Synthesis and Characterization of Thermochromic VO_2 Nano Material by Chemical Bath Deposition Method for Energy Efficient Glass Windows

Adisu Tsige

A Thesis Submitted to

The department of Material Science and Engineering

School of Mechanical, Chemical and Materials Engineering

Submitted in Partial Fulfillment of the Requirement for the Degree of Master's in Materials Science and Engineering

Office of Graduate Studies

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Supervisor's/Advisor's approval sheet

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Subject: Thesis Submission

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I hereby declare that this MSc Thesis is my original work and has not been presented for a degree in any other university, and all sources of material used for this thesis have been duly acknowledged.

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ACRONYMS AND SYMBOLS

AA/APCVD	Aerosol assisted chemical vapor deposition.
AC	Alternating current
Acac	Acetylacetone.
APCVD	Atmospheric pressure chemical vapor deposition.
AR	Antireflection
CBD	Chemical bath deposition
CHFS	Continuous Hydrothermal Flow Synthesis
DC	Direct current
EACVD	Electric-field assisted chemical vapor deposition
FBCVD	Fluidized Bed Chemical Vapour Deposition
FESEM	Field-emission scanning electron microscopy
FWHM	Full width at half maximum
HiPIMS	High power impulse magnetron sputtering
IP	Ionic product
IR	Infrared
JCPDS	Joint Committee on Powder Diffraction Standards
MS	Magnetron sputtering
M-Phase	Monoclinic phases
MIT	Metal insulator transition
MOCVD	Metal-organic chemical vapor deposition
NIR	Near Infrared
PECVD	plasma enhanced chemical vapor deposition
PLD	Pulsed laser deposition
PVP	Polyvinylpyrrolidone
RF	Radio frequency

R-PLD	Reactive pulsed laser deposition
S	Degree of supersaturation
SEM	Scanning electron microscopy
SP	Solubility product
SMT	Semiconductor-to-metal transition
SPT	Structural phase transition
T	Transmittance
ΔT	Change in transmittance (shielding)
T_c	Critical transition temperature
T_{lum}	Luminous transmittance
T_{vis}	Visible transmittance
ΔT_{sol}	Change in Solar transmittance
TEA	Triethanolamine
T_{width}	Transmittance switching relaxation
V	Vanadium
VO_2 M	Vanadium oxide in monoclinic phase
VS	vapor-solid
XAS	X-ray absorption spectroscopy
XRD	X-ray diffractometer

Abstract

Thermochromic vanadium dioxide (VO_2) is successfully deposited on microscope glass substrate by chemical bath deposition method for the first time using potassium hydroxide (KOH), Triethanolamine (TEA) as complexing agents and Polyvinylpyrrolidone (PVP K-30), as a surface modifying agent. The common synthesis methods for thermochromic VO_2, which are chemical vapour deposition and physical vapour deposition, does not make this material commercialized due to scalability and cost effectiveness problems. The chemical bath deposition (CBD) method applied in this project includes, selection and optimization of appropriate chemicals for the synthesis by powder preparation using three trials then annealed in nitrogen gas at 570 ºC. Based on the result found on the three trials the one, which shows better formation of pure phase VO_2 is further used for the thin film deposition. During the thin film deposition process, the microscope glass is pre coated with Polyvinylpyrrolidone to assist the surface modification and selectively attract VO_2 phases towards the substrate so that better adhesion with high purity VO_2 thin film is formed. The thin film material are prepared with different conditions, by varying deposition time, in such way that a 15 minutes, 30 minutes and 80 minute deposited thin film and annealed at 450 ℃, 500 ℃ and 570 ℃ in nitrogen gas. Differential thermo gravimetric (DTG). The Nano martial produced shows thermochromic transition behavior at average of 69 ºC based on Differential scanning calorimetry (DSC) studies. UV-VIS spectrophotometer analysis for 15 minutes and 30 minutes deposited thin film shows shielding of near infrared region (NIR) wavelength 3.7 % and 5.5 % respectively. Based on the XRD studies of the film two dominant peaks at 27.6 degree and 39.5 degree are observed with (011) and (020) planes of VO_2 respectively. In addition to this, crystallinity increases with annealing temperature as the FWHM shows 0.00380 rad and 0.00320 rad for 500 ℃ and 570 ℃ annealing temperature respectively. Scanning electron microscope (SEM) analysis done for 30 minute deposited thin film shows increase in grain size and decrease in grain boundary with increase in annealing temperature. Based on the results of analysis, thin film material prepared using chemical bath deposition (CBD) have shown promising properties for future application in smart window application to regulate indoor temperature without applying external energy.

Key words: Vanadium dioxide, Thermochromic, Metal insulator transition, Critical transition temperature, Infrared radiation, Chemical bath deposition

CHAPTER 1 INTRODUCTION

1.1 General introduction

Materials that exhibit changes in their optical properties due to some external stimulus are called “Chromogenic” materials. The most common of these are photochromic, thermochromic and electrochromic materials, where the stimuli are irradiation by light (photons), change in temperature, and an applied electric field, respectively. Thus, a thermochromic material changes properties upon reaching a characteristic ‘transition temperature’. Thermochromism is the temperature-dependent changes in the optical properties of a material (VO_2). Typically, the thermochromic effect occurs over a range of temperatures, which is observed as a gradual colour change, i.e. continuous thermochromism. Discontinuous thermochromism involves a structural phase change at a specific transition temperature. This phase change can be first- or second-order in nature, and may be reversible or irreversible, as governed by the thermodynamics of the system [1]. Thermochromism offers potential for technological applications, for example, in thermometers (fever indicators, gadgets, design applications, etc.), temperature sensors for safety, laser marking, or warning signals. As well as inorganic oxides, many different compounds, for instance, liquid crystals, conjugated oligomers, leuco dyes, are all commonly known to exhibit the ability to reversibly change colour with temperature. However, thermochromic dyes are usually based on organic compounds, which show irreversible colour changes on heating.The world's energy consumption is continuously increasing and this creates a heavy demand for renewable energy sources to be developed. The emission of carbon dioxide and other pollutant gases are posing a problem not only to the environment but also to human health as well [2]. This coupled with the increase of the general standard of living has shown an increase in demand of energy.

The current energy-environment problem, and the challenges it imposes on society, is one of the driving force behind many energy concerning researches and development. Beside to this concentration of carbon dioxide in the Earth’s atmosphere is rising drastically; it was ~315 ppm at the end of the 1950s and now regularly exceeds ~400 ppm [3]. Furthermore, the rate of increase has almost tripled during this time span. The increased amount of CO_2 fossil fuel based energy generation system , specifically unrestrained burning of coal, oil and gas which are believed to be very influential for global warming and rising sea levels [4].

In addition to that, population is growing rapidly and expected to be 50% larger by the year 2100 than it is today [5]. This population is increasingly agglomerated in urban centers, and it is expected that 70% of all people will be living in such areas by the year 2050 [6]. The centers behave as "urban heat islands" and may reach temperatures that can be several degrees in excess of those in the surrounding countryside. Hence, the "urban heat island" effect exacerbates CO_2-induced climate change [7] for the majority of the world's population.

Due to the different in geological era between Anthropogenic and Holocene i.e., the period prior to the Industrial Revolution, known as the Holocene and the Anthropogenic is considered from starting of industrial revolution [8].

It is evident that the global energy sector must be decarbonized, and this realization points sharply to the importance of improving buildings, which are said to be responsible for about 40% of the world's total annual energy consumption due to the excessive use of lighting, air-conditioning and heating of primary energy [9]. The impact of buildings is presently increasing in many parts of the World, and their part of the energy use in the USA, for example, was 34% in 1980 and this number increase to 41% in 2010 [10], and nothing indicates that this trend is changing. Another important fact to consider in buildings, in developed counties peoples spend as much as 80%–90% of their time indoors [11].

There are many "green" technologies, often with Nano-technology attributes, that can be harnessed [12,13], and energy-efficient glazings i.e., a way which uses thin film coatings on building glazing in order to limit the amount of solar radiation entering or blackbody radiation leaving a building, which are one of the most important options. Most of currently available glazing does not consider energy flows, which necessitates waste of energy to control in door environment conditions.

One principle solution to this conundrum is to make the glazings small, but this is not acceptable in practice since precious indoors–outdoors contact and day lighting are then curtailed, and both of these features are essential for human well-being and task performance [14]. However, energy efficiency can be achieved with glazings permitting variable amounts of solar energy and visible light to be transmitted. These glazings are often referred to as "intelligent" or "smart" and are based on stimulus-responsive "chromogenic" materials [15].

The behavior of a thermochromic window is that, for temperatures below the transition, the material has a low infrared reflectance; consequently, the solar radiation and associated heat will

reach the interior of the building, as it will not be reflected. For *T*>Tc, the opposite is true, part of the energy from the sun will be reflected, due to the higher material's infrared reflectance. In this way, the heat gain from the solar radiation will be high in winter and much lower in summer reducing the need for cooling and heating respectively [16].

For the thermochromic effectiveness in energy saving, the thermochromic material should have some specific characteristics. The thermochromic coating should ideally be transparent in the visible region, to allow all the light from the sun to reach the interior of the building. In this way, there will no (or very little) reduction in the visibility, with no necessity for additional artificial lighting. Moreover, no significant change in the visibility should be associated with the phase change [16].

The change of the optical properties in the infrared region, on the contrary, should be as high as possible. With a much higher reflectance for T > Tc, for instance, less solar energy will reach the inside of the building; however, if the increase in the reflectance is lower, the process will be less effective. The value of the transition temperature is also another important parameter; indeed, for the material to be used on a glassy window as solar controller, the change in the optical properties should take place for temperature values close to room temperature, ideally between 20 and 25 ℃ in order to maximize the time the coating spends in the higher temperature, reflective state [16]. A semiconductor-metal transition temperature of 68 ℃ is too high for this application and must therefore be reduced. At present, there are two approaches to reduce the transition temperature, the substitution of part of the vanadium cations (with concentration of less than 2 at %) in by other metals such as tungsten [17], molybdenum [18], or niobium [19, 20] or the substitution of part of the oxygen anions by other elements e.g fluorine [21]. By applying those techniques and others, researchers are trying create applicable thermochromic material in this era. The present study conducted in this project creates a way to produce thermochromic thin film materials to be produced easily and cost effectively by applying chemical bath deposition method that will contribute for commercial application.

1.2 Vanadium Dioxide (VO_2)

VO_2 belongs to the class of smart materials‖, which generally react to temperature variations, electric or magnetic fields and/or pressure variations and have capabilities of sensing, actuating and switching, relying on an intrinsic property of the material. Modern buildings have large windows and glass facades in order to give desired indoors - outdoors contact as well as good day-lighting. These glazings are often detrimental to the energy efficiency of the building and let in or out too much energy. This needs to be compensated by indoor space cooling or heating, depending on the season. In particular, the need for cooling has increased dramatically in recent years. Chromogenic glazings based on thermochromism or electrochromism can regulate the inflow of visible light and solar energy between widely separated limits and hence achieve good energy efficiency [22]. Whereas electrochromic smart windows are beginning to appear on the market, the thermochromic option has so far been little used in practical applications. However, thermochromic smart windows have potential advantages in terms of simplicity of operation and have been intensively researched in recent years [23].

There are two types of thermochromic materials: inorganic and organic. The inorganic ones are transition metal compounds, but of those only vanadium dioxide (VO_2) exhibits a switching temperature in the vicinity of room temperature [24].The switching takes place in the near infrared (NIR) and infrared wavelength regions from a low temperature transmitting state to a high temperature reflecting state. There also exist a large number of organic polymer-based thermochromic materials [25]. In particular, the ligand-exchange systems may be promising for niche applications. They switch mainly in the visible wavelength range from a low-to-medium absorbing state to a highly absorbing state as the temperature increases.

1.2.1 Structure of vanadium dioxide (VO_2)

The atomic number of vanadium (V) is 23, and it is a transition metal. The electron configuration of vanadium is $[He]3d^3 4s^2$ so it has partially filled 3*d* and 4*s* subshells. Thermally activated metal-insulator transition in VO_2, is accompanied by a structural phase transition (SPT) from a low-temperature insulating phase to a high-temperature metallic phase. The phase that exhibits metallic behavior above the transition temperature MIT has a tetragonal unit cell. Since the structure of the metallic phase resembles that of a rutile structure, the phase is known as R phase. In R phase, the vanadium atoms form a body-centered tetragonal lattice and are surrounded

by an oxygen octahedron [26]. The insulating phase, which exists below MIT temperature, has a monoclinic unit cell, and it is known as M phase. Its unit cell is two times larger than that of the metallic phase, and it is formed by the distortion of the tetragonal structure [26, 27]. In M1, all the vanadium atoms both pair and tilt with respect to the c-axis of the tetragonal R phase, i.e. cR-axis [27]. Figure 1.1 presents the two different crystalline structures, the VO_2 M phase. On the left, the low temperature phase presents a monoclinic lattice with a P21/c group, while on the right, the high temperature tetragonal structure presents a rutile P42/mmm structure. While not trivial, a direct translation of the monoclinic cell onto the tetragonal cell is possible with the monoclinic cell including 2 tetragonal cells along its c rutile axes [26].

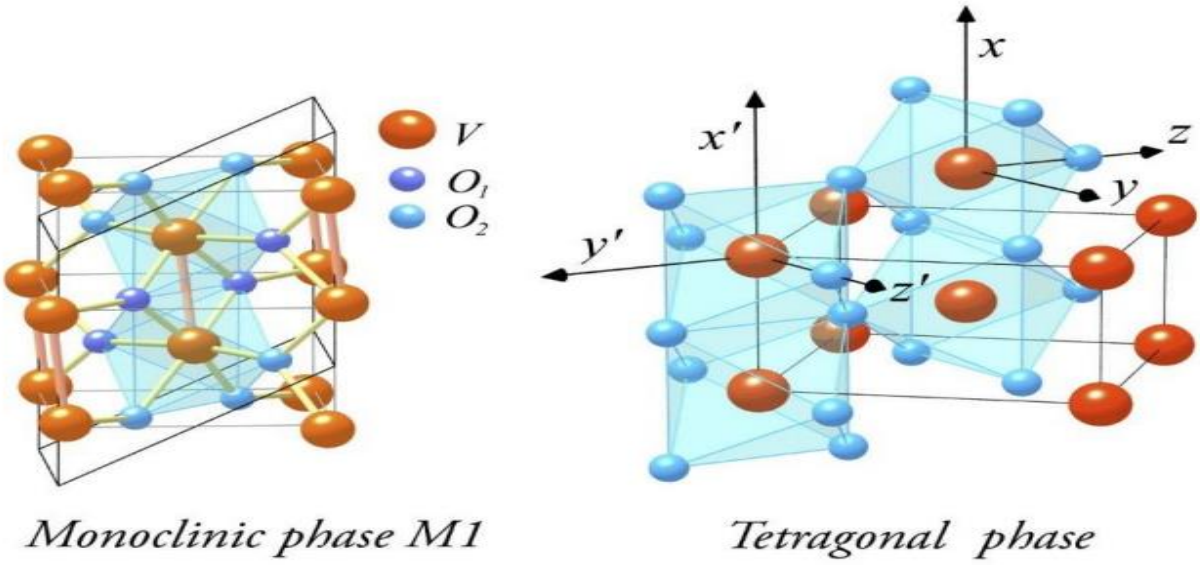


Figure 1.1: Structure diagram of thermochromic VO_2 crystal cells. The left panel shows the low temperature insulator monoclinic cell while the right panel shows the high temperature conductive tetragonal cell [28]

1.2.2 Band structure of vanadium dioxide (VO_2)

In Mott-Hubbard picture, the unusual insulating behavior and the corresponding formation of a band gap stems from the split 3*d* band as a consequence of strong electron-electron [29]. The 3*d* band structure for both the metallic and the insulating phases of VO_2 has been presented by Goodenough, and it is explained as follows [27].

In the metallic phase, the 3d states of the V^{4+} ion are first split into e_g and t_{2g} states, and the latter is further split into $3d_{\|}$ and the $3d\pi^*$ states by the tetragonal crystal field [26, 30]. The $3d\pi^*$

and 3d|| orbitals overlap and are situated around Fermi level, but the 3dπ* band lies higher in energy because it is more hybridized with the O 2p orbitals [26, 30]. Because Fermi level now lies within the conduction band, the material exhibits metallic properties.

In the insulating phase, the monoclinic distortion causes changes in the V-O hybridization which upshifts 3dπ* band to even higher energy so that the band now lies above Fermi level and becomes empty [26]. Furthermore, the 3d|| band, which is aligned along the cR-axis, is split into a filled and an empty state due to pairing of the V atoms [30]. Because of these changes, an energy gap is formed between the 3d|| valence band and 3dπ* conduction band. The majority carriers in the insulating phase are recognized to be of n-type, which are thermally activated into the conduction band [31]. The band structures for the insulating and metallic phases are schematically presented in Figure 1.2, which has been modified from the O 2p levels are situated well below the V 3d states [28, 32].

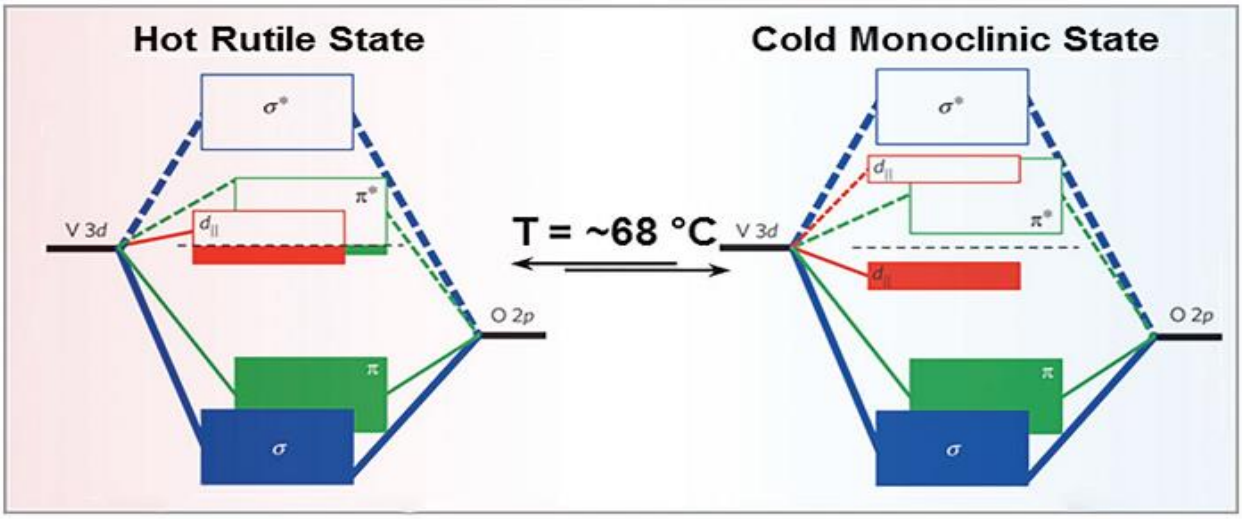


Figure: 1.2. Band structure of VO_2 for the insulating and metallic phases [32].

The 3d-band structure of VO_2 has been well-investigated by Shin et al. using spectroscopic methods [30]. They observed clear changes in the 3d band across the metal-insulator transition and obtained some energy gap values. In accordance with the description given by Goodenough, Shin et al. found the 3dπ* and $3d_{||}$ states near Fermi level in the metallic phase and observed the rise of the 3dπ* band by about 0.5 eV in the insulating phase [30]. They thought that this band shift may be the driving force of MIT and estimated the band gap to be 0.7 eV [30]. Furthermore, they observed the splitting of the 3d|| band and estimated the energy splitting to be about 2.5 eV [30]. The splitting was explained to occur due to strong correlation between the d||-electrons, and the

correlation energy (Uc) was estimated to be about 2.1 eV [28]. Using ultrafast electron microscopy, Grinolds et al. have also observed the opening of a band gap caused by splitting of the 3d|| band in the insulating phase, which occurs in ultrashort time scale [33].

Originally, Goodenough proposed that MIT in VO_2 stems from the increased *p-d* overlap due to distortion of the VO_6 octahedra and that the change in the symmetry of the structure would split the 3*d*|| band [26]. Hence, the reason for the opening of the band gap would be in the electron-lattice interaction. In contrast, Zylbersztejn and Mott suggested that the strong electron-electron interaction splits the 3*d*|| band and generates the gap. They stated that pairing of the V atoms has little effect on the gap and emphasized the importance of the correlation energy *Uc* [34]. They approximated the energy gap to be U_c - ½B_1 where B_1 is the width of the $3d_\pi^*$ band [34]. Later on, Paquet & Leroux-Hugon build up a band model for VO_2 which started from the tight-binding approximation and included both Mott-Hubbard and Peierls mechanisms. They concluded that electron correlations are the driving mechanism stabilizing the monoclinic distorted phase which, in turn, is a consequence of this primary mechanism [35].

The importance of the band structure to MIT characteristics has been experimentally verified. Ruzmetov *et al.* pointed out that the $3d_{||}$ band has an important role in the appearance of MIT in VO_2 using X-ray absorption spectroscopy (XAS). They reported that there exists a clear correlation between the increase of the spectral weight of the $3d_\pi^*$ band and the strength of MIT. The changes of the $3d_\pi^*$ band was attributed to it being overlapped with the $3d_{||}$ band which strengthens due to electron-electron correlation [36].

1.2.3 Mechanisms of VO_2 phase transition

Various phase transition mechanisms for VO_2 have been proposed in the past [37]. However, understanding the nature of the transition itself remains a challenge. Generally, VO_2 can be classified to a Peierls insulator because of the strong dimerization and the fact that this phase is nonmagnetic [38]. However, VO_2 was proved to be pretty similar to a Mott–Hubbard insulator according to some experimental studies [39]. Previous studies showed that the insulating state results from the strong Coulombic repulsion between electrons, indicating that the electron–electron correlation plays an important role. Driven by the thermal excitation, electrons can cross the potential barrier to the metallic state. Based on Goodenough's model [40], the tilting of V–V atoms in the insulating monoclinic phase raises the anti-bonding 3dp band above the Fermi level, with the half-filled $3d_{II}$ band. The debate on the mechanism behind metal–insulator transmit (MIT)

is around whether the V–V pairing and the unit-cell doubling causes the additional splitting of the $3d_{II}$ band. This is the point of Peierls transition. The opening of a correlation gap resulted from carrier localization, which is the heart of Mott–Hubbard mechanism [37].

To find out the factors determine the transition, whether the transition is strain-induced, photoninduced and/or electric filed-induced, and develop methods to control the transition have attracted significant interest. Recent studies [41, 42] showed that a metallic domain-like state could be observed in the monoclinic phase of VO_2 (M) and the rutile phase is not essential to show the metallic behavior. Zhu et al. reported that the band theory - the modified Becke-Johnson exchange potential was applied to understand structural, electronic, and magnetic features of MIT from the rutile phase to the monoclinic phase of VO_2 [43]. To investigate the role of the structural transformation in MIT, Xie et al. applied X-ray absorption fine structure spectroscopy to monitor the fine variations in atomic and electronic kinetics when MIT occurs. They pointed out that the change of the closest V–V atoms may contribute significantly to the evolution of the electronic structure, of monoclinic structure [44].

The adjustments of the phase transition in VO_2 have also been carried out. Aetukuri et al. found that the metal–insulator transition can be controlled by modifying orbital occupancy [32]. The transition temperature and the structural distortion across the transition depend on the orbital occupancy in the metallic state. Wall et al. reported that ultrafast structural transitions can be measured through optical probes [45]. They examined the photo-induced structural phase transition in VO_2 and found that, above the phase transition threshold, photoexcitation completely changed the lattice potential on an ultrafast timescale. Electrolyte gating with ionic liquids was reported to be a powerful tool to suppress the metal–insulator transition by the formation of electric field-induced oxygen vacancy. The metallic phase can be stabilized to lower temperature. By photo-exciting the monoclinic semiconducting phase, an induced transition to a metastable state was observed, which retained the periodic lattice distortion characteristic of the semiconductor but also acquired metal like mid-infrared optical properties.

1.2.4 Optical Properties of VO_2

Pure thermochromic VO_2 thin films transit noticeably between the semiconductor and metallic state at the transition (T_C) 68 °C. At temperatures below T_C the material is transparent in both the infrared and visible part of the spectrum, thus allowing solar radiation to pass through the window maximizing the heating effect of sunlight and black body radiation within the building.

Hence there is high optical transmission in the semiconducting state of VO_2 thin films. At elevated temperatures above T_C the coating is transparent in the visible, more reflective in the infrared part of the spectrum (see figure 1.3). This prevents the thermal part of solar radiation from heating the building interior. This also allows for the greatest use of natural light which is highly desirable as internal lighting contributes towards the buildings energy use and maintenance costs [46]. At the transition temperature (68 ºC) vanadium (IV) dioxide is too high to be effective in maintaining a comfortable temperature (18 – 25 ºC). The use of dopant has been shown to affect the transition temperature. This may increase or decrease depending on factors such as dopant size and dopant charge [47] as well as the changes in electron carrier density. Tungsten has been shown to be the most effective dopant to lower the T_C of vanadium (IV) dioxide with a 2 atom% tungsten loading reducing T_C to around 25 ºC in films prepared by physical vapor deposition and sol-gel coating [47].

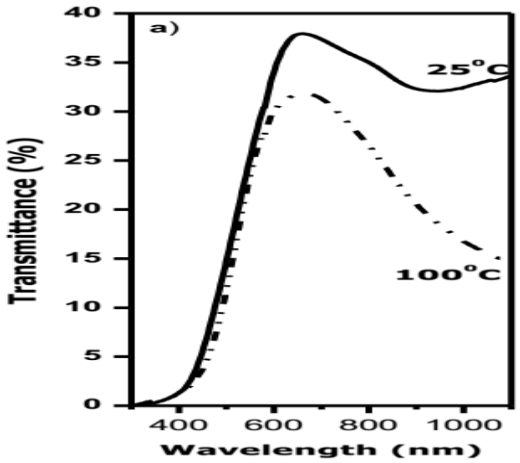


Figure 1.3 Optical switching mechanism of VO_2 thin films between semiconductor and metal state [48].

Fluorine has also been used to dope vanadium (IV) dioxide. Fluorine doping [49] into VO_2 thin films by radio frequency sputtering usually forms films of VO_xF_y, resulting into improved transmittance properties and lead to a decrease in T_{tr}. Fluorine doping has however been reported to decrease the sharpness of thermochromic transition, potentially reducing their usefulness in glazing.

1.3 Statement of the problem

Vanadium dioxide have been produced with different synthesis method, but the methods applied does not commercialize this material for application purpose due to sophistication of the preparation technique, which creases difficulties in scalability and cost effectiveness. The common synthesis method, which have been used for decades such as chemical vapour deposition method, and physical vapour deposition method require expensive device to produce very small thin film coatings even for laboratory applications. Other processing technique, which uses solution synthesis method such as sol-gel method also need another device (such as spin coater) to coat already produced powders. All this limitation together affected the application and development of this technology.

1.4 Objectives of the Study

1.4.1 General Objective

In General the objective of this research is to prepare thin film using chemical bath deposition method of synthesis and conduct the effect of optical parameters. The optical efficiency for shielding property of vanadium dioxide in NIR region of the wave length and transmittance properties in the visible region of wave length with two different temperature (above and below critical transition temperature) condition of temperature, and characterize the properties associated with it.

1.4.2 Specific Objectives

This work will specifically consider the parameters that could be controlled by using chemical bath deposition (CBD) techniques and their effect on the thin film products, which are:

- ✓ Optimizing the condition for chemical bath deposition method synthesis of vanadium dioxide, by testing applicable chemicals.
- ✓ Optimizing the chemicals and condition of deposition method and creating better thin films by CBD.
- ✓ Analyzing thermochromic property of the film including the critical transition temperature with its relation to the optical properties.

- ✓ Analyzing crystallinity, phases present in the film, phase uniformity, average crystal size properties, thickness, deposition time and annealing conditions, annealing temperature, in such a way with its relation to efficiency of the thin films.

1.5 Scope of the Study

This work will be conducted based on the chemical bath deposition to prepare thin film and characterize the product, the experimental work includes effects of parameters that control the properties of coating such as temperature, pH, concentration, heat treatment conditions, deposition time and the characterization technique of coated substrate will be done using XRD, UV-VIS absorption spectroscope, DSC, DTG and SEM. Therefore, the optical properties of the thin film will be studied in different techniques.

1.6 Significance of the study

The significance of proposed project is as follows:

- ✓ Developing thermochromic material (VO_2) with properties mentioned in the specific objective is a global challenge.
- ✓ CBD is not explored for synthesis of thermochromic materials (VO_2), this work contributes application of CBD technique for thermochromic (VO_2) film preparation.
- ✓ Contribute for understanding thin film barrier coating (IR shielding), photonic materials and optical devices.

Thermochromic materials (VO_2) is not known for commercial application, this work will have contribution towards commercialization due to the simplicity in production using CBD.

CHAPTER 2 LITERATURE REVIEW

2.1 Thin films Optical Coatings

Deposition process of thin film is referred optical coating when thin layer materials deposited on optical materials, which can interact with light (optics). Optical coatings are applied for antireflection purposes, as interference filters on solar panels, as plate glass infrared solar reflectors, and for laser optics [49]. More complex optical coatings exhibit high reflection over some range of wavelengths, and anti-reflection over another range, allowing the production of dichroic thin-film optical filters.

The choice of deposition method is governed based on the specific required application of the films, taking into account requirements with regard to the deposition temperature and/or compatibility of the solution chemistry with the substrate. At the start of any deposition sequence stands the formulation of a precursor that can be composed of true solutions (e.g. dissolved metal salts), metal-organic solutions (e.g. sol, gel) or nanoparticle dispersions.

For nanoparticle and sol gel based precursor solutions, spin and dip coating are the most prominently applied coating methods and the preparation of transparent and conductive metal oxide (MO) layers has been demonstrated.

The methods summarized in table 2.1 are often capable of producing films defined as thin films, i.e. 1 μm or less and films defined as thick films, i.e. 1 μm or more. However, there are certain techniques, which are only capable of producing thick films, and these include screen-printing, glazing, electrophoretic deposition, flame spraying and painting.

Table 2.1: Summarized thin film deposition methods [50]

PHYSICAL		**CHEMICAL**	
Sputtering	**Evaporation**	**Gas Phase**	**Liquid Phase**
Glow discharge DC sputtering	Vacuum Evaporation	Chemical vapour Deposition	Chemical bath deposition (CBD)
Triode sputtering	Resistive heating Evaporation	Laser Chemical vapour deposition	Electro-deposition
Getter sputtering	Flash Evaporation	Photo-chemical vapour deposition	Electro less deposition
Radio Frequency sputtering	Electron beam Evaporation	Plasma enhanced vapour deposition	Anodisation Liquid phase Epitaxy
Magnetron sputtering			Sol- gel Spin Coating
Ion Beam sputtering			Spray-pyrolysis technique (SPT)
	Arc		Ultrasonic (SPT)
	R. F. Heating		Polymer assisted deposition (PAD)

2.2 VO_2 Coating Methods

The variation of synthetic conditions may affect the product morphology and structure, which greatly influence the phase transition characteristics and functional properties. In the past, a number of methods have been developed to form VO_2 films. VO_2 deposition processes can be divided in two families: a) direct synthesis of VO_2 in thermochromic crystalline form, and b) the indirect one that necessitates post-treatment, vacuum annealing, or post-oxidation to transform the deposited film into VO_2 [28]. According to the reaction media involved, these methods can be grouped into two main categories: gas-based deposition and solution-based deposition. Gas-based

deposition is a very popular method, which mainly consists of chemical vapor deposition (CVD) and physical vapor deposition (PVD) [38].

2.2.1 Physical Vapor Deposition (PVD) Method

PVD is one of important gas-based technology to fabricate thin films [51, 52]. It usually involves four steps: evaporation, transportation, reaction and deposition. Materials to be deposited, known as targets, are usually solid-state metals, which are bombarded by a high-energy source (such as a beam of electrons or ions) under reduced pressures. PVD method is more suitable for synthesizing ultrathin films, due to requirements of low temperatures, environment-friendliness, compatibility to a wide range of substrates, and convenience of developing multi-layer thin films [53].The common type of sputtering techniques are three: direct current, radio frequency (RF) and magnetron sputtering methods.

From this a processes that demonstrate the best scalability of thermochromic VO_2 are based on the magnetron sputtering (MS). This is a standard approach to obtain high-value coatings in the glass and polymer industries, and therefore it is of interest to the thermochromic VO_2 deposition. Next chapter will offer a more complete presentation of magnetron sputtering processes, and their application to deposit VO_2. MS is a plasma-based physical vapour deposition process. Plasma ions are accelerated toward a solid target to volatilize it. The sputtered atoms condense on a substrate in a line of sight manner. In comparison to diode sputtering, MS entraps the plasma within its magnetic field, at the target vicinity, thus increasing the plasma density, sputtering- and deposition rates. Magnetrons exist in different shapes (circular, planar, cylindrical) and sizes depending on the intended applications. Cylindrical magnetrons of up to 4 m length are common for fabrication of low-e coatings on glass.

Magnetron sputtering of vanadium dioxide has been used since the end of the 1940s at laboratory scale [54], and VO_2 since the end of the 70s [55]. For The thermochromic performance improvement of VO_2 films, Batista et al. reported the deposition of Nb-doped VO_2 by using pulsed-DC magnetron sputtering with a high purity metallic vanadium target in an oxygen/argon atmosphere [56]. Oxygen and argon were introduced into the chamber separately through two gas mass flow controllers. Pure VO_2 film deposited by using this method showed improved thermochromic behavior as compared to the VO_2 film prepared by using the conventional DC sputtering. VO_2 films were also grown on SiO_2-coated float glass by reactive DC and pulsed DC magnetron sputtering in a given oxygen/argon atmosphere [57].

Niklasson et al. applied reactive DC magnetron sputtering to deposit Mg-doped and pure VO_2 were on glass and carbon substrates [24]. The nanocomposite structure prepared display much improved luminous transmittance and solar energy modulation as compared to homogeneous VO_2 thin films. This result is also enhanced by addition of antireflection (AR) properties Long et al. deposited thermochromic $WO_3/VO_2/WO_3$ sandwich structure by a reactive magnetron sputtering technique [58]. With enhanced antireflection (AR) layer to enhance the luminous transmittance (T_{lum}) of VO_2. Joushaghani et al. used reactive radio frequency (RF) magnetron sputtering to deposit VO_2 thin films to show geometry-dependent scaling of current-induced phase transition in VO_2, which resulted in miniaturized threshold current for the phase transition of VO_2 devices, as well as an increased separation between the two steps in the phase transition [59]. Geery. Grow thin films using a DC magnetron sputtering process to show a correlation between the structural properties of VO_2 thin films and their ability to transition from an insulator to a metal [60]. Tadjer et al. deposited amorphous vanadium dioxide (VO_2) films by atomic layer deposition (ALD). To demonstrate that the structural properties of VO_2, which determine the resistivity profile and are already sensitive to multiple factors such as doping and strain, must be carefully tuned in order to obtain the desired electrical response [61].

Crunteanu et al. prepared VO_2 by electron-beam evaporation of a vanadium target on different substrates (sapphire, oxidized silicon and fused silica) and showed substrate effect on electrical and optical properties variations as the material undergoes a metal-insulator transition under thermal and electrical stimuli. Sapphire substrates are mono-oriented and present electrical resistivity changes of up to five orders with sharp variations in the optical characteristics [62].

High power impulse magnetron sputtering (HiPIMS) is a novel sputtering method, developed recently for the deposition of VO_2 films [63]. It is characterized by its high ionization degree of the sputtered species, which allows the control the film microstructure through the ion bombardment. This is helpful to achieve a transmission modulation in the near-IR region for films deposited at lower substrate temperature of 300 °C without using a seed layer. VO_2 films deposited by using this method showed lower transition temperatures than the bulk material, with Tc being brought down to 50 °C for thicker films.

In the early 1980s, PLD and reactive PLD (R-PLD) was introduced, it uses a short pulse from high energy excimer laser focused onto a metallic target. At sufficient laser fluence, an equilibrium plasma is formed at the interface, named plasma plume. Atoms from the target are vaporized and diffuse toward the substrate holder to condense.

The deposition rate of the PLD process is directly proportional to the repetition rate of the laser, and a minimal change of the laser plume is observed in reactive deposition. An exhaustive review [64], reports large-scale production of PLD films with thickness uniformity of 7% over 150 mm substrates. This is large-scale for a PLD process, but still laboratory-sized and unsuited for industrial applications toward "smart windows" or SRD. Nevertheless, this is a reference process for a case study of VO_2 either through doping or substrate effect [28].

The development in the sputtering technology, known as a two-step process, is a combination of the sputtering process and another process such as post-annealing or oxidation. Xu et al. reported a simple but novel sputtering oxidation coupling process to fabricate high quality VO_2 film. According to their method, VO_2 films were first fabricated by using DC-magnetron sputtering process and then oxidized at a high temperature in air. The sample obtained exhibited a promising phase transition near room temperature [65].

2.2.2 Chemical Vapour Deposition (CVD) method

CVD was used for the first time to deposit VO_2 in 1967 [66]. CVD is one of commonly used to technique for depositing high-quality and high-performance thin films. Since then, this method has been used extensively. CVD methods are mainly based on the use of vanadium-based organometallic precursors such as VO $(acac)_2$, [67] $V(acac)_3$, [68] $VO(OC_3H_7)_3$, [69] and halides such as $VOCl_3$, [70] VCl_4. [76] CVD methods have been subdivided into metal-organic chemical vapor deposition (MOCVD) [71], atmospheric pressure chemical vapor deposition (APCVD) [70], aerosol assisted chemical vapor deposition (AACVD) [68], and so on, depending on the variation of fabrication conditions such as precursor compositions, humidifying methods and deposition conditions.

This method offer a higher scalability and higher deposition rates. In CVD, precursor vapours are fed into a chamber: then either through heating, plasma or a combination of both, energy is provided in order to dissociate the precursors. Once fragmented, the precursors become highly reacting molecular or atomic radicals. Depending on the pressure and on the diffusion rate, radicals

react in the gas phase to form powders or at the substrate surface to form a film [72]. This chemical based process allows the use of multiple chambers configurations.

Precursors are molecules specifically formulated to be in vapour form and provide easy extraction of the reaction by-product. For metal, two precursor families are available, halides and organometallics. Additional gas such as H_2 or Ar may be incorporated to stabilize the deposition and optimize halogen removal. Either in thermal-CVD or assisted with additional plasma energy, the commonly used precursors are halides like vanadium oxychloride ($VOCl_3$), vanadium tetrachloride (VCl_4), or organometallics such as vanadyl tri-isopropoxide ($VO(OC_3H_7)_3$), vanadyl tri-isobuxide ($VO(C_4H_9O)_3$) and vanadium acetylacetonate ($V\text{-}C_5H_8O_2$) [73]. Most of them contain additional elements besides V and O such as C, H and Cl. Such elements can remain in the final film, partially degrading its TC performance. While CVD processes can be classified as direct techniques, very frequently additional annealing under neutral atmosphere is needed to reduce the most stable V_2O_5 phase to VO_2.

G.Bodurov et al. deposited mixed W-V-O using APCVD technique using a new mixed precursor based on W hexacarbonyl and Vanadyl acetylacetonate. Appling that a thin films of single oxide of VO_2 films with well oriented crystals distributed in amorphous-like phase were obtained [74]. R. Binions et al, used APCVD reactions of vanadyl acetylacetonate, tungsten hexachloride and 2% oxygen to produce tungsten doped or un-doped vanadium (IV) dioxide films on glass substrates, which showed the enhancement of thermochromic properties due to preferential growth orientation of crystallites along (001) [75]. M.J. Powell, Deposited Multi-layer films of $VO_2/SiO_2/TiO_2$ synthesised by APCVD which is a specialized Fluidised Bed Chemical Vapour Deposition (FBCVD) for the project [76]. Using the reaction of VCl_4 and ethyl acetate to synthesize high quality VO_2 films. Which allows controlling thickness of the film and producing improved visible light transmission to be achieved along with high solar modulation when compared to single film VO_2 analogues.

T.D Manning et al. applied APCVD of $V_{2-x}M_xO_2$ (M = Mo, Nb; X = 0.01–0.003) thin films by using precursor reaction of $VOCl_3$, H_2O and MCl_5 [77]. The films showed reduction in the thermochromic switching temperature, down to 47 °C. narrow temperature hysteresis loop 4–6 °C. L. Hongwei et al. a conventional CVD furnace for synthesis of VO_2 nanowires through a vapor-solid (VS) approach with V_2O_5 power as the precursor [78]. Based on that it found that the phase transition temperature decreases with decreasing nanowire diameters, due to increasing

surface defect density with decreasing nanowire diameter. Controlling the MIT due to size effect could be taken as new approach to control the critical temperature for desired purpose.

One of the Development of CVD is the electric-field assisted chemical vapor deposition (EACVD) method. Electric fields have been shown to affect crystallographic orientation, reduce particle size and decrease T_c of VO_2 films. Effects of types (alternating current (AC) and direct current (DC)) and strength of electric fields as well as the deposition time have been systematically studied.

2.2.3 Sol-Gel method

One of the most studied low-cost processes are the sol-gel methods. Here, V_2O_5 is put into solution using various processes and stirred until adequate viscosity is obtained. Then the sol is spin-coated onto the substrate, dried to form the gel, and annealed to solidify the film. The annealing step also reduces V to its 4^+ oxidation state. It has been extensively used to synthesize VO_2 films, especially for films doped with other metals, because it allows fine control of chemical compositions, even with small quantities. The sol–gel process was first used in 1983 by Greenberg et al. to deposit VO_2 films, with $VO(OC_3H_7)_3$ as the vanadium source. In the sol–gel process, the basic idea is to create an oxide network by a polymerization reaction of chemical precursors dissolved in a liquid medium [79]. Two main challenges accompanying sol-gel methods are dissolution of V_2O_5 and the annealing steps. V_2O_5 can be efficiently dissolved from powder using three processes. The first one uses an acidic solution of H_2O_2 at 30 volume % at controlled temperature [80]; this reaction is strongly exothermic. The second one uses organic solvents mix, for example, isobutanol and benzyl alcohol at a medium temperature of 110 °C, above the flash point of both solvents. Finally, molten V_2O_5 at 800 °C (melting temperature: 690 °C) is poured into water at room temperature and stirred until the solution is homogeneous [81]. The high reactivity of such methods is complex to implement in a strictly regulated academic laboratory, but can be managed at an industrial scale. Another way is to employ vanadium siloxanes, but in this case a high concentration of contaminants will be present in the final film [28].

The next critical step is annealing. For example, in the previously presented methods of sol preparation, the annealing temperature ranges from 440 °C to 750 °C, which hampers the deposition of VO_2 thin films onto polymer substrates or even low melting point, glass [80]. To avoid high-annealing temperature, one can choose to embed already crystalline nanoparticles into a matrix. The matrix can then be chosen to offer a much lower solidification temperature, especially if a polymeric matrix is used. Such a method is proposed by Lu et al., who used chemical

precipitation to generate Nano sized powders before embedding them in a polysiloxane matrix. The reacting agents for VO_2 powder precipitation were vanadyl sulphate hydrate – $VOSO_4$:H_2O – and ammonium bicarbonate – (NH_4) HCO_3. Afterwards, the powder was recrystallized at 800 °C in a controlled atmosphere before milling to reduce the particle sizes. The resulting specular spectral transmission at room and high temperature. One can observe that an increased fraction of VO_2 particles improves the transmittance modulation (*ΔT) 2500 nm*. However, the visible transmission is strongly reduced above 4% of VO_2 in the matrix [82].

An inorganic sol–gel process was reported by Huang's group for the preparation of VO_2 films and elemental cerium (Ce) and/or W doped VO_2 films. The inorganic vanadium sol was obtained by mixing water with molten vanadium pentoxides (V_2O_5) powder [57]. By using this precursor, VO_2 phase was obtained at relatively low annealing temperatures (400–600 °C). The thermal stability of VO_2 films on muscovite (011) substrate prepared by the inorganic sol–gel method was investigated in detail by annealing films in air at different temperatures. VO_2 film was quite stable in air below 200 °C, with steady phase transition properties.

Using Chemical processes for VO_2 coating can provide large area coating, but present traditional issues of wet organic chemistry: the abundant use of solvents, organometallics and halides such as $VOCl_3$. All vanadium precursors present significant toxicity and flammability; therefore, good control of the waste byproduct is needed. It is also to note that reactions using V precursors or even the milling of V containing powders are strongly exothermic, increasing the explosion risk when working with a large batch of materials. All those concerns may make implementation of chemical processes complicated for the industry in "green" economy. Recently it was rediscovered that annealing in a SO_2 atmosphere at T> 600 °C reduces the V_2O_5 into VO_2. This reaction is a by-product of catalytic reaction of SO_3 with V_2O_5 to produce sulfuric acid [83].

Vanadium dioxide (VO_2) thin films deposited on mica substrates with different annealing temperatures by an organic sol–gel method was applied by j.wu et al. to show Effect of annealing temperature on thermochromic properties. Vanadium dioxide thin films which is annealed 440 °C, 460 °C, 480 °C, 500 °C and 520 °C shows a transition temperature of 72 °C and the hysteresis loop shown in the table 2.2 [84].

Table 2.2: Hysteresis width versus the annealing temperature [84]

Temperature (°C)	440	460	480	500	520	540
Hysteresis width (°C)	18	18	18	8	18	18

In recent years, a new vanadium precursor was prepared, which is by adding vanadium oxyacetylacetone (VO (acac)$_2$) to methanol [85]. VO_2 films with excellent thermochromic properties were prepared by spincoating of this vanadium solution on glass followed by annealing at 440–600 °C. After annealing at 440 °C, the film had a Tc as low as 42.7 °C. The value of T_c can be reduced simply by selecting the annealing temperature that induced local nonstoichiometry. The porous microstructure and pure metal-phase of VO_2 gave obtained films a synergetic optical performance with a good visible transmittance and excellent near-infrared modulation abilities. For a 59 nm thick VO_2 film, the integral values of visible transmittance (T_{vis}) for the metallic and semi-conductive states were 54.1% and 49.1%, respectively, while the near infrared switching efficiency was found as high as 50% at 2000 nm.

2.2.4 Hydrothermal Method

One of commonly used techniques in recent years for deposition of thermochromic vanadium dioxide is hydrothermal processing technique, as it allows different nanostructure and nano scale morphology of thermochromic thin film materials.

Hydrothermal synthesis, involving water-soluble precursors at a low temperature, is cost effective and sensitive to synthesis parameters such as time, temperature, pH, concentration, pressure, and reducing agents, which are useful to obtain desired morphology and explore new phases. Because of these unique features, hydrothermal method has been demonstrated to be a feasible method to synthesize VO_2 nanostructures. The pH dependent morphology and pressure-dependent phase formation have been reported in the case of VO_2 polymorphs [86].

Recently worked research on hydrothermal processing of VO_2 has its focus on the formation of phase-pure VO_2 (M) with controllable morphology or fabrication of VO_2 nanocomposites with enhanced thermochromic properties. Pollet et al. proposed an indirect way to obtain VO_2 (M) by annealing VO_2 (B) under vacuum for 1 h. Phase-pure VO_2 (B) platelets can be obtained by a rapid hydrothermal process, with a combination of low temperature and duration

(180 °C for 2 h or 220 °C for 1 h) [87]. R.Chen et al. prepared Pure phase $V_{1-x}W_xO_2$(M/R) nanorods with superb metal-insulator transition properties, which is obtained in tungsten (W)-doped level ranges from 0.5 to 2.0 at % using a one-step hydrothermal treatment without additional annealing steps [88]. The result shows combined nanostructuring and atomic doping synthetic strategy is a good approach to improve the thermochromic property for the VO_2-based materials for several technical applications.

VO_2 nanobelts with metal–semiconductor properties were prepared through low temperature hydrothermal reaction and post annealing by X. Xiao et al. applying this technique one dimension VO_2 nanostructure is formed that shows excellent thermochromic properties [89].

In addition to this, hydrothermal method can also be successfully used to prepare VO_2 nanocomposites. Li et al. reported a TiO_2 seed-assistant hydrothermal method to prepare molybdenum (Mo) -doped VO_2 (M)/TiO_2 composite nanocrystals. Generally, a certain amount of rutile TiO_2 nanocrystals with average size of about 15 nm was added to the solution of appropriate amount of oxalic acid, vanadium pentoxide and molybdic acid. The resultant solution heated in a sealed autoclave at 220 °C for 2 days. It was found that excessive Mo doping could promote formation of the VO_2 (M) phase, and rutile TiO_2 seed was beneficial to the morphology control, size reduction, and infrared modulation of Mo-doped VO_2 (M) nanocrystals [90].

2.2.5 Summaries of VO_2 synthesis methods

The advantages and disadvantages of each synthetic technique for the deposition of solid-state thermochromic thin films were succinctly mentioned when discussing each method. Here, a summary and comparison of each procedure is presented. Table 2.3 summarizes the film preparation methods. It is noted that each method has advantages and disadvantages.

Table 2.3: Summarized Preparation methods of VO_2 films [38]

	Synthesis Methods	Advantages	limitations
PVD	Pulsed-DC MS HIPIMS PLD Electron Beam Evaporation Atomic Layer Deposition OAD	✓ Suitable for multi-layer thin films or ultrathin films ✓ Precise control of process ✓ Compatible to a wider range of substrates	✓ Expensive equipment ✓ Lower growth rate ✓ Reduced pressure or vacuum
CVD	APCVD EACVD AA/APCVD	✓ Easily integrated into the float-glass production process ✓ No expensive vacuum systems High purity ✓ High-performance thin film	✓ Complex equipment ✓ Difficult to achieve controllable stoichiometry
Sol–gel		✓ Feasible for metal doping ✓ Complete coverage of the substrate ✓ Fine controlling of chemical compositions ✓ Low cost ✓ Even thickness	✓ Specific precursors required ✓ Not easy with very large areas of glass
Hydrot-ermal		✓ Unique morphology and structure Control ✓ Low temperature ✓ Cost effective	✓ Ununiformed ✓ Low purity ✓ Multiple steps

2.3 Chemical bath deposition (CBD)

Thin films have different processing possibilities, among all the methods, the chemical methods are found to deliver economical and easier processing challenges. Most of the chemical methods are cost effective, but their full potential for obtaining devise quality films has not been fully explored [91]. In general, it is difficult to find ideal method to prepare thin films, which will satisfy all specified requirements.

One of the thin film deposition method, Chemical Bath Deposition (CBD) is probably the most simplest method available for this purpose and it is also known as Chemical Solution Deposition (CSD) or Chemical Deposition (CD). The only requirements of these methods are a vessel to contain the aqueous solution and the substrate material to be coated. In addition to this, various complications such as some mechanism for stirring and a thermostated bath to maintain a specific and constant temperature are options that may be useful.

Chemical Bath Deposition technique involves controlled precipitation of a compound from the solution on a suitable substrate. This technique offers many advantages over the more established vapour phase routes to semiconducting thin films, such as CVD, MBE and spray pyrolysis. The first CBD thin films were prepared in 1884 and this method was limited to PbS and PbSe for a long time [92]. After the deposition of CdS, a wide range of chalcogenide and chalcopyrite materials have been prepared by this method. In CBD a wide range of substrates such as ebonite, iron, steel, porcelain and brass were specifically used apart from glass. The films were uniform, adherent and able to withstand considerable friction. Around 1980, the focus of CBD films slowly turned towards solar energy applications. One of the earlier developments towards this method was in solar absorber coatings. Application in the field of solar control coatings was suggested in 1989 [92]. The first general review on this topic was published by Chopra et al. in 1982[93]. Next review was published by Lokhande [94]. Then a comprehensive and general review was published by Lincoln et al. in 1998 [95].

2.3.1 Principles of CBD Method

The CBD technique can be used to control the film thickness and chemical composition by different parameters described in section 2.3.4. The ability of this method to coat large areas in a reproducible and low cost process is the most attractive advantage. This method depends on the deposition of thin films from aqueous solutions either by passing a current or by chemical reactions under appropriate conditions. By the nature of their preparative conditions, these films are generally not of high purity. With appropriate control of the deposition parameters definite composition of thin films can be obtained. In CBD process, thin films are deposited on a solid substrate when it is immersed into a dilute solutions of one or more metal salts (M^{P+}), a source of chalcogenide, X (X=S, Se, Te) ion and a suitable complexing agent in an aqueous solution.

The deposition of the film occurs on the substrate when the value of ionic product exceeds the solubility product, otherwise it is precipitated out. CBD can be carried out both acidic and alkaline solutions, most of the CBD reactions have been carried out in alkaline solutions. The metal ions are usually complexed by a suitable complexing agent, which would then gradually release metal ions during the course of reaction. The formation of metal-complex ion controls the rate formation of solid metal hydroxides which leads to the formation of solid film. Thus, the metal ion must be complexed in order to prevent precipitation of metal hydroxide. The strength of the complexing agent should not be too weak or too strong in ordered to prevent bulk precipitation or to deposition of the desired film. The basic principle of CBD is to control the chemical reaction so as to effect the deposition of thin film by precipitation [96]. The process depends on the slow release of chalcogenide ion into an alkaline solution in which the free metal ion is buffered at a low concentration. This concentration is controlled by the formation of metal complex species given by the reaction.

$$M(A)^{2+} \leftrightarrow M^{2+} + A \qquad \text{.....2.1}$$

Where M represents the metal ion and A represents complexing agent.

In chemical bath deposition (CBD) method, deposition of metal chalcogenide semiconducting thin films occurs due to substrate maintained in contact with dilute chemical bath containing metal and chalcogen ions [97].

2.3.2 Solubility and ionic product basics

Sparingly soluble salt, AB, when placed in water, a saturated solution containing A^+ and B^- ions in contact with undissolved solid AB is obtained and an equilibrium is established between the solid phase and ions in the solution as [98]:

$$AB\ (S) \quad \rightleftharpoons \quad A^+ + B^- \qquad \ldots\ldots 2.2$$

Applying the law of mass action, we get

$$K = [C_{A^+} \,.\, C_{B^-}] \,/\, C_{AB} \qquad \ldots\ldots 2.3$$

Where C_{A^+}, C_{B^-} and C_{AB} are concentrations of A^+, B^- and AB in the solution, respectively. The concentration of pure solid is a constant number, i.e.

$$C_{AB}\ (S) = \text{constant} = K' \qquad \ldots\ldots 2.4$$

$$K = [C_{A^+} \cdot C_{B^-}]/K' \qquad \ldots\ldots 2.5$$

$$KK' = C_{A^+} \times C_{B^-} \qquad \ldots\ldots 2.6$$

Since K and K', are constants, the product of KK' is also constant, say Ks, therefore (2.6) becomes

$$K_s = C_{A^+} \cdot C_{B^-} \qquad \ldots\ldots 2.7$$

The constant, Ks, is called solubility product (SP) and ($C_{A^+} \cdot C_{B^-}$) is called the ionic product (IP). When the solution is saturated, the ionic product is equal to the solubility product. But when the ionic product exceeds the solubility product, i.e.

$$IP/SP = S > 1 \qquad \ldots\ldots 2.8$$

The solution is supersaturated (S = degree of supersaturation), precipitation occurs and ions combine on the substrate and in the solution to form nuclei. Temperature, solvent and particle size affect the solubility product. For any formation of thin film, there is some minimum number of ions or molecules, which produce a static phase in contact with solution, called nucleus [98]. Nucleation on the substrate of surface starts at local homogeneity. The rate at which nuclei forms on the surface of the substrate, depends on the degree of supersaturation. The chemical bath deposition involves two steps, nucleation and particle growth, and is based on the formation of a solid phase from a solution [99].

2.3.3 Mechanism of Chemical Bath Deposition

In spite of the fact that CBD has been in use for a long time and that the reactions involved appear to be quite simple, the growth mechanisms of the CBD process is often ambiguous. There are several different mechanisms of CBD. These can be divided into four fundamentally different types [92, 100].

- The simple ion by ion mechanism
- The simple cluster (hydroxide) mechanism
- The complex decomposition ion - by - ion mechanism
- The complex decomposition cluster mechanism

Among the various chemical deposition methods, chemical bath deposition has attracted a great deal of attention because of its overriding advantages over the other conventional thin film deposition methods.

The chemical bath deposition method for the preparation of thin films has recently been shown to be an attractive technique because of its simplicity, convenience, low cost and low temperature, and it has been successfully used for depositing ternary metal chalcogenide thin films. Understanding of the chemistry and physics of the various process involved in a deposition processes has now made possible to obtain undoped/doped, multicomponent semiconductor thin films of usual/unusual and metastable structure.

2.3.4 Factors Influencing the Deposition Process

The formation of thin film by chemical bath deposition is influenced by the factors such as;

- Bath temperature
- Nature and concentration of the precursors
- Nature and concentration of complexing agent
- pH of the solution
- Deposition time
- Nature of the substrate

I. Bath Temperature

An important factor that influences the rate of reaction is the bath temperature. As temperature increases, dissociation of the metal complex to release free metallic ions and hydrolysis of the chalcogenide source increases. The kinetic energy of the molecule also increases leading to greater interaction between the ions. This result in more increase or decrease in the film thickness depending on the extent of super saturation of the solution. Studies by Srinivasan et al. on the effect of temperature on the structural and optical properties of PbS thin films, shows that the crystallinity of films were improved when the temperature was increased [101].

II. Nature and concentration of the precursors

Influences the composition of the product. The growth kinetics also depends on the nature of the precursors. For example, when metal sulphate is used to deposit the metal Selenide film, the rate of deposition decreases and the thickness increases. Here the SO_4^{2-} ions obtained from the metal sulphate reduce the concentration of selenide ions [102].

The deposition rate and terminal thickness initially increase with an increase in the ionic concentration of precursors. However, at higher concentrations the precipitation becomes very fast leading to decrease in film thickness.

III. Nature and concentration of complexing agent

The Nature of complexing agents may influence the final products. For example, when ammonia is used as a complexing agent for the preparation of ZnS thin film, it is found to result in $ZnO/Zn(OH)_2$ phase rather than ZnS. However when two complexants ammonia and hydrazine are used, the oxide and hydroxide phases could be avoided largely.

Generally in a reaction, metal ion concentration decreases with the increase of complexing ion concentration. As a consequence, the rate of reaction and hence the precipitation are reduced leading to a large terminal thickness of the film. Even more important, if the complexing agent to metal ion ratio increases above a certain value, the mechanism of deposition may changes (commonly from a hydroxide cluster mechanism to ion-by-ion deposition) [102].

IV. pH of the solution

When the pH of the reaction bath increases, the metal complex usually becomes more stable reducing the availability of free metal ions. This will decrease the reaction rate resulting in higher

thickness of the film. pH can cause complexing agents to be protonated; thus causing them to be unable to bind to the metal center creating free excess metallic ion [103].

V. Deposition time

Deposition time is one of the parameter which affects thin film deposition in CBD method. In most cases, it has a great influence on structural, morphological and optical properties of thin films showed the effect of Deposition time on the crystal orientation of thin films as well as crystallite size, strain and dislocation densities of PbS films [104].

In general, the growth of good quality thin films proceeds at a slower rate. The CBD method is suitable for producing uniform thickness films in the range of 0.05 - 0.3 μm. The dependence of thickness of the film on the duration of deposition has been studied in detail for different semiconductors [105].

VI. Nature of substrates

Substrate plays an important role in the reaction kinetics and adhesion of the deposited films. Hence, cleaning of the substrate surface is the first step in the thin film deposition. Higher deposition rates and thicknesses are observed for those substrates whose lattice parameters were well matched with those of the deposited material [38].

2.3.5 Advantages and disadvantages CBD

The major advantage of CBD is that it requires in its simplest form only solution containers and substrate mounting devices. Chemical bath deposition yields stable, adherent, uniform and hard films with good reproducibility by a relatively simple process. The growth of thin films strongly depends on growth conditions, such as duration of deposition, composition and temperature of the solution, and topographical and chemical nature of the substrate the most advantageous properties of CBD techniques are listed below [92].

- CBD technique is the simplest cost effective method for thin film synthesis
- The possible to deposit multi compound chalcogenide thin films over a wide range of stoichiometry with this technique
- Chemicals do not require high vacuum and it can be carried out even at room temperature

- Large area deposition is possible by carefully lying down the substrate on a shallow tray containing the deposition bath
- Produces uniform well adherent and reproducible thin films for photovoltaic applications
- An inexpensive method for large scale industrial applications
- The material consumption is low and minimizes the loss
- The crystallite size of the CBD films is very small

The major drawback of this technique is the nature of their preparative conditions, the films are generally not of high purity due to the technique (chemical reaction) used could form small amount of undesired products. Above all this wastage of solution after every deposition, because it is impossible use chemical once used for coatings. Among the various methods, chemical bath deposition has attracted a great deal of attention because of its overriding advantages over the other conventional thin film deposition methods [92].

2.4 Gaps in the Literature

Based on the limitations described synthesis methods, there are different requirements for Selection of Deposition Process, There are no single techniques ideally suited for preparation of large area thin films with all the desired properties, each applied will have its own merit and demerits. Hence, choice and selection of deposition process plays a vital role in the formation of good quality thin films, the choice of deposition methods of thin films depends on several factors to avoid the limiting factors described in section 2.2.5, commonly known are listed below [47]:

- The nature of the material to deposit.
- Nature of the substrate to be used.
- The stoichiometry desired.
- Film microstructure and deposition rate should be controlled.
- Stoichiometry should be maintained as that of the starting materials.
- Adhesion of the film on the substrate.
- Cost effective of the technique.
- Scaling up of the process.
- Control on film substrate interface and defects created in the film.

The processing techniques mentioned for production of thermochromic vanadium dioxide does not make the thermochromic materials to be used for commercial purpose as the processing techniques are complicated to apply and difficult to use from economical point view. The processing is expensive and device used for are costly, more than this processing techniques used for thermochromic materials have difficulties in scalability to the commercials [106,107]. The science of thermochromic materials application in real world is insignificant, Based on the requirements mentioned above the chemical bath deposition technique is used for this experiment. Even if chemical bath deposition method has been developed for decades with different thin film deposition method, up to recent time there are no reported papers for vanadium dioxide (VO_2) synthesis technique using chemical bath deposition. By applying the chemical bath deposition processing techniques it beloved to solve most of the limitation occurring with other processing techniques.

In general there is no ideal processing technique for specific applications of thin films, instead the processing's are selected based on their advantageous parts which override their limitations, based on this, CBD technique fulfill most of the requirements required. There for the processing method applied during this project is chemical bath deposition method.

CHAPTER 3 MATERIALS AND METHODS

3.1 Material Selection

3.1.1 Ammonium metavanadate (NH_4VO_3)

NH_4VO_3 is bought from Loba Chemie with 99 % purity of AR/ACS grade and molecular weight of 116.98 g/mol. Ammonium metavanadate is used as a source of vanadium metal ion, due to its solubility in water at lower temperature, easily reduced from it V^{5+} oxidation state to V^{4+} oxidation state. However, this compound should be used carefully for its hazardous effect during inhalation, the effect would be seen in long term.

3.1.2 Potassium hydroxide (KOH)

KOH is bought from Loba Chemie with 99 % purity of AR grade and have weight of 56.1056 g/mol. The metal ions are usually complexed by a suitable complexing agent for this purpose KOH is found better for its rate of formation of metal complex other than NaOH, which would then gradually release metal ions during the course of reaction. The formation of metal-complex ion controls the rate formation of solid metal hydroxides which leads to the formation of solid film. So that by using KOH rate controlling mechanism is achieved.

3.1.3 Hydrochloric acid (HCl)

Hydrochloric acid is bought from Loba Chemie with 99.0 % purity and it molecular mass of 36.46 g/mol. The HCl acid have its important in this chemical reaction to control the pH of the solution, as well as the formation of precipitates.

3.1.4 Triethanolamine (TEA) ($C_6H_{15}NO_3$)

TEA is bought from Samchun pure chemical co.,Ltd (99.0 % pure) and have 101.19 g/mol molecular weight. This compound is a viscous organic compound that is both a tertiary amine and a triol. This compound is used most commonly in chemical bath deposition process as a complexing agent due to its different properties, most importantly in this project it used to control the rate of release of metal ion precursor, which is very important to form the required VO_2 phases.

3.2.4 Polyvinylpyrrolidone K - 30 (PVP) ($C_6H_9NO)_n$

PVP K-30 is from Junsei Chemical co., Ltd. It has been reported earlier that polyvinyl pyrrolidone (PVP), a water soluble polymer, it has excellent wetting properties, most commonly used in chemical bath deposition of CdS due to its wetting properties, it readily forms a film, PVP could be generally used in thin film formation due its attractive properties such as solubility in water, physiological compatibility, non-toxic, chemical inert, temperature resistance (150 °C melting point), non-ionic and colorless polymer. Therefore PVP K-30 is chosen in this project in order to assist formation of VO_2 thin film on glass substrate and also have a properties of preventing agglomeration. In addition to this; PVP have shown to assist formation of V^{4+} oxidation state to form VO_2, which is very important for this research purpose. The general look of the materials selected for this research purpose as a package is shown in figure 3.1.

Figure 3.1: Materials selected for the research purpose from left to right polyvinylpyrrolidone k - 30 (PVP), ammonium metavanadate, potassium hydroxide (KOH), hydrochloric acid (HCl) and triethanolamine (TEA)

3.2.5 Substrate

The substrate used for this experiment is an ordinary microscope glass from star labs, which have a size of 76.2mm × 25.4mm ×1.1 mm as it is shown in figure 3.2 d and it have transmittance (T %) of ~80 % for visible range of wavelength (390 – 700 nm). Based on this coating process is applied on. The figure 3.2 below shows the materials selected after they are unpackaged.

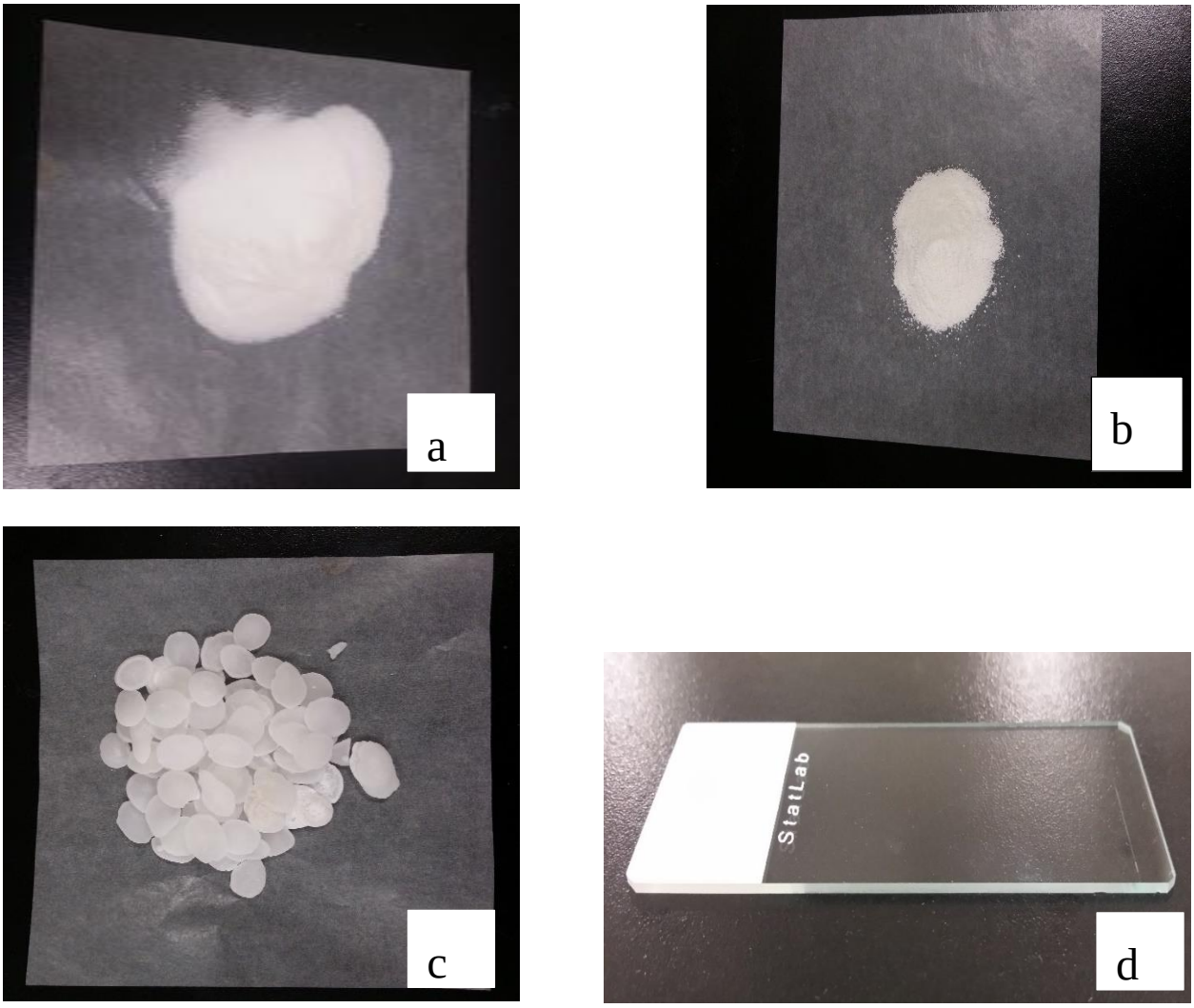


Figure 3.2: a) PVP powder b) ammonium metavanadate c) KOH powder d) glass substrate used.

3.2 Thin Film Synthesis

3.2.1 Cleaning process

Before the start of chemical bath deposition synthesis, all the equipment to be used in the experiment including the beaker, spatula, small containers undergo a cleaning process in such way

that first hand wash with running water using detergent to remove any dust and impurities. Then it undergo ultrasonic cleaning steps at 60 °C in HCl solution for 20 minutes to remove some remaining impurities, finally washed with water and rinsed with deionized water. More than this special attention was given for substrate cleaning steps first washed with detergent then using solution of HCl, ethanol and acetone in ultra-sonication for 30 minutes for each solution to remove any possible impurities available including organic maters and handprints, finally it is washed with deionized (DI) water in the sonicator and rinsed by DI water. After completing cleaning processes, all the samples were dried in oven at 100 °C and made ready for applications.

3.2.2 Synthesis procedure

The synthesis flow chart is given below to describe procedure included CBD.

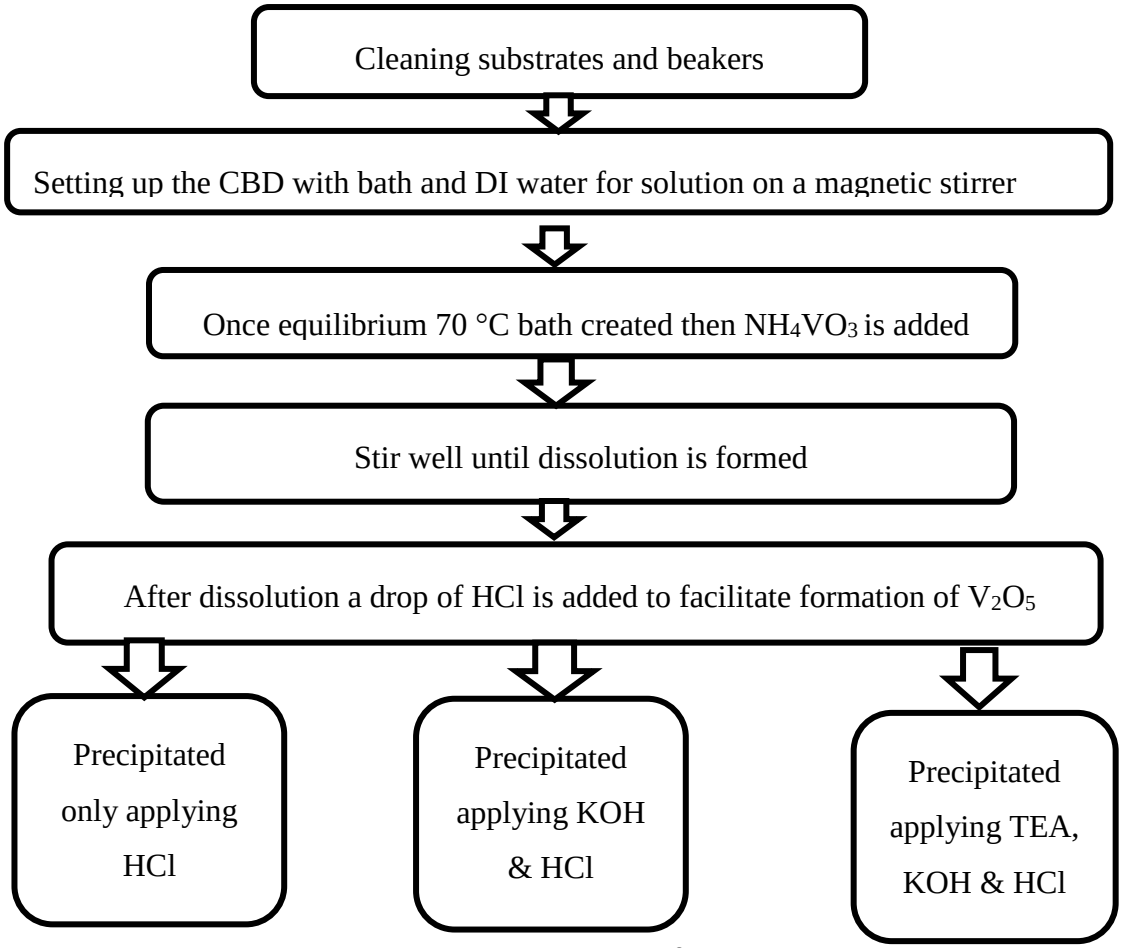


Figure 3.3: Flow chart showing the general procedure of CBD.

1. Before the formation of thin film, I have worked out three trial to get combination of elements taking previously done CBD process on thin films such as PbS, CdS and others as base, to check

for the process and compounds that should be used to get the best pure phase of VO_2. The three trials includes 1) using HCl, only 2) using KOH, HCl and 3) using TEA, KOH & HCl.

2. Based on the result found in the three trial, the deposition process extended for thin film deposition of VO_2 i.e the one that shows formation of better VO_2 phase.
3. To achieve this first of all CBD method is formed in such a way that 0.05 M of 100 ml NH_4VO_3 Solution (0.5853 g of NH_4VO_3 powder in 100 ml deionized water) is formed in water filled bath of 250 ml beaker. The bath in this experiment is used to control the temperature of solution easily and facilitate measuring the solution temperature using thermometer without directly inserting the sensor in to solution (that could create impurities), to determine the amount of powder a digital balance is used.
4. The experimental set up of the bath is shown in figure 3.4, so that solution containing beaker is inserted in a larger beaker filled with water (the bath could be filled with other liquid based on requirements, such as oil). The temperature of bath is set ~ 70 °C, in which the dissolution of NH_4VO_3 will be facilitated.

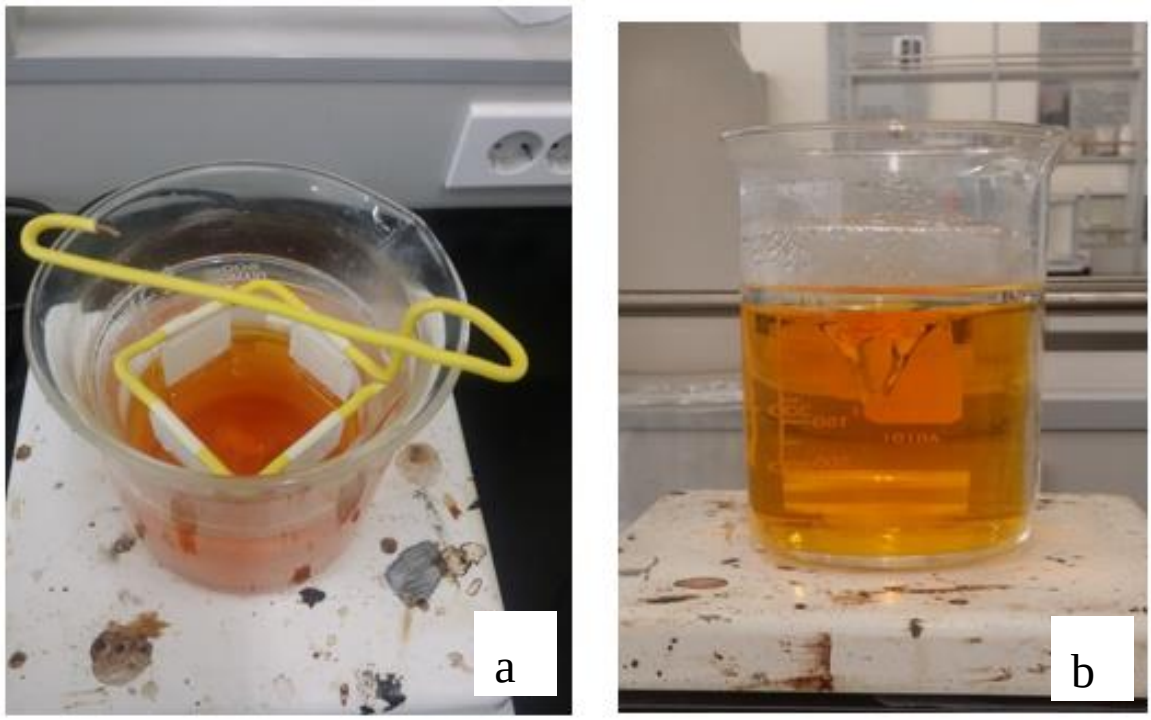


Figure 3.4: a) The experimental setup of the chemical bath deposition of VO_2 b) The yellow colour appearance of the solution after addition of HCl.

5. The 0.05 M concentration once formed, for the first trail 1), I created precipitate using HCl in drop wise, with each drop of 0.1 ml. with addition of the HCl the solution colure immediately transform from transparent to yellow color as shown in figure 3.4.

   N.B from different experiment trials for this project I have done I realized, precipitation in vanadium compounds occur in acidic condition (in the basic condition no precipitate occurs) in addition to this, the 0.05 M concentration is applied for different literatures for CBD and other techniques [108, 109] and I found it is optimum level for this experiment based on my trial.
6. The very bright yellow color in solution formed indicates V^{5+} oxidation state, [110] it is formed by addition of only 0.1 ml HCl. By continuous addition of the HCl, the pH of the solution changes from neutral 7 to around 3.5 at which the precipitate forms, pH of the solution is controlled using pH indicative litmus paper shown in figure 3.5 a. During each steps of reaction the solution is well stirred until equilibrium formation in each steps, and temperature is maintained constant at 70 °C.

   N.B for this trial I preferred the powder form due to facilities available, to easily identify the phase formed using XRD.
7. Once the precipitate formed, rinsed with deionized water and extracted from the beaker as shown in the figure 3.5 b & c, and dried at 50 °C, using the higher temperature could affect the precipitate before it is characterized as transition temperature of VO_2 is around 68 $\pm$2. This process is done frequently to get enough amount of powder samples for XRD characterization.

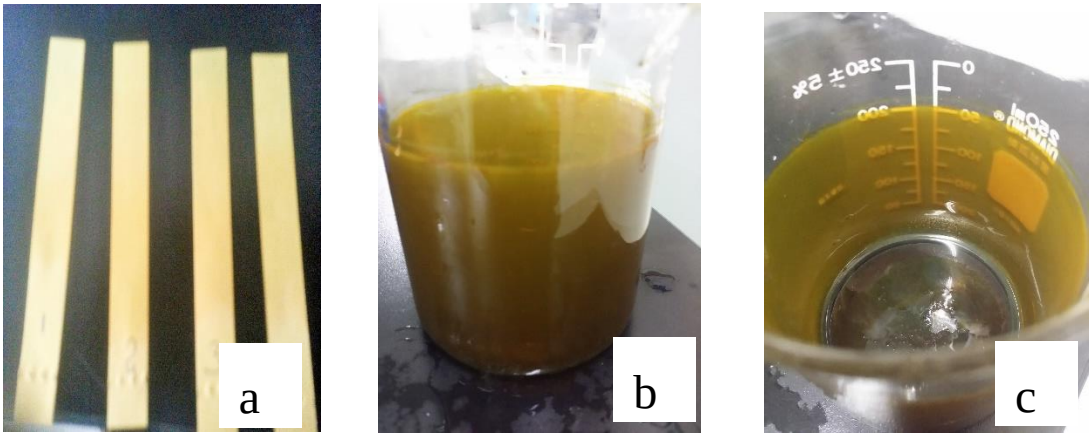


Figure 3.5: General aperance of a) the litmus paper b) and c) the general appearance after the precipitatio on the beaker.

8. For precipitate formation of trial 2**)** using KOH, HCl, is done in same procedure as previous, but for this experiments once the dissolved NH_4VO_3 formed, only a small drop of ~0.1 ml of HCl

is added (which facilitate V_2O_5 formation and preferable for subsequent reduction towards VO_2), after this KOH is added, the amount of KOH used for the 100 ml solution is 0.2 g in pellet form as shown in the figure 3.2 c , with addition of KOH solution shows reduction process from V^{5+} towards V^{4+} then V^{3+}. When blue black color is formed i.e indicative of V^{4+}, for VO_2 formation [111]. Once this color is shown then the solution pH is lowered using HCl acid to ~ 3.5 by drop wise addition.

The precipitate formed and extracted with the same procedure for trial 1 above. (the amount of KOH used is preferred according to the excepted chemical reaction predicted, using higher amount of KOH makes it uncontrollable based on their color of oxidation state), During each steps of reaction the solution is well stirred until equilibrium formation and throughout the process temperature is maintained constant at 70 °C which is measured using the digital thermometer putting the sensor in the bath.

9. For precipitate formation of trial 3) using TEA, KOH & HCl, is done in same procedure as previously mentioned for trial 2, but in this case 0.8 ml TEA is added, addition of TEA shows slow transition in color of the solution which indicates reduction process is slow and easy to control. (the amount used according to different literatures on CBD involving TEA and experimental expected reaction shown in reaction mechanism) [112] once blue black color is seen, then the solution pH is lowered using HCl acid to 3.5 by drop wise addition. The precipitate formed and extracted with the same procedure for trial 1 mentioned above. During each steps of reaction the solution is well stirred until equilibrium formation and temperature is maintained constant at 70 °C.
10. After the precipitate extracted for the three trial, it is annealed at 570 °C as shown in figure below using inert gas furnace for 2 h, and one powder sample of trial 3 at 570 °C in ordinary air furnace. This temperature selected based on the DTG analysis and literatures form other thin film materials [113]. i.e at high temperature vanadium dioxidizes to its higher valance state V_20_5 if heat treated in air.

Based on the results found from XRD results, the third trial shows better VO_2 formation comparative to the rest of trials the result is shown in figure 4.1. Accordingly the thin film is prepared by using TEA, KOH & HCl chemicals. The chemical reaction which is expected as a mechanism for the formation of VO_2 phase is described below [114,115].

In addition to this, PVP is used as a surfactant, because the deposited thin film formed without using PVP is not good enough, shows agglomeration and easily peeled off from the surface after coating. As a solution to prevent this and create better thin film, PVP is incorporated to create thin film which is stable after deposition. Above all this PVP have properties of attracting V^{4+} described on the discussion parts. Addition of PVP possibly can help formation of better thin film as described in different literature and helps its formation [116, 117].

In this project I designed another technique that helps to attach as much as possible vanadium in its V^{4+} state, which is very important steps of VO_2 formation instead of other unwanted phase of vanadium formed on the glass substrate. Briefly described on the discussion part.

The mechanism I have designed is that instead of formation of solution by addition of PVP, the glass is covered with PVP solution before using it for vanadium coating so that it will have selective attraction for VO_2 phases towards the glass substrate surface to be coated. The thin formation mechanism is described in the steps below.

1. The solution of PVP is formed in 100 ml beaker, by addition of 1.5 gram PVP, K-30 powder in 50 ml deionized water heated at 60 °C. The amount of PVP for this design is considered with literature which used PVP in the solutions [116, 117]. The solution stirred very well for a while until dispersed solution is formed. i.e using cool water the dissolution and the uniformity is affected.

   N.B In this case, as PVP is only needed to cover the thin film, the amount used is above the described extent on literatures. Higher concentration of PVP have also negative effect on the thin film.
2. After formation of dispersed solution, the clean glass substrate is inserted in to the solution for 30 second, as PVP have sticky properties, 30 second is enough to cover the glass surface. After this PVP covered glass is dried in an oven at 80 °C for 40 minutes [117].

   All of glass substrates used in this project for thin film preparation are pre coated with PVP.
3. The process used for thin film formation is trial 3 using TEA, KOH & HCl. The process followed is the same as described above for trial 3, in this case just before formation of precipitates the PVP coated glass is inserted in to the solution and the stirring is stopped, to create uniform deposition. Four glass substrates are inserted together at time the general setup is shown in figure 3.6 a and figure 3.4 a.

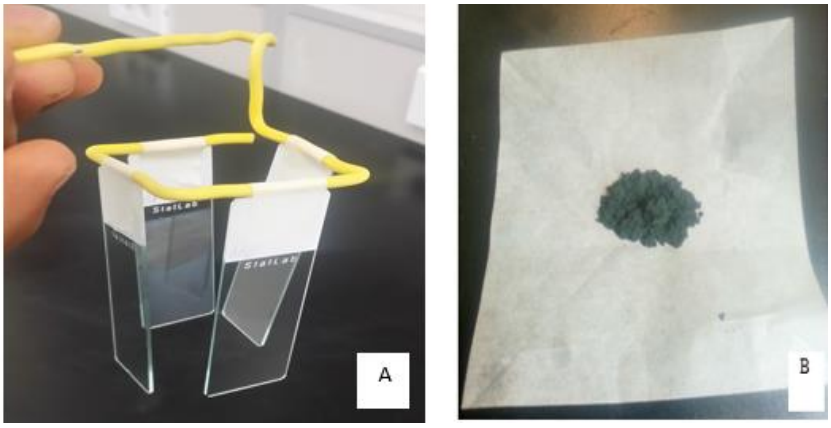


Figure 3.6: a) The setup of the glass to coat 4 substrate at a time. B) Powder samples extracted from precipitate.

4. After the deposition process of vanadium dioxide, it is rinsed in deionized water and dried at a temperature of 50 °C.
5. The deposition process was done at different time of coating at 15 minutes, 30 minutes and 80 minutes shown in figure 3.7. The thin film prepared at 80 minutes is made thicker so that it possible to characterize it as a thin film on XRD, it could not be used for spectrophotometric measurement as it appears almost opaque.

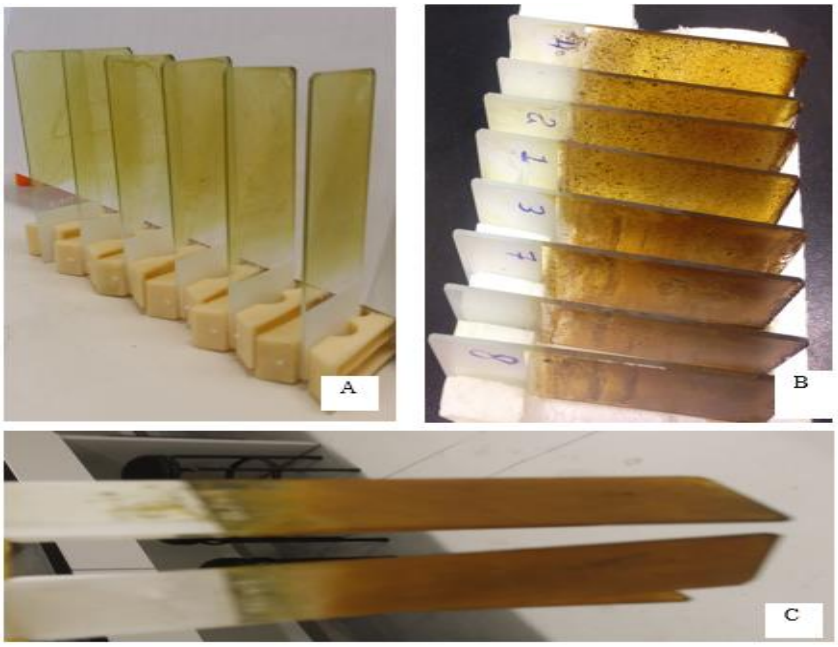


Figure 3.7 Showing thin film after deposition process a) 15 minutes deposition b) 30 minutes deposition c) 80 minutes deposition.

6. After this, thin films are annealed in different temperature of 450, 500 and 570 °C for 2 h [129].

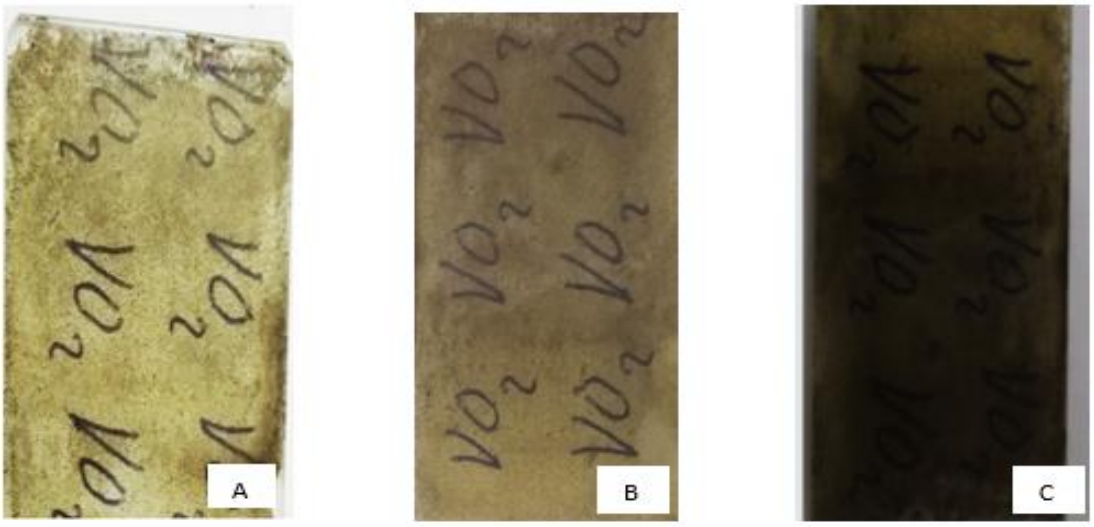


Figure 3.8: Showing thin films after annealing at 570 °C for 2 h a)15 minute b)30 minute c) 80 minute deposition times.

3.2.3 Experimental Samples names

Samples prepared in this experiment are named as presented below to be used for specification of each samples. This nomenclature will be used from this point. All of them are annealed for 2 h in inert gas furnace with nitrogen, except for X5 annelid in air for 2 h to compare the effect.

Code	Description of code name
X1.	Powder sample prepared using HCl chemical and annealed at 570 °C.
X2.	Powder sample prepared using HCl and KOH chemicals and annealed at 570 °C.
X3.	Powder sample prepared using HCl, KOH and TEA and annealed at 570 °C.
X4.	Powder sample prepared using HCl, KOH and TEA before annealing.
X5.	Powder sample prepared using HCl, KOH and TEA annealed at 570 °C in air.
1S1	15 minute deposited thin film using HCl, KOH, TEA and PVP annealed at 450 °C
1S2	15 minute deposited thin film using HCl, KOH, TEA and PVP annealed at 500 °C
1S3	15 minute deposited thin film using HCl, KOH, TEA and PVP annealed at 570 °C.

2S1 30 minute deposited thin film using HCl, KOH, TEA and PVP annealed at 450 °C

2S2 30 minute deposited thin film using HCl, KOH, TEA and PVP annealed at 500 °C

2S3 30 minute deposited thin film using HCl, KOH, TEA and PVP annealed at 570 °C.

3S1 80 minute deposited thin film using HCl, KOH, TEA and PVP before annealing.

3S2 80 minute deposited thin film using HCl, KOH, TEA and PVP annealed at 450 °C.

3S3 80 minute deposited thin film using HCl, KOH, TEA and PVP annealed at 500 °C.

3S4 80 minute deposited thin film using HCl, KOH, TEA and PVP annealed at 570 °C.

3.2.4 Reaction Mechanism

Deposition of vanadium dioxide thin film involves controlled release of vanadium ions from its complex. The formation of VO_2 involves the following steps: [114,115].

$NH_4VO_3 + HCl \rightarrow V_2O_5 + NH_4Cl + H_2O$ ……..3.1

$V_2O_5 + 6HCl \rightarrow 2VOCl_2 + 3H_2O$ …….. 3.2

$NH_4VO_3 + 8HCl \rightarrow 2VOCl_2 + 2NH_4Cl + Cl_2 + 4H_2O$ …….3.3

$VOCl_2 + TEA \leftrightarrow VO\ (TEA)^{2+} + 2Cl^-$ …… 3.4

$VO\ (TEA)^{2+} \leftrightarrow VO^{2+} + TEA$ ……. 3.5

$KOH + OH^- \leftrightarrow K^+ + OH^-$ ……. 3.6

$VO^{2+} + 2OH^- \leftrightarrow VO\ (OH)_2$ ……..3.7

$VOCl_2 + KOH \leftrightarrow VO\ (OH)_2 + KCl$ ……...3.8

$VO\ (OH)_2 \leftrightarrow VO_2 + H_2O$ ……3.9

3.3 Characterization techniques

3.3.1 XRD and morphology characterization

The characterization technique is used to show, the structure and phase present in the prepared materials especial to select the processing technique which will give better product of VO_2, this is done using (SHIMADZU, XRD-7000 X-RAY DIFRACTOMETER) which uses 40 kV and 30 Ma. To do this powder diffraction technique is used by preparing fine powders from all trials, the samples tested as powder form first annealed at 500 °C in nitrogen gas and air. The phases of VO_2 tested are confirmed with JCPDS files (JCPDS # 43-1051) for VO_2, to see the existence of the required phase, based on the results found on this technique then thin films are produced.

The thin films characterized in this technique are specially prepared for the XRD purpose that deposited for 80 minutes, because the peak from 15 and 30 minutes deposited thin films was not clear enough for characterization purpose. Thin film characterization is done by inserting perfectly cut glass in sample placemen area, to characterize samples, target = Cu (λ =1.5405 Å), voltage = 40.0 (kV) current = 30.0 (mA) are applied.

Based on the results found from XRD peaks of thin films, the average crystallite sizes (D) were calculated from the full width at half maximum (FWHM) of the diffraction for the dominate peaks of using the Debbye–Scherrer formula [118].

$$D = \frac{K\,\lambda}{\beta COS\,\theta} \qquad \text{3.10}$$

Where the dimensions shape factor k=0.94, λ =1.5405 Å, β= FWHM of the peak in radian, θ=angel of diffraction using the mentioned conditions the results are analyzed.

The morphology of thin film samples prepared from the experiment is analyzed using optical microscope (HUVITZ HR-300) with its maximum magnification of 1000 x. For observation of general form of deposition and arrangements.

The scanning electron microscope (SEM) device used for the analysis of the surface morphology with a magnification of 30, 000 X, and 10 KV is used in which the effect of temperature on the microstructure of the film is studied, in such a way by comparing the image obtained from SEM, to analyze grains, structures, particles and growth of microstructures.

3.3.2 Thickness of the thin film calculation

The thickness of thin film is calculated based the weight deference, this is done by finding the weight of coated substrate. In such a way, that substrate is measured before and after the coating process. The equation is as given below [119].

$$T = \frac{m}{\rho 2A} \quad \text{……..……3.11}$$

Where T, represents thickness of the film, ρ represents the density of VO_2 in the bulk state which is 4.57g/cm^3, m represents the weight difference of the substrate before and after coating, A represents the area of coated substrate in this case. In this case it used as 2A, because the substrate is coated in both sides. The area is found by measuring the coated portions of the substrate using digital measuring equipment.

Based on this calculation, the thickness of the film is evaluated for the three deposition time, with their difference in annealing temperature, the result given in the discussion part table 4.2.

3.3.3 Optical properties

The optical properties were evaluated by the UV-VIS spectrometer at a wavelength range of 250-1100 nm. The device used for this analysis is (AZZOTA, SM-1600 SPECTROPHOTOMETER).

The technique used to measure the transmittance value is by setting the wavelength number for each wavelength transmittance value, so that for each measurement by selecting specific value from 250- 1100 nm, with increment of 25 nm, based on that the values are such as 250nm, 275nm, 300nm, 325nm, etc.

The figure is plotted connecting those points, to measure the transmittance at higher temperature (100 °C), as device does not contain heating unit, it is done by setting an oven beside the spectrometer, so first the thin film is heated to 110 °C in an oven until the sample get uniform heat for about 10 minutes, then taking out the sample from the oven and immediately measuring its transmittance, during this the transmittance measurement for one wavelength value takes about 15 second, so that with in the 15 seconds the sample heat decrease from 110 to 100 °C, so that the spectrometer will show its transmittance for the specified wavelength at 100 °C, and based on this technique its transmittances are evaluated.

3.3.4 Thermal analysis

The temperature properties of this samples are the important parameter required for this research as properties of VO_2 is based on thermochromic transition behavior. This is done using two devices the first device used is differential thermo gravimeter (DTG) (SHIMADZU, DTG - 60H) using the powder synthesized with trial 3, to analysis the properties prepared powder samples under heat treatment set the condition and temperature of annealing to be used for the thin films produced. This done using 15 mg of fine powder sample with heating rate of 7 °C in both condition under of nitrogen and air, in a range of 30 - 600 °C . Based on this results of exothermic and endothermic peaks found the annealing condition is optimized.

The second device used for thermal application is Differential scanning calorimetry (DSC), the device used in this research (SHIMADZU, DSC -60 PLUS). Based on the above analysis powder samples prepared from trial 3 after annealing process in nitrogen gas are used for testing. This testing is done from 25 °C- 100 °C in nitrogen gas atmosphere with heating rate of 5 °C to see the thermochromic transition behavior of the prepared samples, based on this thermochromic behavior is analyzed using endothermic peaks shown from the results, and this is taken as the transition temperature of sample shown in the discussion part.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 XRD Diffraction analysis

The phase identification conducted by using XRD results of each processed sample in this experiment, so that the other thin films synthesis are produced using results found from the powder analysis technique.

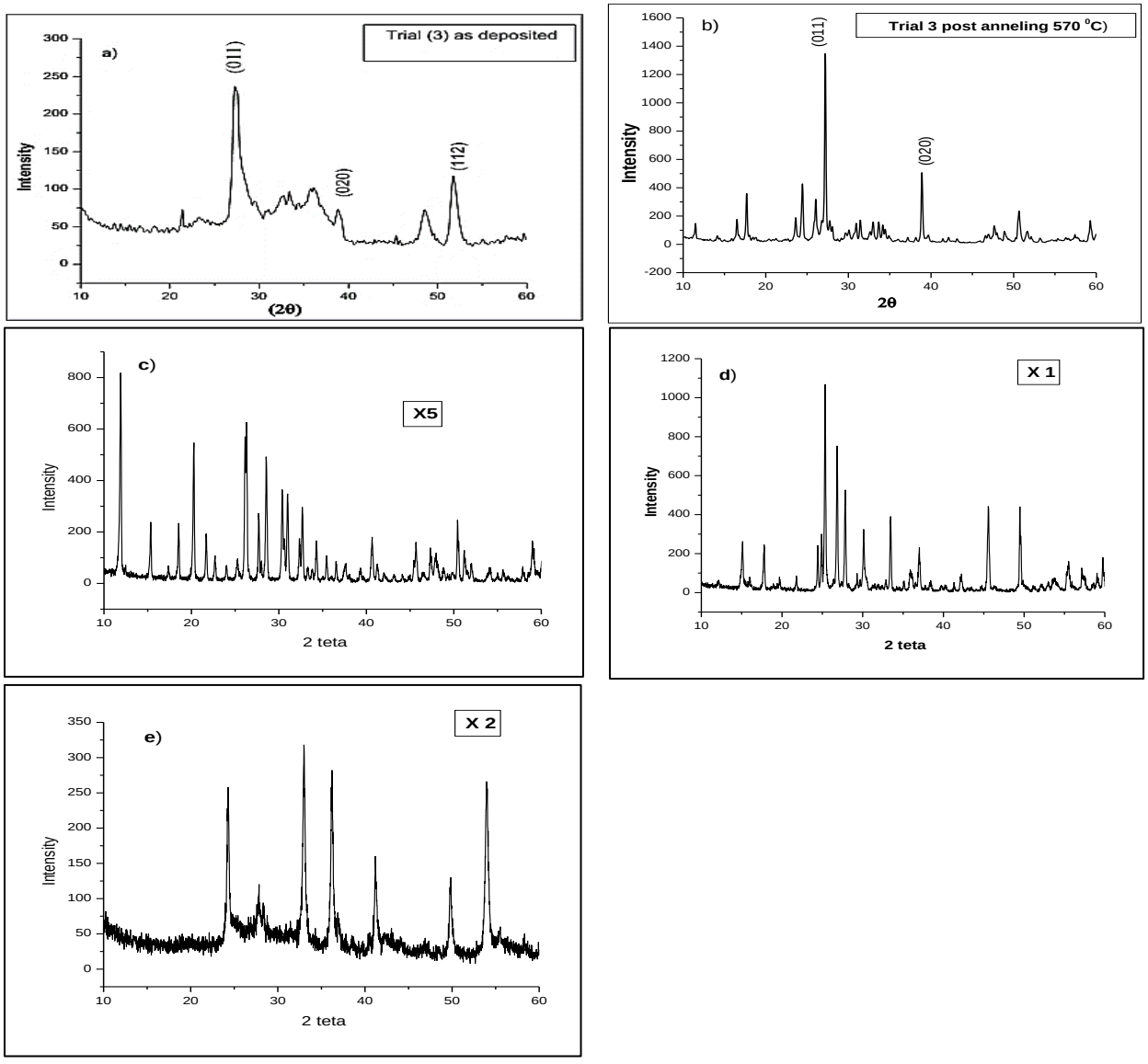


Figure 4.1: The XRD of a) trial 3 before annealing (X4) b) trial 3 after annealing at 570 °C in N_2 gas (X3) c) trial 3 after annealing at 570 °C in air (X5) d) trial 1 after annealing at 570 °C in N_2 (X1) e) trial 2 after annealing at 570 °C in N_2 (X2). The units of the intensity are all in (a.u)

Formation for VO_2 phase as shown in figure 4.1 a, b. The dominant phases are due to VO_2 which is indexed to (011) at $2\theta = 27.6°$ and (020) indexed with $2\theta = 39.5°$ [116,117,120]. The other results as trial 1 shows a dominant pick at (210) at 2θ of 25 ° which shows that V_2O_5 is more dominate phase of the results, for trial 2 the result shows a combined existence of V_2O_3 and V_2O_5 phases as indicated in figure 4.1 e.

In addition to the formation of better VO_2 phases using trial 3, the effect annealing condition of the final results have significant effect as V element could oxidize very easily in high temperature.

The effect of annealing in normal environment is shown in figure 4.1 c, which shows that even if the processing technique used is trial 3 (which forms VO_2), But the annealing condition have almost completely destroyed the required VO_2 phase by creating differ undesired phases and polymorphs of vanadium. Compering the results found in figure b and c, in which annealing in N_2 gas is very important steps for the VO_2 phase formation.

The above result is taken as reference for the thin film processing technique to be done using trial 3. Because the method used in trial 3 observed to show better result comparative to the other.

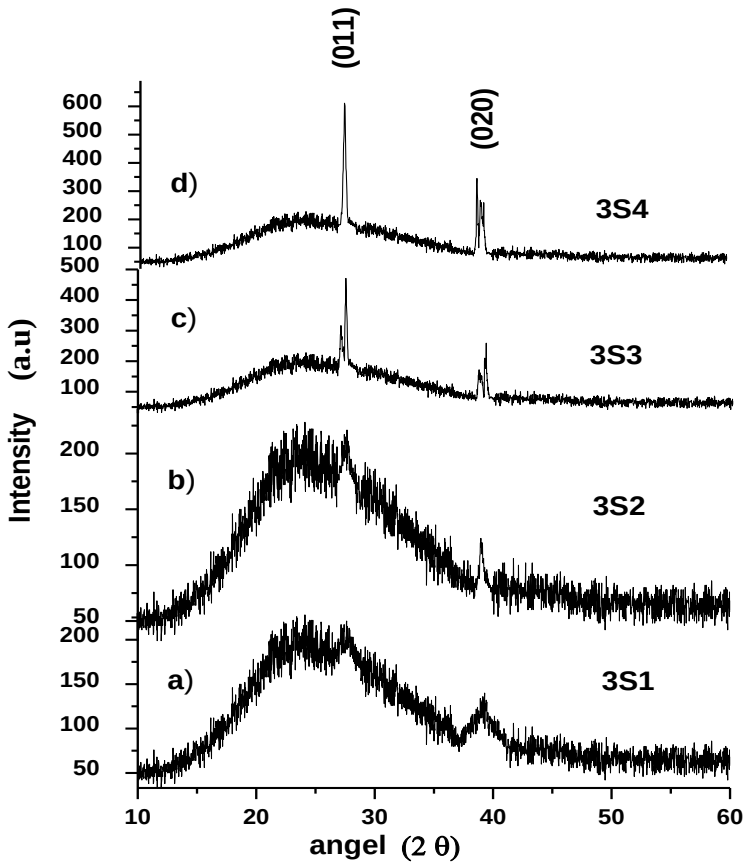


Figure 4.2: The XRD results of low temperature monoclinic phase 80 minute deposited thin film samples a) 3S1 before annealing b) 3S2 annealed at 450 °C c) 3S3 annealed at 500 °C d) 3S4 annealed at 570 °C.

The XRD figure 4.2 shown above are prepared by increasing the deposition time to 80 minutes so thicker film will be found which is easier to be analyzed, and for the thinner films (lower deposition time) finding the XRD pick is challenging. The XRD result found are in line, the dominant diffraction peaks could be indexed to the monoclinic crystalline VO_2 (JCPDS # 43-1051) [120]. The peaks observed are dominant enough, indicating the high purity and high crystallinity of the products. The higher VO_2 purity is attributed to the PVP pre deposited film which have a properties attracting and interacting with V^{4+} ions from its VO^{2+} state selectively. This properties of selection is more clearly seen when we compare the relation on figure 4.1 which shows dominate phases of VO_2 with other less dominant phases of vanadium compound, but when we see the figure 4.2, it

shows only the dominant phases of VO_2. This shows that the PVP used have direct contribution to the formation of VO_2 on the substrate selectively [116, 117].

The effects of PVP on the stabilization of the precursor solution were due to interactions of the negatively charged carbonyl groups in PVP with VO^{2+}. Furthermore, it has been reported that the interactions between the metal ions and the carbonyl groups from different PVP molecules increase the apparent viscosity, where metal ions act as cross-linking points between different PVP molecular chains, improving the film formability.

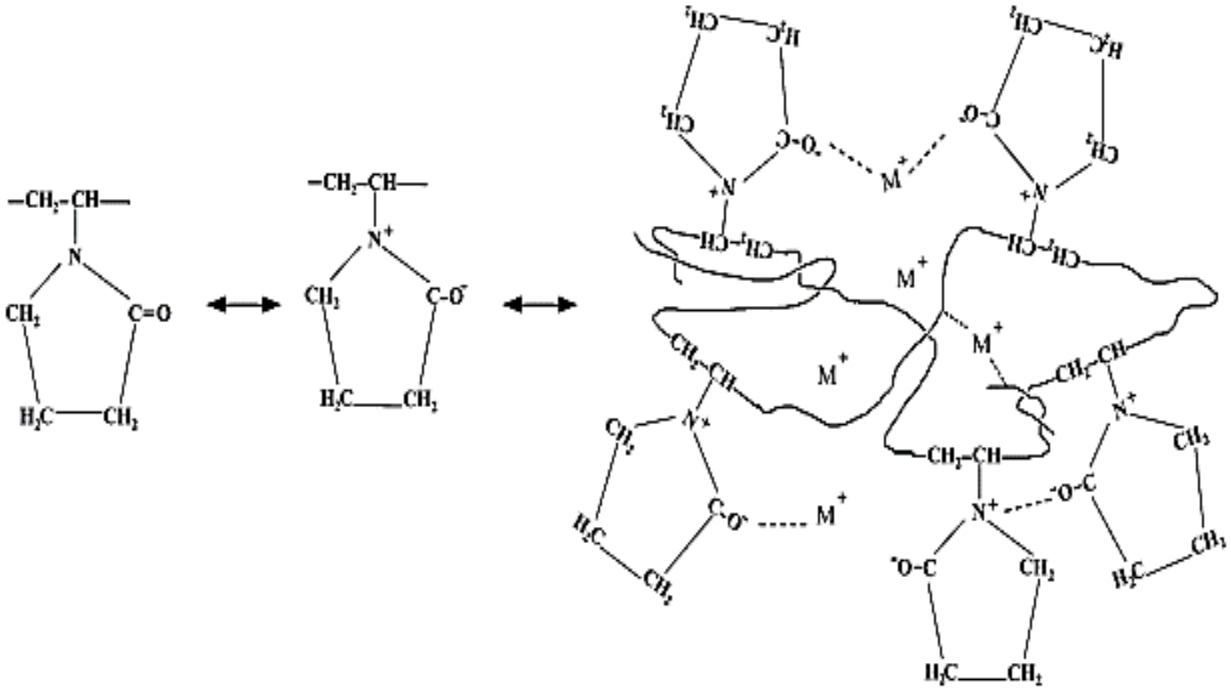


Figure 4.3: Schematic illustration of the interactions between VO^{2+} (M^+) and PVP as well as the film-forming mechanism [117].

The figure above shows a schematic illustration of the film-forming mechanism. The interaction among polymer molecules via the oppositely charged groups, along with those between the carbonyl groups and the metal ions, ensure the formation of cross-linked high quality. In addition, steric entangling of the polymer chains enhances the cross-linking.

Based on the result confirmed from the XRD data, the mechanism employed to create VO_2 by pre coating the PVP was effective technique, which gives the desired products expected.

Table 4.1: The FWHM and average crystal size value of thin film sample calculated using Debye scherrer approximation

Samples	FWHM (011) 2θ= 27.6°		FWHM (020) 2θ= 39.5°		Average crystal size of (011)	Average crystal size of (020)
	degree	radian	degree	radian	Angstrom (Å)	Angstrom (Å)
3S3	0.2175	0.003806	0.2485	0.004348	391.8024	353.8408
3S4	0.1829	0.003200	0.1547	0.002707	466	568.3413

All samples are 80 minute deposited with 3S1 (before annealing), 3S2 (annealed at 450 ºC in N_2), 3S3 (annealed at 500 ºC in N_2), and 3S4 (annealed at 450 ºC in N_2)

As it is known, the FWHM are inversely proportional to the degree of crystallite structure based on table 4.1. The calculated average crystal size is of the two planes show different results, this is attributed the difference in the growth process, due to the preferential orientation of the plane with the PVP and also the substrate used.

It is clearly seen that 3S4 sample have shown high crystal quality in relative to others, the FWHM value appears the smallest, this crystal quality increase for 3S4 is attributed due to it higher annealing temperature(570 °C) [121].

The degree of crystallinity decrease when the annealing temperature decreases, because those samples (3S2, 3S3) are not fully crystalized due to the range of annealing temperature. The table 4.1 shows that with increase in annealing temperature the average crystal size also increases.

In general the degree of the preferred crystallographic orientation in thin films is greater when the annealing temperature is higher, due to the greater mobility of growth species. The average grains size of the thin film increases when the annealing temperature is increased [121,122]. This trend is in line with the increase in average crystalline size with increase in temperature.

4.2 Thermal analysis

4.2.1 Differential thermo gravimetry (DTG) analysis

Thermo gravimetric analysis of VO_2 powered prepared from trial 3 was carried out in order to see the variation of properties in relation to temperature change, especial to clearly understand the optimum temperature for the annealing steps (where crystallization process began ~ 400 ºC).

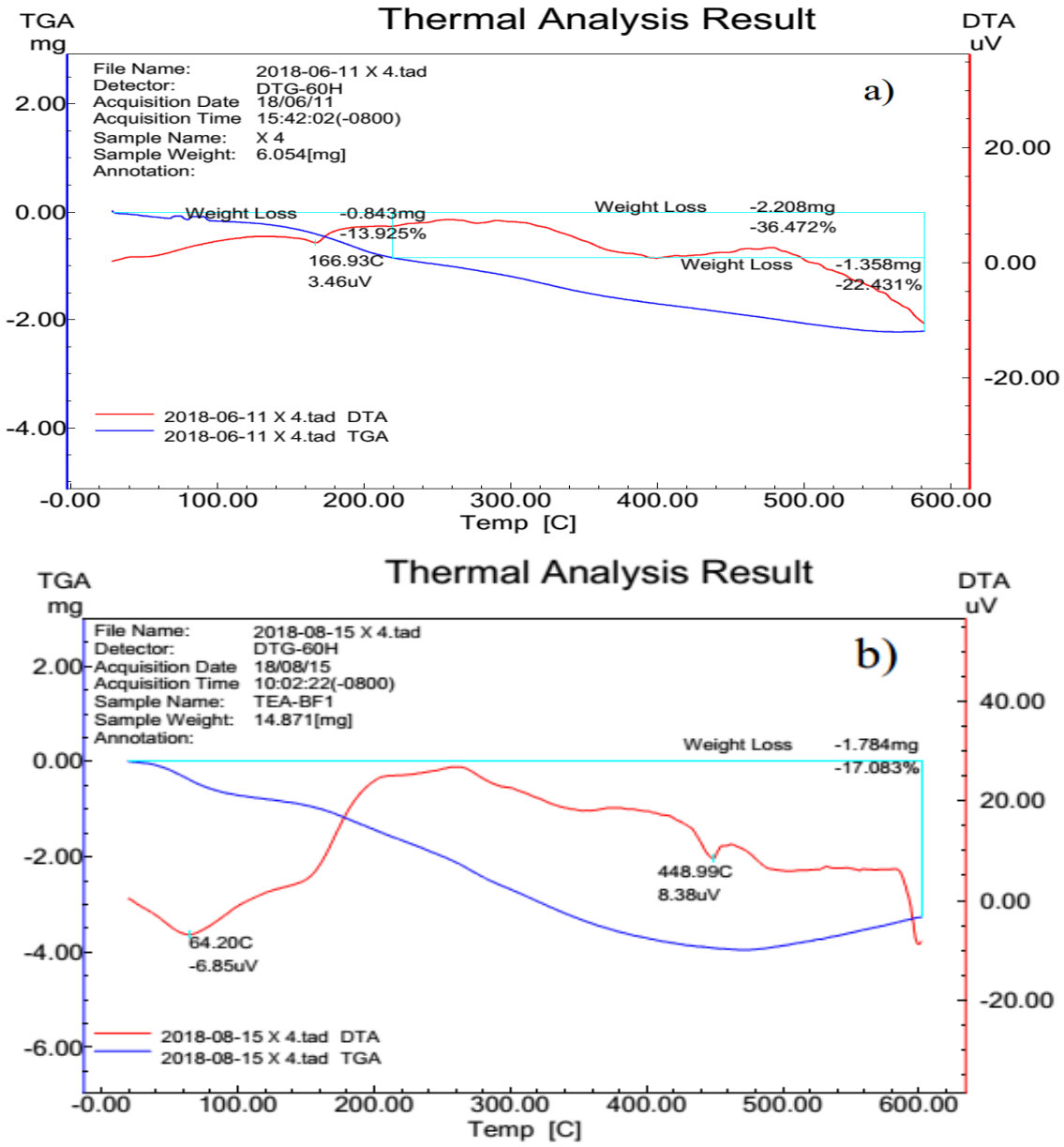


Figure 4.4: DTG results of a) using nitrogen gas, b) without applying nitrogen gas in normal environment condition.

In addition to this TGA thermal analysis give concrete data based on temperature change which is expected to occur such as dehydration process, decomposition of constituents and crystallization related information can be found. The figure 4.4 shown presents two differ TGA analysis in different condition. From the curve above, we can clearly point out the weight loss associated with heating at different stages of temperature in the range from room temperature to 600 °C. First mass loss from room temperature to around 100 °C, which is around 6 % of the weight, confirming the loss of water from the surface. The preceding loss in weight are due to removal of water from the lattice, which ranges from 100 to 200 °C associated with 7.6 % weight loss. For the remaining weight, losses are associated with the decomposition and removal of incompletely reacted substances which remains in the precipitate such the TEA from the solution [116]. The DTA curve from figure 4.4, shows that there is a crystallization process starting around ~390 °C. the crystallization peak is not very clear due to overlay of the exothermic crystallization peak and the endothermic decomposition peaks cancel each other.

The analysis of DTG is also studied in nor environment (in air) as shown in figure 4.4 b. result shows nearly same curves up 280 °C with one analyzed in nitrogen gas due to the process of dehydration occurring in both condition around this temperature, above 280 °C the curves are distinguished due, the one which treated in air shows different endothermic and exothermic peaks, those peaks are expected results, because heating process vanadium compound in air will facilitate the oxidation process consequently forming different phase and polymorphs of vanadium such V_2O_5, V_2O_3,V_3O_5,V_6O_{11} and others as it was shown in in XRD result figure this is associated with an increase in the weight of sample as clearly indicated in figure 4.4 b [121], starting from 450 °C. In addition to this compering the results of total weight losses, 1.78 mg on figure 4.4 b and 2.21 mg on figure 4.4 a. this result shows that even if there is weight loss in both condition, but heating in air shows relatively smaller loss of weight which is compensated by addition of oxygen from air [123].

This result found on DTG analysis is used to optimize the annealing condition and temperature for thin film sample heat treatment.

4.2.2 Differential scanning calorimetry (DSC) analysis

Thermochromic materials shows reversible first order transition under temperature stimulation. In case of VO_2 it transform from monoclinic structure to tetragonal structure at 68 °C when heated [110]. Figure 4.5 shows the thermochromic transition behavior of the samples.

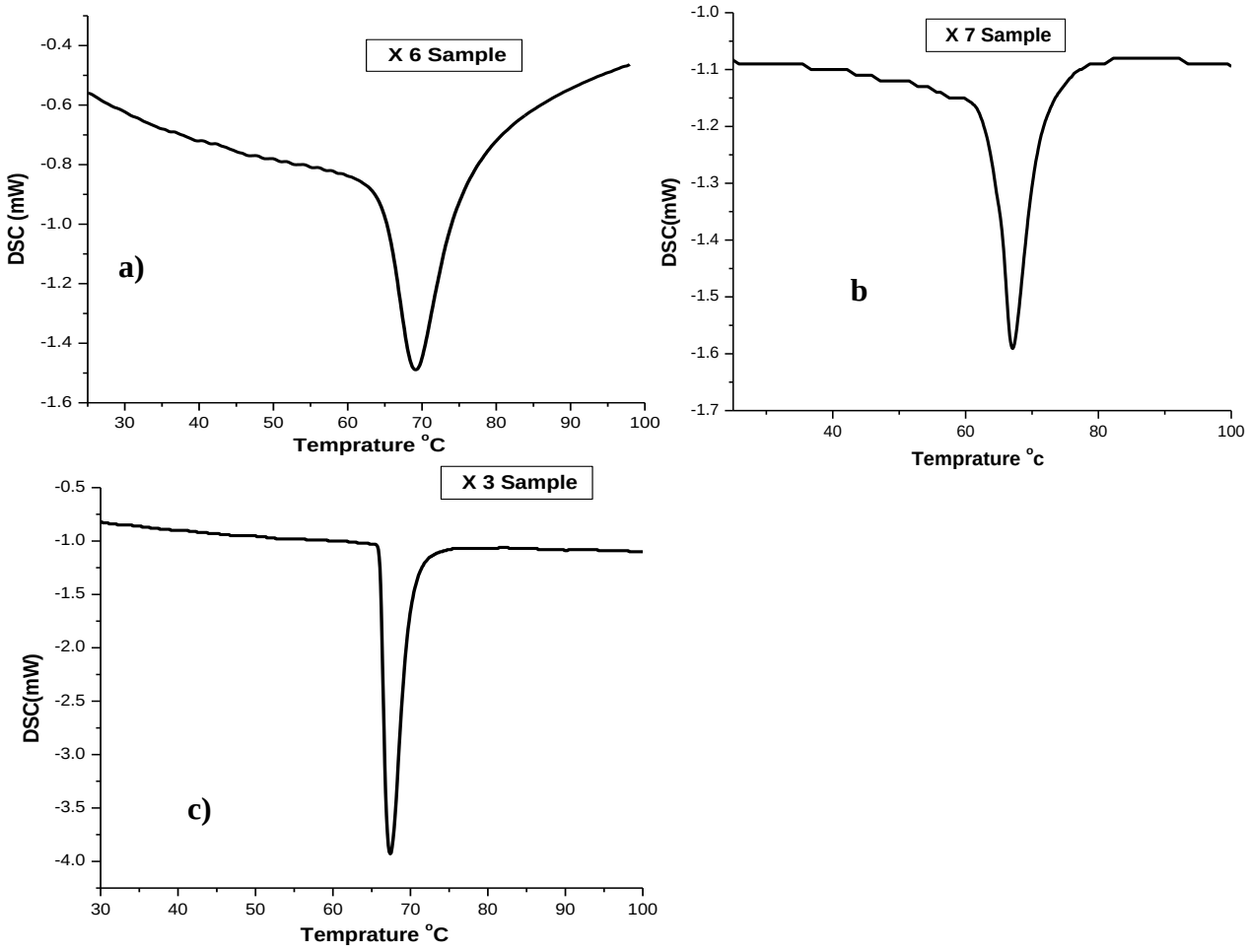


Figure 4.5: DSC result for three samples prepared a) annealed at 450 °C, b) annealed at 500 °C, c) annealed at 570 °C.

Based on results, the thermochromic transition occurs at around ~ 69 °C, which is nearly the same to literatures reported on subject, which is 68 °C [124,110]. the shape of the figures get sharpening with increasing in annealing temperature, based on the picks observed on XRD, the one which is annealed at 570 °C shows higher crystalline structure and higher quality of thin films with better thermochromic transition [121]. The transition peaks in the DSC curve gets sharper when there is

an increase in crystalline structure and purity of the coated substrate, which is also associated with decrease in grain boundary. Both of this behavior (increase in crystalline structure and decrease of impurities) are observed with increase in annealing temperature [121]. The XRD figure above clear indication of increase in crystalline structure with annealing temperature, the DTG figure also shows that increase in annealing temperature more impurities are removed from the sample.

The total factor condition reavails better thermochromic materials are found at 570 °C annealing temperature, due the higher crystalline structure the first order transition behavior from low temperature monoclinic state to high temperature tetragonal state are observed with perfection.

4.3 Thickness of the thin film

The average value of measured thin film thickness is as shown in table below. For the 15, 30 and 80 minutes deposition time, the coating process is done in both side of the glass, this result shows one side of its thickness. To find the total thickness this result is multiplied by two.

Table 4.2: Thin films average thickness value.

Annealing temperature (°C) ↓	**Deposition time (minutes)**					
	15		**30**		**80**	
	Before annealing (nm)	After annealing (nm)	Before annealing (nm)	After annealing (nm)	Before annealing (nm)	After annealing (nm)
450	279.9	178.3	412.4	284.3	867.5	648.4
500	279.9	147.8	412.4	237.8	867.5	576.8
570	279.9	107.4	412.4	186.5	867.5	503.4

As the table 4.2 clearly shows, the thickness of the film have variation before and after annealing. This data is calculated based on mass difference, with increasing in annealing temperature, thickness of the film shows decrease in average value as the table 4.2 shows all of the three time

of deposition have negative slope. Above all this, the thickness of the thin film is shown to be directly proportional to the deposition time up to 80 minute deposition in this case.

As it is expected the deposition time have clearly an effect on the thickness profile as shown in figure 4.6 a, b and c. this is because when the time of deposition increases, more ions are released from the solution bath and deposited on the surface of substrate based on the result found [92].

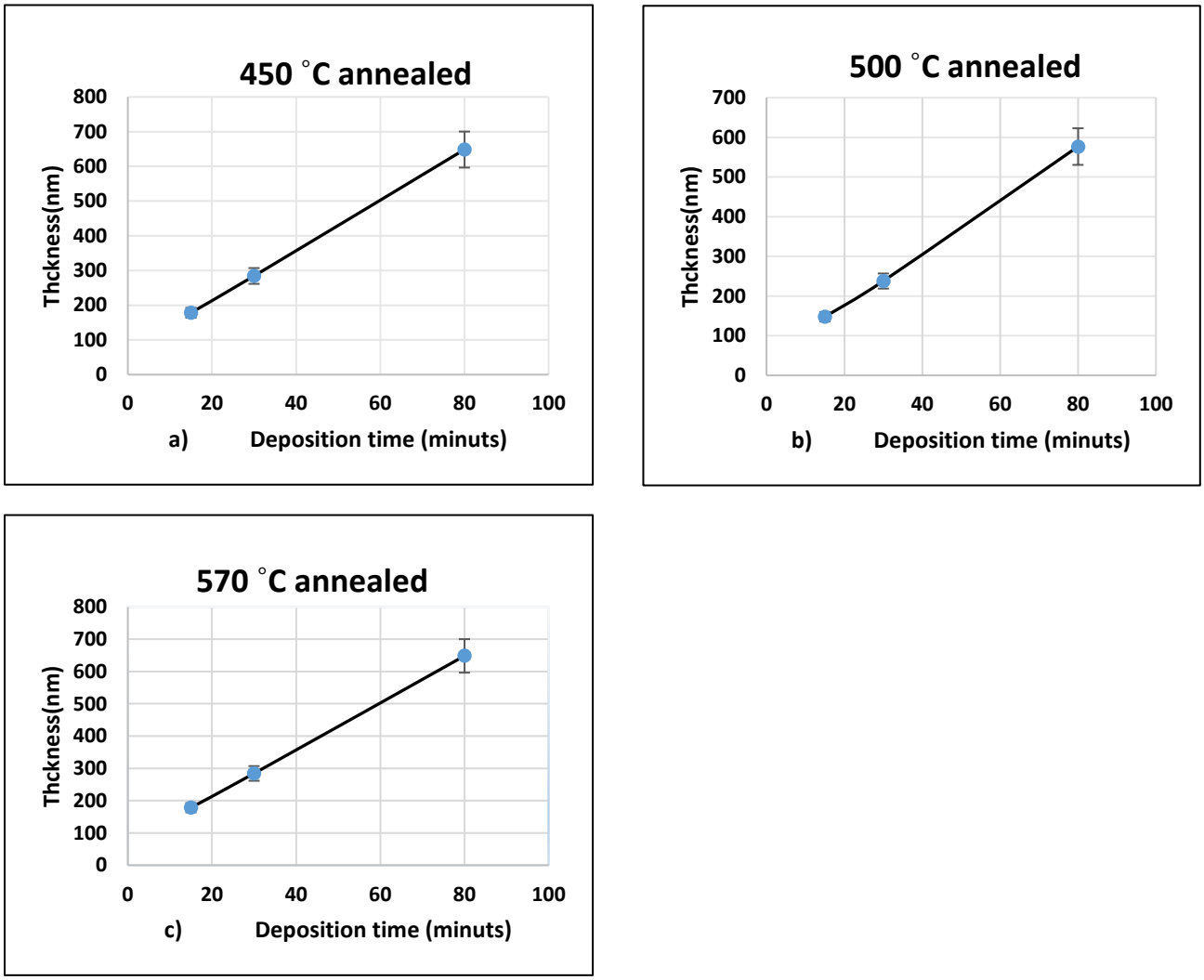


Figure 4.6: Thickness profile showing as function of deposition time for a) 450 °C, B) 500 °C, c) 570 °C annealing temperature in N_2 gas.

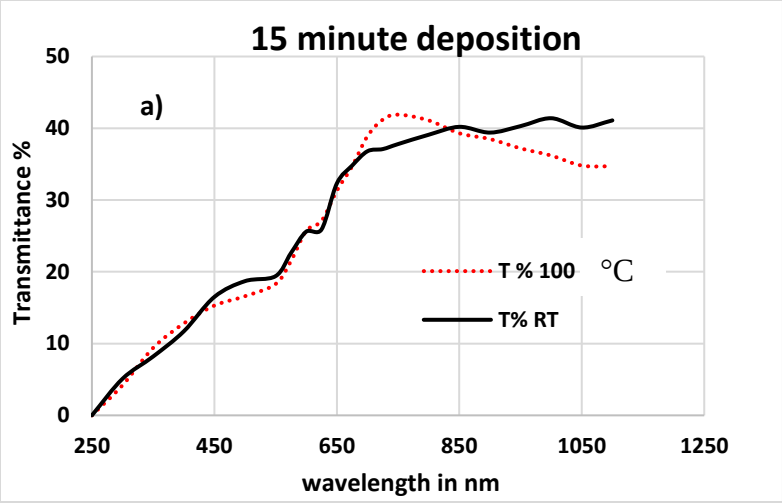
The larger amount of loss in mass during annealing is occurred because first the deposition process is done in chemical deposition method, which means there will be some loosely attached precipitates and aqueous solution found on the films, in addition to this there was pre deposited PVP surfactant on the substrate which decomposed during annealing are the factors related to the

decrease in mass consequently the thickness profile [117]. This values are gives general profile of the thickness value, but the exact value could have small variation from this one because, the density used for calculation is the bulk density of VO_2 ($4.57g/cm^3$) and this value is expected to have small variation with one which is coated precipitate. Based on this it is expected that the bulk density of VO_2 will be higher than the coated material, the effect of variation will make the measured thickness value shown above to be slightly higher than the real value.

4.4 Optical properties

One of the important parameter for thin film materials are their optical properties, thermochromic materials change their properties when heated above the transition temperature, which is around 68 °C. Thin film materials prepared by appling trial 3. Thin films on this project are charaterized using spectrophotometer at different temprature(ar room temprature and at100 ºC) which yeilds the figure 4.7 shown below.

Based on the two representative figure 4.7 a & b tranamitance behavior of the thin film varies accoriding to the change in wave lengeth range , and also the chenge in temprature of the condition of the samples. The maximum transmitance observed are 41 % and 28 % for 1S3 and 2S3 respectivly. The difference of the sample is their deposition time. The result on this experiment shows transimance behavior of the thin film is inversly proportional to the deposition time for the two deposition times (15 and 30 minutes). The difference in transmitance occures, as the deposition time is higher formation or accumlation of the preciptating substance occure, so that higher accomlation of the substance belieaved to block the transmited wavelenegeth [16].



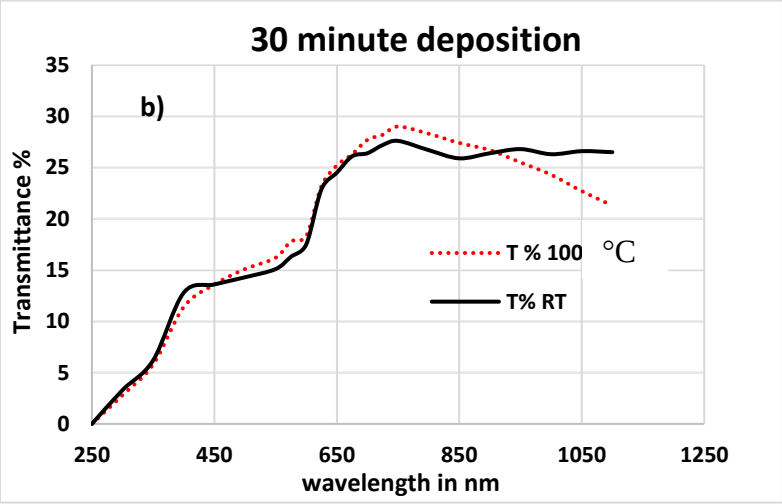


Figure 4.7: Transmitance value of a) sample 1S3, 15 minute deposition and anneild 570 °C, b) sample 2S3, 30 minute deposited and anneild 570 °C.

The change in temprature of the sample also showes to affect the transmitance behavior on the thin films. From the figur 4.7, it is shown that when the temprature increases from room temprature to 100 °C, the transmitance of especialy in wave lengeth range of above the visible light (>790 nm), transmitance strates to show difference [120]. The sample which are found at high temprature, their transmitance gradualy decrease when compared with the one measured at room temprature. The behavior of transmitance variation in samples occurred due the thermochromic behavior of the thin films, as we have seen in DSC curve of the materials, thermochromic transition occures at ~ 69 °C.

The transition properties are accompined with monclinc to tetragonal transition, in the monoclinc state(at room temprature) transmitace does not show apprecable decrese in wavelegeth region of >790 nm, this occurred because the monoclinic state of VO_2 does not show shielding effect, when the temprature increase the monclinc state changes to tetragonal state (at high temprature), this tetragonal state of VO_2 have shielding effect for NIR and IR region of wave lenegeth, due to this effect transmitance deacrese for tetragona state at higher wavelengh range [116].

The change in optical transmitance(ΔT) with temprature change as a stimulant is core point of IR and NIR shielding properties the one which showes higher difference in transmitance with the change in temprature are required (that could shield IR and NIR at high temprature and transmit IR and NIR at low temprture). Based on this the thin films prepared for this project showes appricable change in optical transmitance (ΔT) between monclinic(which show higher transmitance for NIR region) and tetragona state(which shows lower transmitance for NIR region), based on the figure 4.7 above, the transmitance at 1100 nm shows 21 % for tetragonal state, 26.5 % in monoclinic state, and transmitance difference between the two is 5.5 at 1100 nm for 30 minutes deposited films, and for 15 minutes deposited films 36 % for tetragonal state, 39.7 % in monoclinic state, and transmitance difference of 3.7 at 1100 nm for 15 minutes deposited films. From this two observed change in optical tranmitace for the wavelength of above visible region , the one with higher deposition time (30 minuts) is observed, to show better shielding properties (the transmitance difference between monoclinic and tetragonal state is higher for the NIR wavelength region), but at the same time when the deposition time increases even if shielding properies increase, the transmitance in general is also degraded. In case of 15 minuts deposition the transimitance obseved higher, but change in shielding effect relativly lower, so that for better shielding properties and good transmitance during monoclinin state, should be manged for application purpose of this materials [117].

The litratures in this area have shown that the differnce in optical transmitace increaese with increase in wavelengeth region above 1100 nm [116], based on the figure above this tranmitance difference is expeced to increase at higher wave lengeth region in such way that low temrature monoclinc phase increase towards higher transmitance and high temprtaure tetragonal phase transmitance decreasing to towardes lower transmitance with over all effect of higher shielding properties ralative to the obseved results on the figure 4.7.

4.5 Morphological analysis

The Optical image data analysis observeved shows uniform coatings, with comact morphology of arrengement. In addition to this, the change in the time of deposition does not seem to show morophological change which tels that the dopsition time is not affecting the morphology in this case.

The surface morphology of the thin film is also studied with SEM in which the result is shown in figure 4.8

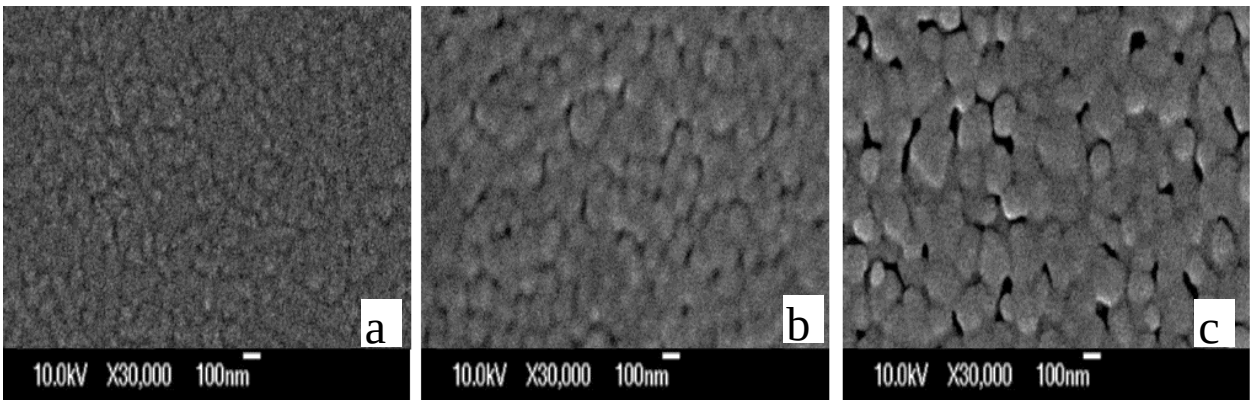


Figure 4.8 30 minutes deposited VO_2 SEM image after annealing N_2 (with 30, 000 x magnification) a) annealed at 450 °C, b) annealed at 500 °C, c) annealed at 570 °C.

Based on the SEM image obtained the morphology of the film looks uniform with pore like opening in between the particles the spaces are created due to the PVP pre deopsited film, in which during the annealing condition the polyemers decoposed from films. This can be clearly seeen by large mass loss during DTG analysis is caused by polymer parts decomposing from the substrate.

In addition to this morphology of thin film shown clearly notify that, for lower temprature annealing grains are smaller and bounderies of the grains are not clear enough, when the annealing temprature increases the grains show an increment in such way that grain boundiesrs of the thin film can be seen clearly. This is due to the the grain growth occuring with incraese in annealing temprature as it is also described in by average crystalin size calculation from the XRD peak. The result found from the XRD peak is in line with SEM result found showing an increment in size. the effect of larger particles size can be seen on the DSC curve of transition in such a way that

smaller the averge crystalin size the wider temprature range of transition is observed. Above all of this in thermochromic materials the range of the transition temprtaure is an important variable, for future appliction of this materials very spacific transition temprature will be rquired this can be achived through grain growth, which can be seen in DSC curve of X 3 sample with sharp transition peak.

CHAPTER 5 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In the present study of chemical bath deposition method is found applicable for thermochromic thin film VO_2 fabrication for future development of smart window application, which regulate temperature without external energy applied. In this project, the synthesized thin film materials show thermochromic transition behavior at ~69 °C according to the DSC study, which is nearly the same to transition temperature reported before. The UV-VIS measurement done at high and low temperature shows that the thin film produced exhibit reflection of NIR wavelength regions due to the tetragonal structure formed at high temperature and NIR transmitting behavior in its low temperature condition due to formation of the monoclinic phases.

The thin films produced at different deposition time shows change in thickness. The annealing temperature also affected thickness of the film. The results observed for this were thinnest film of 107.4 nm for 15 minutes deposition at 570 °C annealing and maximum thickness for 648.4 for 80 minutes deposition process at 450 °C annealing. Based on the results thickness difference have an effect the optical transmittance behavior that the larger deposition time, then it will have lower transmittance value.

The XRD studies of the thin film shows two dominant peaks at 27.6 degree and 39.5 degree which are indexed to (011) and (020) planes of VO_2 respectively, the crystallinity increases with annealing temperature as the FWHM shows, 0.00380 rad and 0.00320 rad for, 500 °C and 570 °C annealing temperature respectively

In addition to this thin films with thicker deposition for 2S3 sample (30 minutes deposition) shows higher shielding effect for the NIR regions wavelength, which is an important property for the smart window application, the 2S3 and 1S3 samples exhibit 5.5 % and 3.7 % optical transmittance difference at 1100nm respectively.

The morphology study observed shows uniform morphology of thin films for the VO_2 phases, due to the systematic mechanism used by applying PVP surfactants on the surfaces before VO_2 thin film coating.

In general, by applying the chemical bath deposition technique, it is possible to create better thin film materials with uniform phase of VO_2 materials and its accompanying thermochromic properties for future commercialization of smart window application.

5.2 Recommendation

Based on the research done on this project I recommend the CBD process to be done very intensively especially, which will have tremendous advantage towards creating smart windows applicable for houses and buildings without external energy applied. More than this I recommend this research to be conducted in future to lower the transition temperature towards room temperature by doping elements such as Nb^{5+}, Mo^{6+}, W^{6+} and Ta^{5+}, which could possible create thermochromic transition to occur at Rome temperature [38]. In addition to this, the transmittance to visible range of the light and shielding effect to IR region is inversely proportional, so that I recommend for the optimization of this two variables to be done in future works.

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