the transition temperature quite difficult if not impossible. Through transmission electron diffractograms obtained, it can be stated with certainty that we dealt with polycrystalline films. Presence of polycrystalline films, was further attested to by the films good switching behavior up to a thousand cycles.

The transition temperature was found to decrease with increasing number of cycles. The reduction is by three degrees after the first ten cycles, by six degrees after a hundred cycles and by eight after a thousand cycles. This reduction indicated a convergence to a particular transition temperature in relation to the number of cycles. Similar trend was observed for the hysteresis loop width, which was also an indicator of a good quality film upon cycling. These results clearly point to a need for heat treatment of the films in order to stabilize the transition temperature and the hysteresis loop width.

The spectral normal transmittance results showed very slight variation, upon the films being cycled as compared with the as-deposited, in the infrared wavelengths for temperatures above and below the transition temperature. It is this kind of behavior of vanadium dioxide films in the infrared wavelengths that really shows its suitability for use in energy efficient windows.

The sheet resistance was found to increase slowly with increasing number of cycles at both the semi-conducting and metallic state. The sheet resistance ratio at semi-conducting and metallic state decreases slightly but maintains same order as the as-deposited, upon cycling. Grain structure, as well as stoichiometry and the
crystallographic phase contribute to the resistivity ratio. The fact that there was no much variation of the sheet resistance pointed towards stable grains, good stoichiometry and unchanging crystallographic phase. This behavior is admirable for the vanadium dioxide films in their technical application.

A reasonable value of the refractive index was obtained as expected and in comparison with other workers. The values of the extinction coefficient were quite unreliable and added to the discrepancy observed by others. We speculate that the problem is more experimental than theoretical, as earlier observed.

5.2 Suggestions for further work

The results obtained show a promising use of VO₂ films on glass windows but the studies we undertook examined this material at temperatures far above the room temperature. We would therefore suggest that the stability of these films be investigated when VO₂ films are doped to lower the transition temperature close to room temperature. This could be done for tungsten doped VO₂ for which an optimized dopant level has been established as reviewed in the literature.

The values of the optical constants, especially the extinction coefficient, looked very unreliable when the ellipsometric method was used. We would therefore suggest that other methods of determination of the constants be adopted. An example is by use of reflection and transmission coefficients to compute the optical constants.
The cycling was done manually by switching on and off the heater. It would therefore be advisable to automate this and be able to do the cycling for thousands of times and hence establish more exactly the trend set by our results especially on the shifting transition temperature and eventual stabilization.

Exact microstructure of the films obtained before and after thermal cycling could lead to a better understanding of these materials. It is therefore suggested that beyond the diffractograms obtained the X-Ray Diffraction (XRD), Transmission (TEM) and Scanning Electron Microscopy (SEM) analysis be carried out.

Annealing reduces intrinsic stress and increases the stoichiometry. Our films were not annealed and it would therefore be advisable to try out the cycling with annealed films. It would also be interesting to study the stability of the films upon aging.
References

Adler D. (1972), 'Electronic phase transitions', DTIC Technical Report AD741459

Annakarin J. (1998), 'Preparation and Characterization of Sputtered Vanadium Dioxide Thin Films', Master's Degree Project, Uppsalla University School of Engineering


Case F.C. (1990), 'Improved VO₂ Thin Films for Infrared Switching' Appl. Opt. 30, 28, 4119-4123

69


Granqvist C.G., 1988 'Window Coatings for the Future; Research Aspects', Proc. of the Workshop for planning of network projects in materials science and solar energy, Nairobi-Kenya


Lorrain P. and Corson D. (1970), 'Electromagnetic fields and waves', California, Sanfransisco


Appendix (I)

FORTRAN PROGRAM TO COMPUTE THE REFRACTIVE INDEX \((n)\) AND THE
EXTINCTION COEFFICIENT \((k)\) FROM THE ELLIPSOMETRIC
PARAMETERS

Program nk

Real*8 c1, c2, c3, c4, a, x1, x2, q, b, c, n, n2, k, E1, E2

Integer sgnb

\(\pi = 3.1415926\)

Write (*,*)"---------------
Write (*,*)" n & k calculations from"

Write (*,*)" Ellipsometric Parameters"

Write (*,*)" using Ditchburn relations"

Write (*,*)"

Pause

Write (*,*)" ***************
Write (*,*)"Enter the value of PHI in Degrees"

Write (*,*) "PHI=

Read*, PHI

Write (*,*)"Enter the value of PSI in Degrees"

Write (*,*) "PSI=

Read*, PSI

Write (*,*)"Enter the value of DELTA in Degrees"

Write (*,*) "DELTA="
Read*, DELTA

C CALCULATION OF E1(n*n - k*k) AND (2*n*k)
C

C BY FIRST CONVERTING PHI, PSI, AND DELTA IN RADIANS

RPHI=PHI*PI/180.0
RPSI=PSI*PI/180.0
RDELTA=DELTA*PI/180.0

SPHI=DSIN(RPHI)
S2PS=DSIN(2*RPSI)
S4PS=DSIN(4*RPSI)
SDE=DSIN(RDELTA)
C2PS=DCOS(2*RPSI)
CDE=DCOS(RDELTA)
TPHI=DTAN(RPHI)

C1=SPHI**2
C2=TPHI**2

C3=(C2PS**2)-((S2PS**)*(SDE**2))
C4=(1+S2PS*CDE)**2
C5=(SPHI**2)*(TPHI**2)*S4PS*SDE

E1=C1*(1+(C2*C3)/(C4))
E2=C5/C5

C *********************************

C SOLVING QUADRATIC EQUATION

a= 4
b = -4*E1

c = -(E2**2)

C DEFINING THE FUNCTION sngb

IF(b.GT.0) GOTO 40

sgnb = -1

GOTO 45

40 sngb = 1

C SOLVING QUADRATIC EQUATION

45 q = -0.5*(b + ((sgnb)*DSQRT((b*b)-(4*a*c))))

x1 = g/a

x2 = c/q

IF (x1.GT.x2) GOTO 50

50 n2 = x1

C END SOLVING QUADRATIC EQUATION.

C******************************

70 n = DSQRT(n2)

k = E2/(2*n)

WRITE(*,*)

WRITE(*,*)"REFRACTIVE INDEX, n, =", n

WRITE(*,*)

WRITE(*,*)"EXTINCTION COEFFICIENT, k, =", k

STOP

END
### Appendix (II)

Table 3 Vertical Magnifications for the Metric Chart Paper

<table>
<thead>
<tr>
<th>Magnification</th>
<th>Recorder Chart Values</th>
<th>Full Scale</th>
<th>Each Division*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>x 10&lt;sup&gt;3&lt;/sup&gt; Angstroms</td>
<td></td>
</tr>
<tr>
<td>Classification</td>
<td>Values</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lower</td>
<td>5 x 10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>120</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>1 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>60</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>2 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>30</td>
<td>1</td>
</tr>
<tr>
<td>Mid</td>
<td>5 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>12</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>1 x 10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>6</td>
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</tr>
<tr>
<td></td>
<td>2 x 10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>3</td>
<td>0.1</td>
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<tr>
<td>Higher</td>
<td>5 x 10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>1.2</td>
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<tr>
<td></td>
<td>1 x 10&lt;sup&gt;6&lt;/sup&gt;</td>
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<td>2 x 10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>0.3</td>
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</table>

*The metric chart paper has 2 mm division