Thermochromic VO$_2$-based materials for smart windows

Progress towards applications in buildings

YUXIA JI

Vanadium dioxide is a well-known thermochromic material, whose optical properties can be varied reversibly in response to fluctuation of temperature. It is attractive in various fields due to its unique properties as well as its prospective applications. Especially, it is the most favorite candidate for smart window applications which can significantly lower energy consumption. Ideally, VO$_2$-based thermochromic windows can regulate solar radiation gain dynamically according to the exterior environment conditions. However, commercial utilization of VO$_2$ thermochromic windows is still on the way. There are still a few issues needed to be overcome, such as high phase transition temperature, the unfavorable yellow-brown color, low luminous transmittance and weak solar energy modulation ability.

Vanadium oxides are known to have rich polymorphs and devices using thermochromic effect often require absence of impurities, so that stringent process control is crucial for practical manufacturing of VO$_2$ materials. In this work, a novel route for fabrication of VO$_2$ thin films was developed thermodynamically and verified experimentally. Another concern related to VO$_2$-based materials is the relatively short durability of their desirable properties as VO$_2$ is not the most thermodynamic stable species. Hence the lifetimes of the thermochromic VO$_2$ films under various environmental conditions were evaluated. Furthermore, studies have been made to investigate the impacts of substrates on VO$_2$ film growth.

For window coating applications, the light scattering is of importance. Therefore, the light scattering effect for particulate VO$_2$ film was studied. Additionally, the low luminous transmittance of VO$_2$ film can be substantially increased by use of a top coating with suitable refractive index. In our study a TiO$_2$ top layer was used, which leads to improved thermochromic behavior. Moreover, incorporation of VO$_2$ plasmonic pigments into a matrix is a useful way to overcome the unsatisfied thermochromic performance of conventional VO$_2$ films. A composite film of VO$_2$-SiO$_2$ was fabricated and its optical properties were studied. Besides, phase-pure VO$_2$ nanospheres were synthesized via chemical route and their thermochromic properties were investigated.

In general, these studies promote development and progress of VO$_2$-based material further to be used in heat and light regulation applications.

Keywords: Thermochromic, Vanadium dioxide, Smart windows

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To my family
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


IV. Y. Ji, A. Mattsson, G.A. Niklasson, C.G. Granqvist, L. Österlund, TiO₂/VO₂ bilayer coatings for glazing: Synergetically enhanced photocatalytic, thermochromic, and luminous properties, in *manuscript*.


VI. Y. Ji, G.A. Niklasson, C.G. Granqvist, Nanothermochromic VO₂–SiO₂ composite coatings for energy-efficient glazings, in *manuscript*.

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I. Sample preparation, measurements, data analysis and most of the writing.

II. Sample preparation, measurements, data analysis and most of the writing.

III. Part of the sample preparation and measurements, participate in discussion and writing.

IV. Part of sample preparation, measurements, data analysis and part of the writing.

V. Part of the sample preparation and measurements, participate in discuss and writing.

VI. Sample preparation, measurements, data analysis and most of the writing.
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<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>MST</td>
<td>semiconductor-metal transition</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>VIS</td>
<td>visible light</td>
</tr>
<tr>
<td>NIR</td>
<td>near infrared</td>
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<td>PDLC</td>
<td>polymer dispersed liquid crystal devices</td>
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<tr>
<td>RH</td>
<td>relative humidity</td>
</tr>
<tr>
<td>$T_s$</td>
<td>synthesis temperature</td>
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<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>EDX</td>
<td>energy dispersive X-ray</td>
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<tr>
<td>SPDs</td>
<td>suspended particle devices</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
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<td>GIXRD</td>
<td>grazing incidence X-ray diffraction</td>
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<td>TC</td>
<td>thermochromic</td>
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<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>BE</td>
<td>binding energy</td>
</tr>
<tr>
<td>LSPR</td>
<td>localized surface plasmon resonance</td>
</tr>
<tr>
<td>EMT</td>
<td>effective medium theory</td>
</tr>
<tr>
<td>AR</td>
<td>antireflection</td>
</tr>
<tr>
<td>$\tau_c$</td>
<td>critical temperature</td>
</tr>
<tr>
<td>$c$</td>
<td>speed of light</td>
</tr>
<tr>
<td>$h$</td>
<td>Planck constant</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>wavelength</td>
</tr>
<tr>
<td>$T_b$</td>
<td>the temperature of the blackbody</td>
</tr>
</tbody>
</table>
$i$  
  gaseous species

$j$  
  condensed species

$n_i$  
  number of moles of species $i$

$m_g$  
  number of gaseous species

$m_s$  
  number of condensed phases

$a_{ij}$  
  number of atoms of $j$th element in a molecule of the $i$th species

$g$  
  gaseous phase

$s$  
  condensed phase

$\Delta G_r$  
  Gibbs free energy

$G$  
  total Gibbs free energy

$\mu_i$  
  chemical potential of species $i$

$\mu_i^0$  
  standard chemical potential of species $i$

$a_i$  
  activity of species $i$

$A_j$  
  total number of moles of the $j$th element

$k_e$  
  total number of elements

$R_g$  
  universal gas constant

$T'$  
  temperature

$p_i$  
  partial pressure

$N_t$  
  total mole number in the gas phase

$P$  
  total pressure in the system

$T$  
  transmittance

$R$  
  reflectance

$A$  
  absorptance

$L_o$  
  optical loss

$S$  
  optical scatter

$T_{tot}$  
  total transmittance

$T_{direct}$  
  direct transmittance

$T_{diff}$  
  diffuse transmittance

$R_{tot}$  
  total reflectance
<table>
<thead>
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<th>Symbol</th>
<th>Description</th>
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<tr>
<td>$R_{spec}$</td>
<td>specular reflectance</td>
</tr>
<tr>
<td>$R_{diff}$</td>
<td>diffuse reflectance</td>
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<tr>
<td>N</td>
<td>complex refractive index</td>
</tr>
<tr>
<td>$N_m$</td>
<td>refractive index of the surrounding medium</td>
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<tr>
<td>$\varepsilon$</td>
<td>complex dielectric function</td>
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<tr>
<td>$n$</td>
<td>real part of complex refractive index</td>
</tr>
<tr>
<td>$k$</td>
<td>imaginary part of complex refractive index</td>
</tr>
<tr>
<td>$\varepsilon'$</td>
<td>real part of complex dielectric function</td>
</tr>
<tr>
<td>$\varepsilon''$</td>
<td>imaginary part of complex dielectric function</td>
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<td>$T_{lum}$</td>
<td>luminous transmittance</td>
</tr>
<tr>
<td>$T_{sol}$</td>
<td>solar transmittance</td>
</tr>
<tr>
<td>$\varphi_{lum}$</td>
<td>standard luminous efficiency of human eyes</td>
</tr>
<tr>
<td>$\varphi_{sol}$</td>
<td>solar irradiance spectrum for air mass 1.5</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>collision frequency</td>
</tr>
<tr>
<td>$\omega$</td>
<td>frequency</td>
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<td>$\omega_p$</td>
<td>plasmon frequency</td>
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<tr>
<td>$\tau$</td>
<td>electron relaxation time</td>
</tr>
<tr>
<td>$\theta$</td>
<td>angle</td>
</tr>
<tr>
<td>$\delta_{sp}$</td>
<td>surface plasmon propagation distance</td>
</tr>
<tr>
<td>$\delta_m$</td>
<td>decay distance in the metal</td>
</tr>
<tr>
<td>$\delta_d$</td>
<td>decay distance in the dielectric material</td>
</tr>
<tr>
<td>$a$</td>
<td>sphere radius</td>
</tr>
<tr>
<td>$\varepsilon_m$</td>
<td>dielectric constant of the environment medium</td>
</tr>
<tr>
<td>$\alpha_{pt}$</td>
<td>complex polarizability</td>
</tr>
<tr>
<td>$E_L$</td>
<td>electric field</td>
</tr>
<tr>
<td>$\varepsilon_{eff}$</td>
<td>effective dielectric function</td>
</tr>
<tr>
<td>$\varepsilon_p$</td>
<td>dielectric function of the inclusion particles</td>
</tr>
<tr>
<td>$f$</td>
<td>volume filling fraction</td>
</tr>
<tr>
<td>$L_i$</td>
<td>depolarization factor</td>
</tr>
<tr>
<td>$m$</td>
<td>aspect ratio</td>
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</table>
$r$ reflection coefficient
t transmission coefficient
$\delta$ phase change
$C_{\text{ext}}$ extinction cross section
$C_{\text{sca}}$ scattering cross section
$C_{\text{abs}}$ absorption cross section
$I_{\text{inc}}$ energy flux of the incident irradiance
$W_{\text{sca}}$ scattered energy
$W_{\text{abs}}$ absorbed energy
$x$ size parameter
$Q_{\text{abs}}$ absorption efficiency
$Q_{\text{sca}}$ scattering efficiency
$Q_{\text{ext}}$ extinction efficiency
$\Gamma$ mixed gas ratio
$\phi_{\text{O}_2}$ oxygen flux
$\phi_{\text{Ar}}$ argon flux
d$_{\text{hkl}}$ atomic layer distance
$\Delta\nu$ wavenumber shift
$R_{\text{res}}$ resistance
$R_s$ sheet resistance
$L$ length
$d$ thickness of thin film
$t_h$ time period
$T_h$ temperature of the environment
$\Delta T$ near-infrared transmittance modulation
$R_{\text{rms}}$ root mean square roughness
$V_p$ unit volume
1 Introduction

In the history of the development of human society, materials investigations have always a dramatic impact. As mankind enters the 21st century, the worldwide energy use has already risen significantly and is likely to continue for the foreseeable future. Concerning difficulties of energy supply, exhaustion of traditional energy resources and heavy influences on environment, we have a need to replace fossil fuels with other energy sources and subsequently reduce the energy consumption. The future of the world’s economy relies on scientific and technological progress. A buzzword used in the present era of technology would be “intelligent”.

The global energy consumption of buildings, both residential and commercial, accounts for 30–40% of the primary energy [1, 2]. Concerning the aspects of population growth, comfort level and time people spent inside buildings, energy consumption in buildings will continue the upwards growth trend. The current energy demand forces people to reevaluate the fundamentals of the building design. Therefore, intelligent buildings will emerge. Intelligent buildings are buildings that maximize the service for the inhabitants while in the meantime effectively manage the resources and saving energy.

One essential component of buildings is fenestration which has the greatest direct effect on the building’s future energy performance. Fenestration provides daylight, but it is also often regarded as a less energy efficient building component as it can allow undesirable heat and light exchange. In cold climates, internal heat is lost through fenestration, and in warm climates, exterior heat enters through fenestration, leading to increasing air conditioning loads. The energy loss through windows takes a big part of the total energy consumption in the buildings [3, 4]. In the past few decades, numerous techniques have been developed intensively for improving energy efficiency of existing or new fenestration. From ordinary plate glass, it has been developing into intelligent glazings. Low energy emissivity glazing and solar control glazing are two of the most commonly used energy saving windows for controlling solar irradiation throughput [5]. Besides these, researchers have been working hard on the development of next generation of glazing technologies which is called smart windows [6]. As the name implies, smart windows spectral properties could promptly adapt in response to changes in natural climates or the inhabitant’s intention. Smart windows
have high expectations to achieve desired cost-saving for heating, air-conditioning, lighting and motorized window screens and blinds.

Basically, there are two different types of smart windows, passive and active. The passive type includes photochromics [7] and thermochromics [8] which react readily to environmental variable such as light intensity or temperature. The active type includes polymer dispersed liquid crystal devices (PDLC) [9], suspended particle devices(SPDs) [10], micro-blinds [11] and electrochromics [12] which directly respond to the inhabitants preferences. In comparison to various switchable windows, passive systems with its simple building unit request no additional energy consumption, no electrical power supply and no control unit for operation. Therefore, the passive switching smart windows are of interest to be investigated as they are promising to enhance the energy efficiency of buildings.

The work presented here is focused on one particular passively switching smart window, VO₂-based thermochromic material, which changes its optical properties in response to changing temperature. Ideally, VO₂-based thermochromic windows can keep balance between solar energy gain and heat loss dynamically according to the exterior climate conditions. Thus, thermochromic windows enable to maintain indoor temperature to a comfortable level regardless of the outdoor temperature being higher or lower than the desired comfort temperature. By using thermochromic windows, the energy consumption in buildings can be reduced significantly and solar energy resource could be harnessed more efficiently. The use of thermochromic coatings may provide an additional 10% energy benefit in comparison to a window with non-coated glasses from simulated study [13]. Laboratory prototypes have demonstrated good switching effect from an infrared-transparent state into an infrared-reflecting state. A variety of methods have been developed to prepare VO₂-based materials. The usual physical methods include magnetron sputtering [14], pulsed laser deposition [15], atomic layer deposition [16], and electron beam evaporation [17]. The common chemical methods include hydrothermal [18], sol-gel [19], chemical vapor deposition [20, 21], polymer-assisted deposition [22], and electrochemical deposition [23].

However, a few problems remain in putting the VO₂ materials to practical smart window application. Specifically, the transition temperature of VO₂ film should be depressed to a value close to room temperature while in the meantime luminous transmittance and solar transmittance modulation should be high enough. During the past few decades, a lot of efforts have been made to resolve the aforementioned issues. Transition temperature can be reduced by doping [24-27], grain size [28], stress [29, 30], stoichiometry [31]. To enhance the luminous transmittance and solar transmittance modulation, multilayer structure, such as SiO₂/VO₂, TiO₂/VO₂ and In₂O₃:Sn/VO₂/In₂O₃:Sn, have been proposed [32-34]. More recently, VO₂-based composite materials [35], such as hybridization structure [36, 37] and core-shell structure [38, 39] and highly-porosity structure [40, 41], have been
intensively investigated to achieve more satisfactory performance of luminous transmittance and solar energy transmittance modulation. In addition, unfavorable yellow-brown color, relatively short durability and stability have emerged to attract more attention [42]. Besides, combining VO₂ materials with other functional materials to achieve multifunctional materials and devices is also a research trend. For instance, combination of thermochromic coating and solar cell into one device, smart photovoltaic window, could save energy and generate electricity at the same time [43, 44].
2 Thermochromic smart windows

2.1 The solar spectrum and the blackbody radiation

The effect of solar radiation through fenestration is very significant; thus, energy efficiency of windows is often associated with the solar radiation.

Sunlight is electromagnetic radiation given out by the sun. In particular, sunlight is divided into three major components: (1) ultraviolet light, with wavelengths shorter than 0.4 micrometer, (2) visible light, with wavelengths between 0.4 and 0.7 micrometer, and (3) infrared radiation, with wavelengths longer than 0.7 micrometer. Near infrared radiation (NIR) solar radiation carries about 50% of the total solar energy.

The sun is, to a good approximation, modeled as a blackbody emitter whose characteristics are to absorb all incident radiation and to emit radiation based on its temperature. The radiation power spectrum emitted by the sun is equivalent to a black body radiation with temperature of 5505 °C. When the sunlight reaches the earth surface, it becomes a less regular blackbody spectrum as the sunlight is partially absorbed by various components of the atmosphere. The solar spectrum [45] after traveling through the atmosphere is shown in Figure 2.1.

The spectral irradiance from a blackbody is given by Planck's radiation law:

\[
I(\lambda, T_b) = \frac{8\pi hc}{\lambda^5} \frac{1}{\exp \left( \frac{hc}{\lambda \kappa T_b} \right) - 1}
\]  

(2.1)

where \(c\) is speed of light, \(h\) is Planck’s constant, \(\kappa\) is Boltzmann’s constant, \(\lambda\) and \(T_b\) refer to the wavelength and the temperature of the blackbody.
2.2 Thermochromism

Thermochromism is the property of substances to display a change in their optical properties as a result of a fluctuation in temperature. A wide variety of materials have been discovered to have thermo chromic properties and provide good modulation of the visible light transmission over a range of temperatures [46-50]. However, they don’t have good switching in the near infrared region of the solar spectrum and some of them show irreversible color changes. VO₂ is the well-known thermo chromic material which exhibits a sharp transition from an infrared transparent semiconductor state to an infrared reflective metallic-like state close to room temperature (68 °C) [51-53], while it retains visible transmittance as a thin film. The total transmittance and reflectance of a VO₂ film with 80 nm thickness is shown in Figure 2.2. The transformation of the lattice and electronic structures occurs in less than 500 femtosecond [54]. Such an abrupt transition causes variation of the specific resistance of VO₂ by a few orders of magnitude. The excellent thermo chromic behavior makes VO₂ a leading candidate as a passive energy efficient architectural glazing [55-57].
Figure 2.2. Spectral transmittance and reflectance of a 80 nm-thick VO₂ film made by sputtering technique.

The thermochromic behavior can be visualized in Figure 2.3, where a thermochromic window is schematically drawn. When the temperature is below the transition temperature, the material has high transmittance of infrared radiation, thus the heat from the sun will get through the window and reach the interior of the building. On the contrary, when the temperature is above the transition temperature, the material has high reflectance of infrared radiation; consequently, the heat from the sun will be partly reflected. As a consequence of the thermochromic effect, heat gain from solar radiation is high in the cold winter and heat is blocked from solar radiation in the hot summer.
Figure 2.3. Schematic drawing of a thermochromic coating for building fenestration (a) in a hot day and (b) in a cold day.
3 Vanadium dioxide

It is a longstanding challenge to predict and control the occurrence of polymorphs in the field of material development. It is prominent in the case of vanadium oxides and their related compounds as a consequence of their rich number of stable and metastable structures. It is known that vanadium has high affinity for oxygen and vanadium is found in oxides in a wide range of oxidation states +5, +4, +3 and +2 [58-60]. The V₂O₃-V₂O₅ system is very complicated [61, 62] and the vanadium–oxygen phase diagram in Figure 3.1 shows nearly 20 different stable phases of vanadium oxide with only small variations in composition, such as V₂O₅, VO₂, V₃O₇, V₄O₉, V₆O₁₃. On the other side, vanadium related compounds have received considerable attention for decades due to their unique chemical and physical properties, which make them highly desired in a wide range of promising applications.

V₂O₅ and lower oxides V₄O₉ and V₆O₁₃ have high surface reactivity which have been intensively studied for use as surface catalysts in a class of oxidation reactions [63-65]. Layered structures of vanadium oxides, such as V₂O₅ and VO₂, were commonly involved in cathode materials for reversible lithium batteries [66]. Nanosized vanadium oxides have been reported as prominent sensor materials for the quantitative detection of different compounds such as ethanol vapor, nitric oxide [67-70]. V₂O₅ is additionally a well-known electrochromic material and electrochromism has also been reported for VO₂ [71-73].

Among the various species of vanadium oxides, much interest has been directed towards V₂O₃ and VO₂ [74, 75] for their unique electrical switching properties. As the temperature changes, their electrical conductivity can vary up to five orders of magnitude over the semiconducting-to-metal transition process. The reversible structural transition makes V₂O₃ and VO₂ great candidates in electrical switches applications [76].
3.1 Lattice and electronic structure

The most stable phase of VO\textsubscript{2} is the high temperature rutile which exhibits the characteristics of a metal and has a simple tetragonal lattice (space group \(P4_2/mnm\)). This space group corresponds to a very symmetric structure, the vanadium atoms are at the center of regular oxygen octahedra. Different octahedra share edges and the edge-sharing octahedra form chains along the c-axis and are coupled to each other by sharing corner O atoms. The high-temperature crystal structure is shown in Figure 3.2a.

The low-temperature semiconducting phase of VO\textsubscript{2} is based on a monoclinic crystal structure (space group \(P2_1/c\) shown in Figure 3.2b. In this structure, two vanadium atoms dimerize along the rutile c-axis (monoclinic a-axis) with alternate shorter and longer V-V distances, and also tilt transversely in a zigzag way along the rutile c-axis. The O-octahedra are also distorted due to V-V pairing. The two different distances between vanadium atoms lead to a doubling of the unit cell along the rutile c-axis. The induced distortion leads to lower symmetry of the structure, the vanadium atoms have shifted from the center of the octahedra and form chains that are no longer parallel to the rutile c-axis.
It is worth mentioning that the atomic displacements accompanied with the phase transformation results in only a small 1% volume change in the unit cell [77], suggesting the unit cell size change is small enough to lead a reasonable thermal stability as coating material against heating-cooling cycles.

The semiconductor-to-metal (MST) features during transformation from the high-temperature tetragonal lattice structure to the low-temperature monoclinic distorted structure include hysteresis loop, hysteresis width, MST sharpness and transition temperature. Many factors, for example, crystallinity, stoichiometry, grain size, stress, influence the MST features. A small deviation from stoichiometry, either under or over-stoichiometry could reduce the transition temperature [77]. Small crystallite size or large surface/interface ratio for a thin VO$_2$ film may damage the zigzag chains of the V-V pairs in low temperature phase and destabilize the low temperature phase and as a result decrease the transition temperature.

The pure monoclinic VO$_2$ phase is labeled as $M_1$, since VO$_2$ with dopant refer to another monoclinic structure $M_2$ (space group $C2/m$) [52]. Dopants into VO$_2$ can induce a variation in the length of the V-V distances along the c-axis. Generally, the replacement of V$^{4+}$ by a small amount of penta- or hexavalent ions (such as W, Nb, Mo) can introduce extra electron into VO$_2$ and is favorable for reducing the transition temperature. Low-valent cations (Al$^{3+}$, Ga$^{3+}$, Cr$^{3+}$, Fe$^{3+}$) doping elevates the transition temperature. Moreover, introduction of impurities in VO$_2$ also results in variations of the specific resistance and the optical transmission.

*Figure 3.2. Crystal structure for (a) tetragonal VO$_2$ ($R$) and (b) monoclinic VO$_2$ ($M_1$); blue balls are vanadium atoms and red balls are oxygen atoms.*

The band structure and molecular orbitals of VO$_2$ were first proposed by Goodenough [78]. Each[Ar]4s$^2$3d$^5$ V atom bounds to two $1s^22s^22p^5$ O atoms. Four electrons from V$^{4+}$ fill the O 2p shell and the remaining single electron occupies the lowest 3d level. The closed shell O 2p electrons are tightly
bound and not contributing to the conductivity. The fivefold energy-degenerate 3d level of V$^{4+}$ cation split into a twofold higher energy level (e$_g$) and threefold lower energy levels (t$_{2g}$) in the octahedral crystal field. The two e$_g$ orbitals form V 3d$\sigma$ band and the t$_{2g}$ states split into 3d$\sigma$ and 3d$\pi$ under the strong influence of the crystal field of surrounding oxygen atoms. The hybridization of the V 3d$\pi$ and the O 2p$\pi$ band is stronger than the hybridization of V 3d$\sigma$ and the O 2p$\sigma$ which makes V 3d$\pi$ band have higher energy and wider bandwidth than V 3d$\sigma$ band. The 3d$\pi$ and 3d$\sigma$ bands overlap around the Fermi level. The partially filled V 3d$\sigma$ and 3d$\pi$ bands are the reason for the high temperature phase VO$_2$ having metallic behavior.

In the monoclinic phase ($M1$) of VO$_2$, the V-V pairing along the rutile c-axis and unit-cell doubling cause the additional splitting of the 3d$\sigma$ band into filled bonding and empty antibonding states. In addition, the lattice distortion raises the antibonding 3d$\pi$ band above the Fermi level due to increased overlap between the V 3d$\pi$ band and the O 2p$\pi$ band. As a result, the completely filled lower V 3d$\pi$ band leaves the V 3d$\sigma$ band completely empty. The schematic diagram of VO$_2$ band structure is shown in Figure 3.3 [79, 80]. E$_{g1}$ features the energy gap between the lower filled 3d$\sigma$ band and empty 3d$\pi$ band; E$_{g2}$ represents the gap between the filled O 2p$\pi$ band and V 3d$\sigma$ band; E$_{g3}$ is the energy gap between the lower filled V 3d$\sigma$ band and the upper empty V 3d$\sigma$ band. In general, transition at ~ 0.5 eV is assigned to E$_{g1}$, transition above 1 eV is interpreted to E$_{g2}$ and E$_{g3}$. The bandgap energy has been studied based on many experimental measurements [59-61, 81-83] and theoretical calculations [80, 84].

![Figure 3.3. Band structure of VO$_2$](image)
The mechanism of the MST in transition metal compounds is generally complex as a result of competition among various factors. The factor which gained the largest energy would be the main driving force. The factors governing the MST in VO₂ are electron correlations, Peierls instability or lattice distortion. The prime mechanism remains a decades-long contention, which is whether the additional splitting of the 3dₓᵧ band is dominated by periodic lattice deformations of V-V pairing and unit cell doubling as in a Peierls mechanism [85-88] or by the opening of a correlation gap due to strong electron-electron correlations in the 3dₓᵧ bands with the electron-lattice interactions referring to Mott-Hubbard mechanism [88-91] or a combination of both effects [92-94]. However, since the sharpness of the phase transformation in VO₂ shows a strong dependence on many factors such as exact stoichiometry, microstructure and built-in strain related to substrates, the actual phenomena at MST are difficult to interpret within a simple scenario [15, 95-97].

3.2 Polymorphs of VO₂

VO₂ is a representative binary compound with different polymorphs. Many crystalline phases of vanadium dioxide have been reported, including thermodynamically stable phases of tetragonal VO₂(R) and monoclinic VO₂(M), and the metastable phases of monoclinic VO₂(B) [98], tetragonal VO₂(A) [99], VO₂( despreased) [100], VO₂(C) [101] and VO₂(D) [102]. These VO₂ polymorphs have the same chemical formula, but their crystalline and electronic structures are very different and highly complex. The phase structures have great influence on their physical and chemical properties.

Among the aforementioned polymorphs of vanadium dioxide, numerous efforts have been directed to VO₂(B), VO₂(A) and VO₂(M/R) [59, 103]. The four polymorphs of vanadium dioxides, VO₂(B), VO₂(A) and VO₂(M/R) are all based on a vanadium body centered unit cell and each vanadium atom is surrounded by an octahedron of six oxygen atoms, while the oxygen octahedra are more or less regular. VO₂(M/R) has the oxygen octahedra aligned along two perpendicular directions, but VO₂(B) and VO₂(A) have the oxygen octahedra aligned along one crystallographic direction.

Many effort has been directed toward the preparation and study of the thermochromic VO₂(M/R). Although one-step synthesis of VO₂(M/R) has been reported now and then, metastable phases of VO₂(B) and VO₂(A) are still often present as impurities. Compared to VO₂(M/R), VO₂(B) and VO₂(A) have larger cells and are thus less compact [98]. VO₂(B) has a low-symmetry monoclinic structure with space group C2/m. It is considered to have two layers of identical atoms and the second layer is shifted with respect to the first layer. In this structure, the oxygen octahedra are deformed and as a result the vanadium atoms are not in the center of the oxygen octahedra any-
more. The monoclinic VO$_2$(B) possess an open framework originating from the edge-sharing VO$_6$ octahedra which makes VO$_2$(B) a great electrode material for use in Li-ion batteries [104]. VO$_2$(A) has a tetragonal structure with a space group $P4_2/nmc$. The oxygen octahedra in VO$_2$(A) are less deformed than in VO$_2$(B).

VO$_2$(B) is the most common allotropic phase in the intermediate step involved in the process of producing the final product of VO$_2$(R). VO$_2$(B) can transform into VO$_2$(R) by convenient annealing at elevated temperature. Conversion of the metastable VO$_2$(B) phase to the most stable rutile form of VO$_2$(M/R) by thermal treatment has been extensively reported [105, 106]. It has been shown that the mechanism of the transformation is complex and the transformation at least includes two main steps [107]. The transformation of VO$_2$(B) into VO$_2$(M/R) is irreversible and is crucial for the final morphology which influences the optical performance.

However, concerning the transformation from VO$_2$(B) into VO$_2$(R), the occurrence of the intermediate VO$_2$(A) phase is occasionally observed experimentally [98], but not always. It is known that the presence of VO$_2$(A) phase can only be obtained under certain conditions, such as under low pressure [108].

VO$_2$(B) can transform to VO$_2$(A) at elevated temperature. The change of structural units from B to A is accomplished by a shift of oxygen vacancies along with rearrangement of vanadium atoms [108]. VO$_2$(A) can be further converted to VO$_2$(M) by annealing process.
4 Thermodynamics approach

4.1 V-SO$_2$ system

It is notable that elemental vanadium reacts with oxygen in a simple and direct way to obtain vanadium dioxide according to the overall reaction:

$$V(s) + O_2(g) \rightarrow VO_2(s) \quad (4.1)$$

Many methods to selectively synthesize individual VO$_2$ phases have been reported, such as chemical process, e-beam evaporation, pulsed laser deposition and sputtering [24, 109-112]. However, it can be quite difficult to precisely control the composition. At high temperatures vanadium has a very rapid rate to be oxidized progressively from tetragonal VO$_2$ into monoclinic V$_6$O$_{13}$ and V$_3$O$_7$ until ultimately reaching thermostable orthorhombic V$_2$O$_5$ [113].

Alternatively, using a mild oxidation agent can be a better way to control the oxidation potential. It has been shown that the reduction of sulfur dioxide by active transition metals, such as copper, will form elemental sulfur and metal oxide [114]. Using SO$_2$ as oxidizing agent to oxidize vanadium into vanadium oxide is likely to happen. The oxidation of vanadium by sulfur dioxide is expressed by the overall reaction:

$$V(s) + SO_2(g) \rightarrow VO_2(s) + S(g) \quad (4.2)$$

From the above reaction, if SO$_2$ is completely decomposed, the outputs from the process would be VO$_2$ and S. Elemental sulfur yielded in the reaction chamber can be evaporated and flow away at high temperature. To evaluate the feasibility of this underlying chemical reaction, a theoretical chemical thermodynamic analysis is performed in section 7.1 to provide a basic understanding of the chemical reaction and to make sure that the desired reaction will happen.
4.2 Basics of thermodynamics

In general, the free energy change of a reaction, the Gibbs free energy \( \Delta G_r \), decides the reaction direction. A negative value of \( \Delta G_r \) indicates the reaction is thermodynamically favorable to proceed to its products side, whereas a positive \( \Delta G_r \) implies that the reaction would not occur. If several possible reactions are thermodynamically feasible, the reaction with the most negative \( \Delta G_r \) should ideally occur since it produces most stable products.

For a closed reaction system, equilibrium compositions present under given conditions of pressure, temperature and input concentration can be determined with thermodynamic methods under constraints of mass conservation, constant temperature and constant total pressure.

Minimization of the Gibbs free energy is an equilibrium model which doesn’t require defining the specific chemical reactions. The calculation is based on the thermodynamic rule which states that a chemical reaction will be in equilibrium when the Gibbs free energy of the system reaches a minimal value. Under the thermodynamic equilibrium condition, the total Gibbs free energy of a system is expressed as

\[
G = \sum_i n_i \mu_i \tag{4.3}
\]

where \( n_i \) is the number of moles of species \( i \) and \( \mu_i \) is the chemical potential of species \( i \) which is defined as

\[
\mu_i = \mu_i^0 + R_g T' \ln a_i \tag{4.4}
\]

where \( a_i \) is activity of species \( i \), \( \mu_i^0 \) is the standard chemical potential of species \( i \), \( R_g \) is the universal gas constant and \( T' \) is the temperature.

The activity of condensed species is assumed to be unity; the gaseous species can be treated as an ideal gas, its activity \( a_i \) equals to its partial pressure \( p_i \):

\[
p_i = \frac{n_i}{N_t} P \tag{4.5}
\]

where \( N_t \) is the total mole number in the gas phase and \( P \) is the total pressure in the system.

Combination of above equations, a dimensionless quantity \( G/R_g T' \) is expressed as:

\[
G = \sum_i n_i \mu_i = \sum_i n_i \left( \mu_i^0 + R_g T' \ln a_i \right)
\]
\[
\frac{G}{R_gT'} = \sum_{i=1}^{m_g} n_i \left[ \frac{\mu^0_i}{R_gT'} + \ln P + \ln \frac{n_i}{N_t} \right] + \sum_{j=1}^{m_s} n_j \left[ \frac{\mu^0_j}{R_gT'} + \ln a_j \right] \tag{4.6}
\]

where \( i \) stands for gaseous species, \( j \) stands for condensed species, \( m_g \) is the numbers of the gaseous species and \( m_s \) is the number of condensed phases.

According to the elemental balance, the following equation is obtained:

\[
\sum_i a_{ij}^q n_i^q + \sum_i a_{ij}^s n_i^s = A_j \quad (j = 1, 2, \ldots, k_e) \tag{4.7}
\]

where \( a_{ij} \) is the number of atoms of the \( j \)th element in a molecule of the \( i \)th species, \( g \) and \( s \) denote the gaseous phase and condensed phase, respectively. \( A_j \) is the total number of moles of the \( j \)th element and \( k_e \) is the total number of elements. Then the problem is to find a set of \( n_i \) values which minimize the value of \( G/R_gT' \), the solutions \( n_i \) have to be real non-negative numbers.
5 Optics

5.1 Optical properties of materials

The optical properties of a material represent its interaction with electromagnetic radiation. Light is considered as an electromagnetic wave and consists of particles which are called photons. Material-light interaction leads to a number of phenomena. The light may be transmitted through the sample; or the light might be absorbed by the sample; or the light may be reflected from the sample; or the light may be diffusely scattered by the sample.

The transmitted light can travel in many directions. The part parallel to the incident light is called direct transmittance and the other part is called diffuse transmittance. Likewise, the reflected light which has the same angle to the surface normal as the incident light is called specular reflectance and the other part is called diffuse reflectance. When light strikes a rough or granular surface, the diffuse transmittance and reflectance would become significant. Their relations can be written in the following way:

\[ T_{\text{tot}} = T_{\text{direct}} + T_{\text{diff}} \] (5.1)
\[ R_{\text{tot}} = R_{\text{spec}} + R_{\text{diff}} \] (5.2)

In the presence of absorption and scatter, the law of energy conservation can be written as:

\[ T_{\text{direct}} + R_{\text{spec}} + A + S = 1 \] (5.3)

where \( T_{\text{direct}} \) is the direct transmittance, \( R_{\text{spec}} \) is the specular reflectance, \( A \) is the absorptance and \( S \) is the optical scatter. All these values are dependent on the wavelength of the light. The algebraic sum of absorption and scatter is often called optical loss \( L_o \).

To classify a material with regard to light propagation, two sets of complex optical constants, the complex refractive index \( N \) and the complex dielectric function \( \varepsilon \), are commonly used.

The complex refractive index \( N \) is defined as

\[ N = n + ik \] (5.4)
where the symbols $n$ and $k$ are used for the real and imaginary part, $n$ is the refractive index and $k$ is related to the optical absorption of electromagnetic waves propagating through the medium.

The complex dielectric function (relative permittivity) is defined as

$$\varepsilon = \varepsilon' + i\varepsilon'' \quad (5.5)$$

where $\varepsilon'$ is the real part and $\varepsilon''$ is the imaginary part of the complex dielectric function.

The complex dielectric function and the complex refractive index are closely interrelated by:

$$\varepsilon = N^2 \quad (5.6)$$
$$\varepsilon' = n^2 - k^2 \quad (5.7)$$
$$\varepsilon'' = 2nk \quad (5.8)$$

The two wavelength-integrated optical properties, luminous transmittance $T_{\text{lum}}$ and solar transmittance $T_{\text{sol}}$ are used to characterize a thin film for its architectural functions. The luminous efficiency of the human eye [115] and the solar irradiance spectra are shown in Figure 5.1. The integrated luminous transmittance ($T_{\text{lum}}$, 380–780 nm) and solar transmittance ($T_{\text{sol}}$, 300–2500 nm) were calculated based on the recorded spectra using the following expression:

$$T_{\text{lum/sol}} = \int \phi_{\text{lum/sol}}(\lambda) \ T(\lambda) \ d\lambda / \int \phi_{\text{lum/sol}}(\lambda) \ d\lambda \quad (5.9)$$

where $T(\lambda)$ is the recorded film transmittance, $\phi_{\text{lum}}$ is the standard luminous efficiency function of human eye and $\phi_{\text{sol}}$ is the solar irradiance spectrum for air mass 1.5 (when the sun is standing 37° above the horizon).
5.2 Surface plasmon resonance

The development of control of material geometries in nanoscale enables a variety of exciting possibilities in a wide range of applications. Among the unique physical and chemical properties observed in nanoscale materials, surface plasmon resonance is particularly important for the exotic optical properties which can be relevant for a number of light harvesting and energy conversion applications [116]. The plasmon resonance is most commonly observed in elemental noble metal nanoparticles, such as Au and Ag, which have been extensively studied for using in the field of solar cells, light-emitting devices, photocatalysts and sensors [117-119]. However, due to their high optical loss, alternative low loss materials, for instance, heavily doped metal oxides (such as indium tin oxide) [120], which have low optical losses in the visible and near infrared ranges have been put forward. Of particular note is that VO₂ exhibits large change in refractive index in the infrared wavelength range in its different states.

5.2.1 Surface plasmon resonance

A plasmon is the quantum of the collective oscillation of free electrons in solids. In free-electron like materials, the electrons oscillate in response to the applied electromagnetic field and their motion is damped via collisions occurring with a characteristic collision frequency \( \gamma = 1/\tau \). By using the

![Figure 5.1. Solar irradiance spectrum and luminous efficiency of the human eye.](image)
Drude model, the dielectric constant of such material is obtained as a function of frequency in the following form:

\[ \varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \frac{i\omega}{\tau}} \]  

(5.10)

with \( \omega_p \) denoting the plasmon frequency of the corresponding bulk metal, and \( \tau \) denoting the electron relaxation time of the free electron in the metal. For large frequencies close to \( \omega_p \), the damping is often negligible (lossless), the complex dielectric constant is predominantly real and is expressed as

\[ \varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \]  

(5.11)

Surface plasmons are coherent delocalized electron oscillations that exist at the metal-dielectric interface. When the incident light has the correct incidence angle, surface plasmon resonance occurs. At this so-called ‘resonance angle’, \( \theta \), the photons in the light have a momentum (vector with magnitude and direction) equal to the momentum of the surface plasmons, and the photons are converted into plasmons.

Under resonant conditions, a propagating surface wave is generated along the interface which is called surface plasmon polariton. In this case, plasmons propagate in the x- and y-directions along the metal-dielectric interface, but decay evanescently in the z-direction. Usually, the surface plasmon propagation distance, \( \delta_{sp} \), can reach from a few micrometers up to a millimeter scale. The decay distance in the metal, \( \delta_m \), is in the order of a few nanometers. The decay distance in the dielectric material, \( \delta_d \), is in the order of half wavelength of the associated light. It means the surface plasmon does not penetrate deep into the metal; conversely the surface plasmon can extend a micrometer away from the dielectric surface [121].

5.2.2 Localized surface plasmon resonance

In the case if the lateral dimension of the interface is much smaller than the plasmon propagation distance, for instance, when the light interacts with nanoparticles whose size is much smaller than the incident wavelength. Then there is no traveling wave but there will be a large increase of the electromagnetic field close to the nanoparticle surface hence the surface plasmon is localized. The decay distance in the dielectric material, \( \delta_d \), is much shorter than the regular surface plasmon. Localized surface plasmons are non-propagating excitations of the conduction electrons of metal nanoparticles.

Metal nanostructures usually have unique properties compared to their bulk counterparts, especially their fascinating optical properties. For exam-
ple, nanosized gold and silver exhibit bright colors because their surface plasmon resonances occur in the visible region. For metallic nanoparticles less than 30 nm in diameter, scattering process is negligible. For larger particles, scattering effects become more significant and the resonance decreases in magnitude and becomes broadened and shifts to longer wavelength. The plasmonic absorption strongly depends on the detailed structures of the particles, such as size, shape and aggregation [122]. The solid spherical particles and hollow spheres have only one dipolar plasmon resonance frequency due to their complete symmetry. For structures with lower symmetry, the induced charge distribution on the surface results in more non-degenerate dipolar modes with different resonant frequencies which result in broad plasmon absorption spectra.

The applied field from the light induces a dipole moment in the nanoparticle, the complex polarizability of the sphere with radius $a$ is introduced as [116]:

$$\alpha_{pl} = 4\pi a^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}$$

(5.12)

where $\varepsilon_m$ is the dielectric constant of the environment medium. The localized dipole surface plasmon resonance of a nanoparticle occurs when the polarizability reaches maximum. Under the condition that $|\varepsilon + 2\varepsilon_m|$ is a minimum, which requires the real part of the dielectric function of the particle to be $\varepsilon' = -2\varepsilon_m$, polarizability $\alpha_{pl}$ is enhanced.

Metallic particles in general have large and negative real part of the permittivity $\varepsilon'$ in the visible region and it decreases in the infrared region. Therefore, the plasmon resonance of metals usually occurs in the visible wavelength region. For VO$_2$ in its metallic state, the resonance frequency occurs in the near infrared region [123]. In the case that the effective dielectric constant $\varepsilon_m$ was chosen between glass-like material ($\varepsilon_m = 2.25$) and air ($\varepsilon_m = 1$), the estimation of the resonance frequency lies between 1300 nm and 1800 nm [124].

### 5.3 Maxwell-Garnet effective medium theory

Nanoscaled composite materials often have different optical properties from the constituent materials. If the characteristic size of the nanostructure is much smaller than the irradiation wavelength, then the composite can be considered as one homogeneous optical medium. The optical properties of the composite can be characterized by an effective refractive index and an effective absorption coefficient. The effective medium theory (EMT), specif-
ically the Maxwell-Garnett [125] and Bruggeman-Landauer [126] forms, is developed to study various physical properties of such heterogeneous media.

For a composite consisting of isolated particles, the Maxwell–Garnett model is appropriate, while the applicability of this model is restricted by the size and volume fraction of the metallic inclusion particles. The particle radius shall be much smaller compared to radiation wavelength so that the electromagnetic field is constant over the particle volume. And the spacing in between the particles must be large enough so that the interaction between the inclusions is negligible. In an electric field a small sphere can be replaced by equivalent point dipole \( p = \alpha_p E_L \), where \( \alpha_p \) is the polarizability of the sphere. Hence the finite size of the spheres is ignored. The polarizability of sphere is written as

\[
\alpha_p = \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_m + \frac{1}{3} (\varepsilon_p - \varepsilon_m)} \tag{5.13}
\]

Under the assumption that the composite consists of isolated spherical and uniform inclusion particles randomly embedded in a dielectric matrix, an effective macroscopic dielectric function \( \varepsilon_{\text{eff}} \) could be determined for the composite [127]. The Maxwell-Garnet formula for a strongly diluted suspension of spheres can be written in the form:

\[
\frac{\varepsilon_{\text{eff}} - \varepsilon_m}{\varepsilon_{\text{eff}} + 2\varepsilon_m} = f \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2\varepsilon_m} \tag{5.14}
\]

where \( \varepsilon_m \) is the dielectric function of the suspending matrix, \( \varepsilon_p \) is the dielectric function of the inclusion particles and \( f \) is the volume filling fraction of particles in the composite. Although Maxwell-Garnett considered only metallic particles, in general, the derivation is valid even for pure dielectrics.

The Maxwell-Garnett mixing formula [127] could be also written as

\[
\varepsilon_{\text{eff}} = \varepsilon_m \frac{1 + \frac{2}{3} f \alpha_p}{1 - \frac{1}{3} f \alpha_p} \tag{5.15}
\]

The Maxwell-Garnett theory assumes the particles to be spherical. Cohen et al. [128] have proposed a modified Maxwell-Garnett theory for treating aligned ellipsoidal particles in the case of identical in shape and orientation by including a characteristic depolarization factor \( L_i \) obeying \( \Sigma L_i = 1 \). For the
case of spheres, \( L_1 = L_2 = L_3 = \frac{1}{3} \). The modified Maxwell-Garnett formula follows:

\[
L_i \frac{\varepsilon_{eff} - \varepsilon_m}{\varepsilon_{eff} + (1 - L_i)\varepsilon_m} = \frac{1}{3} \int f \frac{\varepsilon_p - \varepsilon_m}{L_i\varepsilon_p + (1 - L_i)\varepsilon_m} \tag{5.16}
\]

The polarizability for randomly oriented ellipsoids is defined as:

\[
\alpha_{pl} = \frac{1}{3} \sum_{i=1}^{3} \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_m + L_i(\varepsilon_p - \varepsilon_m)} \tag{5.17}
\]

An spheroid (two of the \( L_i \) are equal) can be prolate or oblate with respect to aspect ratio \( m = c/a \) as illustrated in Figure 5.2. The semi-axis \( a \) is the equatorial radius of the spheroid, and \( c \) is the distance from center to pole along the symmetry axis. If \( c > a \), the spheroid is prolate and if \( a < c \), the spheroid is oblate.

![Figure 5.2. Schematic drawing for (a) prolate spheroid and (b) oblate spheroid.](image)

### 5.4 Thin film optics

#### 5.4.1 One interface

The geometry of an interface is sketched in Figure 5.3 where the interface is absolutely flat. The refractive index of the first medium (medium 1) and the second medium (medium 2) is \( N_1 \) and \( N_2 \), respectively. \( \theta_1 \) is incidence angle
and $\theta_2$ is refraction angle. The incidence angle and the refractive angle are connected by Snell’s law of refraction:

$$\frac{\sin \theta_1}{\sin \theta_2} = \frac{N_2}{N_1} \quad (5.18)$$

![Diagram of a single interface](image)

**Figure 5.3.** Geometry of a single interface

The reflection and transmission of light at one interface between the two media are given by the following Fresnel’s equations. For s-polarized light the reflection coefficient $r_s$ is

$$r_s = \frac{N_1 \cos \theta_1 - N_2 \cos \theta_2}{N_1 \cos \theta_1 + N_2 \cos \theta_2}, \quad (5.19)$$

while the reflection coefficient for p-polarized light $r_p$ is

$$r_p = \frac{N_2 \cos \theta_1 - N_1 \cos \theta_2}{N_1 \cos \theta_2 + N_2 \cos \theta_1}. \quad (5.20)$$

The transmission coefficient for s-polarization $t_s$ is:

$$t_s = \frac{2N_1 \cos \theta_1}{N_1 \cos \theta_1 + N_2 \cos \theta_2}, \quad (5.21)$$
and the transmission coefficient for p-polarization $t_p$ is:

$$t_p = \frac{2N_1 \cos \theta_1}{N_1 \cos \theta_2 + N_2 \cos \theta_1}. \quad (5.22)$$

The reflectance of an interface is then calculated as:

$$R = |r_{s,p}|^2 \quad (5.23)$$

Accordingly, the transmittance through the interface is:

$$T = 1 - R = \frac{N_2 \cos \theta_2}{N_1 \cos \theta_1} |t_{s,p}|^2 \quad (5.24)$$

### 5.4.2 Two interfaces

In fact, samples always contain more than one interface. For a film deposited onto another solid material (substrate), the first and third materials are usually different. In the following, it is assumed that all layers have parallel interface. Geometry of two interfaces is sketched in Figure 5.4. The light incident at the interface between medium 1 and 2 will both be reflected and transmitted according to Fresnel’s equations, in section 5.4.1. At the second interface between medium 2 and 3 the transmitted light can then either be reflected or transmitted. If the film layer has a thickness of the order of the wavelength of light or less, interference effects needs to be considered. When the light is passing through the thin film, a phase change occurs. The magnitude of the phase change ($\delta_2$) depends on the path length ($d$) through the medium and the refractive index according to

$$\delta_2 = \frac{2\pi}{\lambda} N_2 d \cos \theta_2 \quad (5.25)$$

If the complex part of the refractive index of $N_2$ is non-zero, the $\delta_2$ term also accounts for the absorption in the layer.
The contribution from each reflectance and transmittance is then summed up, and total amplitude reflectance and transmittance can be obtained by the following equations:

\[
\begin{align*}
    r &= \frac{r_{12} + r_{23}e^{i2\delta_2}}{1 + r_{12}r_{23}e^{i2\delta_2}} \\
    t &= \frac{t_{12}t_{23}e^{i\delta_2}}{1 + r_{12}r_{23}e^{i2\delta_2}}
\end{align*}
\]  

(5.26)  

(5.27)

Subsequently the transmittance and reflectance are expressed as follows:

\[
\begin{align*}
    R &= |r|^2 \\
    T &= |t|^2 \frac{N_3 \cos \theta_3}{N_1 \cos \theta_1}
\end{align*}
\]  

(5.28)  

(5.29)

For multilayer films with more interfaces, the situation becomes more complicated. Calculation of transmittance and reflectance in the present work is based on the Fresnel equations using a transfer matrix method which is described in the work by Pfrommer [129] and Harbecke [130].
5.5 Mie light scattering theory

When the incident radiation encounters an obstacle, the incident light may be redirected due to light scattering or be absorbed by the particles. There are different light scattering theories and the most well-known are Rayleigh scattering theory which is applicable to small dielectric spherical particles and Mie scattering which is applicable to in general all spherical particles. Mie theory was developed by Gustav Mie [131] for handling scattering and absorption of electromagnetic radiation by a uniform isotropic particle.

The optical properties of the sphere are expressed in terms of the scattering, absorption and extinction cross sections. The total extinction cross section is a sum of the scattering cross section and absorption cross section:

\[ C_{ext} = C_{abs} + C_{sca} \quad (5.30) \]

The extinction cross section represents loss of energy from the incident field due to both scattering and absorption generated by the particle.

The absorption cross section and scattering cross section can be obtained as follows: \( C_{sca} = W_{sca}/I_{inc} \), \( C_{abs} = W_{abs}/I_{inc} \) where \( I_{inc} [W/m^2] \) is energy flux of the incident irradiance on the surface of the particle, \( W_{sca} [W] \) is the scattered energy and \( W_{abs} \) is the absorbed energy.

The total scattering cross section and extinction cross section are expressed in units of the geometric cross section \( \pi a^2 \),

\[ C_{sca} = \frac{2\pi a^2}{x^2} \sum_{l=0}^{\infty} (2l + 1)(|a_l|^2 + |b_l|^2) \quad (5.31) \]

\[ C_{ext} = \frac{2\pi a^2}{x^2} \sum_{l=0}^{\infty} (2l + 1)\text{Re}(a_l + b_l) \quad (5.32) \]

where \( x \) is a dimensionless size parameter \( x = \frac{2\pi a N_m}{\lambda} \), \( a \) is the radius of the spherical particle, \( \lambda \) is the incident wavelength, \( \text{Re} \) is the real part of the sum of the complex numbers and \( N_m \) is the refractive index of the surrounding medium.

The Mie solution has form of an infinite series of spherical multipole partial waves. The incident plane wave, the scattering field and internal field are expanded into vector wave functions. By applying the boundary conditions at the surface of the sphere (between the sphere and the surrounding medium), the expansion coefficients \( a_l \) and \( b_l \) for the scattered field can be computed [132].

Scattering and extinction can be normalized by projected cross sectional areas to yield dimensionless parameter commonly known as efficiency fac-
tors or efficiency coefficients. Efficiencies for absorption ($Q_{abs}$), scattering ($Q_{sca}$) and extinction ($Q_{ext}$) are defined as the ratio of its cross section $C_i$ to the total geometric cross–section area $n_t \pi a^2$ of the particles ($n_t$ are numbers of the particles):

$$Q_{ext} = \frac{C_{ext}}{n_t \pi a^2} \quad (5.33)$$

$$Q_{sca} = \frac{C_{sca}}{n_t \pi a^2} \quad (5.34)$$

$$Q_{ext} = Q_{sca} + Q_{abs} \quad (5.35)$$

For the same particle, when the index of the surrounding medium has changed, extinction behavior of particle is affected. Specifically, when the refractive index $N_m$ increases, light becomes weakly confined in the particle which results in less light scattered and absorbed by the particle.
6 Experimental

6.1 Thin film processes

6.1.1 Magnetron sputtering

A variety of thin films production methods have been employed for synthesis of thermochromic VO₂ films such as sol-gel route [133-135], pulsed laser deposition [136, 137], atomic layer deposition [16, 138], chemical vapor deposition [21, 139] and physical vapor deposition [140]. Sputtering is a very common physical vapor deposition (PVD) process to produce thin films. A vapor of a material is produced by physically knocking atoms out from the source material surface using an ionized inert gas. The ejected atoms then build up on the substrate they land on; resulting in the deposition of a thin film.

The sputtering deposition used in this work is a magnetron sputtering system. The target source materials are used as cathode and the substrate and the chamber walls are grounded and serve as anode. In order to obtain highly pure coatings, the chamber is evacuated to remove most of the gas molecules in the chamber. The chamber is then backfilled with a process gas. A negative electrical potential applied to the target source material will cause free electrons to flow from the negatively charged target. When an inert gas, usually argon, is introduced, those free electrons will collide with the outer electronic shell of the argon gas atoms and strip an electron from the gas atoms. The inert gas atoms then become positively charged Ar⁺ ions and are accelerated to the negatively charged target material at a very high velocity knocking off some atomic-sized particles from the target source material due to the momentum of the collisions. Magnetic field generated from magnets behind the target is used to restrict the emitted electrons close to the negatively charged target material surface. This confinement increases the ionization rate of argon atoms and therefore leads to faster deposition rate which is defined as the thickness of material deposited on the substrate per time unit. Target material particles will cross the vacuum chamber in the path that the magnetron is directed and then land on the substrate as a layer of thin film.

Besides argon, reactive gas species (such as oxygen or nitrogen) can be introduced to promote chemical reactions between target material atoms and the reactive gas atoms to form compounds as the end product of the deposition landing on the substrate.
Figure 6.1. Deposition chamber schematics.

A sputtering system based on a Balzers UTT400 unit was used. The targets were 2-inches diameter of circular plates. The distance between the substrate and the target for sputtering was 13 cm. The vacuum chamber was initially evacuated to $10^{-7}$ mbar and then back-filled with argon. The gas flows were adjusted by mass-flow-controlled gas inlets. Pre-sputtering in pure argon was usually carried out for a few minutes in order to remove surface oxides from the source target.

The glass substrate was 1-mm-thick from ThermoScientific and the pre-coated ITO ($\text{In}_2\text{O}_3$:Sn) glass substrate was also 1-mm-thick with a resistance/square of 60 $\Omega$ manufactured by Colorado Concept Coating LLD, Loveland, CO, USA.

The substrates were cleaned in ethanol in an ultrasound bath and then rinsed using deionized water before introduced in the vacuum system. During deposition the substrate was rotated to get uniform films.

The thickness of the films was recorded by a Bruker Dektak XT surface profilometer afterwards.
6.1.2 Deposition of metallic vanadium thin films

Metallic vanadium thin films were deposited on glass substrate by dc magnetron sputtering from a vanadium metal target (99.95% purity). The deposition procedure was as follows: After argon (purity 99.99%) flow of 80 ml/min was introduced and the vanadium target was presputtered for a few minutes, then vanadium films were deposited at room temperature at a discharge power of 6.6 W/cm² without using any reactive gas. The total pressure during sputtering was maintained at 0.01 mbar. The deposition rate was determined to be ~8 nm/minute.

6.1.3 Deposition of vanadium oxide thin films

Vanadium oxide films were deposited on a heated substrate with a very accurate control of the oxygen concentration and other deposition parameters to minimize the content of non-thermochromic oxides in the film. In most cases, substrate temperatures above 400 °C are required in order to obtain VO₂ film with a sharp and strong phase transition. The deposition temperatures also influence the surface roughness, morphology and grain size of the deposited films [141].

The thermochromic vanadium oxide films were made by reactive dc sputtering from vanadium target. Before deposition, the glass substrate was preheated by a substrate heater to obtain a stabilized substrate temperature. The temperature was measured in-situ by using a thermocouple which is mounted on the substrate heater. Calibration measurements with a thermocouple mounted on a glass substrate were made to determine the temperature difference between the sample and the substrate heater. After deposition, the sample was cooled down in vacuum.

The vanadium oxide films in the study of durability under heating and humidity were fabricated on glass substrates at a power of 172 W in an argon and oxygen gas mixture where the oxygen/argon ratio was kept at a constant value of 0.05 during the deposition process. The process pressure in the growth chamber was kept constant at 1.2×10⁻² mbar. The deposition rate was ~7 nm/minute.

For studying substrate effects, vanadium dioxide thin films were grown on three different substrates, indium tin oxide (ITO) coated glass(with resistance/square of 60 Ω), (SnO₂) coated glass and bare glass. The most crucial factor to fabricate the thermochromic VO₂ is the precise control of the oxygen amount in the reactive sputtering. The mixed gas ratio $\Gamma$ is defined as $\Gamma = [\phi_{O₂}/(\phi_{Ar}+\phi_{O₂})]$, where $\phi_{O₂}$ and $\phi_{Ar}$ are oxygen and argon fluxes, respectively. $\Gamma$ was varied in the range of 5.3 ≤ $\Gamma$ ≤ 6.7% and the power density on vanadium target was 8.58 W/cm². In addition, the power density on vanadium target was varied in the range of 3.45~8.58 W/cm² and for each power
setting, the oxygen/argon ratio was optimized to obtain pure phase of VO$_2$ with high thermochromic performance.

6.1.4 Aluminum oxide thin films deposition

A thin film of aluminum oxide was coated onto the as-made VO$_2$ layer by reactive dc magnetron sputtering from aluminum target (purity 99.99%). To avoid degradation of the VO$_2$ film, the deposition was done at room temperature. After pre-sputtering of aluminum in pure argon gas, oxygen was introduced into the system at oxygen/argon gas flow ratio of 0.025, while the working pressure in the growth chamber was kept at 4×10$^{-2}$ mbar. The power of the aluminum target was 200 W and the deposition rate was 20 nm/min.

6.1.5 Deposition of vanadium oxide based composite films

Vanadium dioxide-silicon oxide composite films were deposited by reactive rf magnetron co-sputtering from a metallic vanadium target and an insulating silicon dioxide target (purity 99.9%). The substrate was heated at 450 °C. Numerous experiments were carried out to find best deposition conditions. The optimal oxygen/argon ratio was 0.017 and the corresponding discharge power was 100 W on vanadium target and 200 W on silicon dioxide target, respectively.

6.1.6 Titanium dioxide film deposition

Deposition of the titanium dioxide films were made by reactive dc sputtering from metallic titanium target. An oxygen/argon ratio of 0.045 was used and the sputtering power density on titanium target was 14.9 W/cm$^2$ at a pressure of 1.2x10$^{-2}$ mbar. The substrate temperature was stabilized at 230 °C. The thickness of the titanium dioxide film was around 300 nm.

6.2 Thermal growth of VO$_2$ films in SO$_2$

The sputter-deposited metallic vanadium film on glass substrate was introduced to an in-house built tubular chamber (shown in Figure 6.2) consisting of a 40-mm-diameter quartz tube inserted in a furnace. The sample was placed at position of T2 zone. A nitrogen gas (99.98%) flow of 100 sccm was continuously flowing through the chamber during the process. A ramping rate of 20 °C/min was used to heat up the oven and the temperature was stabilized at desired temperature for half an hour. Sulfur dioxide, SO$_2$ (purchased from Air Liquide, with a purity of 99.98%), used as the reactive gas, was introduced into the oven at a flow rate of 100 sccm. The pressure in the chamber was 18 mbar. The as-made vanadium film was heat treated for 1 h.
at desired temperature in the gas mixture of N₂ and SO₂. The temperature was calibrated with thermocouple at the sample position. Afterwards the sample was cooled down overnight in the nitrogen environment.

![Figure 6.2. The hot-walled tubular oven where T1-T4 are temperature zones.](image)

### 6.3 Nanoparticle synthesis

Two main chemical techniques were used to obtain VO₂(M/R), hydrothermal or reduction of vanadium oxide precursors. Hydrothermal method provides numerous variable parameters (reaction time, pH, reducing agents). However hydrothermal synthesis often produce metastable phase or mixture phases rather than pure VO₂(M/R) phase. Secondly, the essential long reaction time in hydrothermal method generates large particles. Therefore, most soft chemical routes leads to non-spherical 1D nanostructures since VO₂ has preferable growth direction, various morphologies reported in the literature include nanorods, nanowires, nanobelts and nanosheets [142]. Moreover, the reducing agent N₂H₄ often plays a key role [143, 144] in the synthesis process which is highly toxic and dangerous.

Hydrolysis of metal alkoxide [145] is one effective way to prepare high purity spherical metal oxide particles with relative narrow sized distribution. Monodispersed spherical V₂O₅ particles made by hydrolyzing vanadium alkoxide was first reported by Yamamoto [146]. Synthesis of vanadium nanoparticles were performed as follows: acetone (99.9%), pyridine (anhydrous, 99.8%) and deionized H₂O with weight ratio of 6.4g/1.6g/0.05g were mixed in a flask. Then 60 µl vanadium isopropoxide (VO(OiPr)₃, 97%) was injected into the mixture solution under stirring. The reaction solution turned to cloudy orange color intermediately. After stirring for 5 minutes, the orange precipitate was gathered by vacuum filtration and washed with acetone. The resultant powder was dried at 60 °C in a vacuum oven overnight. Then the powder was placed in a crucible and heat-treated in hydrogen gas in a multipurpose-vacuum-furnace.

The as-synthesized VO₂ nanospheres (0.02 g) were added to a 0.1g/ml polyvinylpyrrolidone (PVP) (average molecular weight 38000) ethanol solu-
tion. The solution was sonicated for 45 min and then dropcasted onto 2x2cm glass slides. After drying, the films were subjected to optical measurements.

6.4 Characterizations

6.4.1 X-ray diffraction

X-ray diffraction (XRD)[147] is a commonly used technique to characterize crystalline materials and provide information about grain size, relative crystalline orientation and lattice parameters. A crystalline material is composed of atomic planes separated by distance \( d_{hkl} \). A set of lattice planes can be indexed with the Miller indices \( h, k \) and \( l \). When the X-rays scattered from the atomic planes in a crystal constructively interfere, a diffraction peak is observed at a specific angle. The angle at which a beam of X-rays of a particular wavelength diffracts from a crystalline surface is given by Bragg’s Law.

\[
y\lambda = 2 d_{hkl} \sin \theta
\]

(6.1)

where \( \lambda \) is the wavelength of the incoming X-rays, \( \theta \) is the scattering angle, \( y \) is an integer representing the order of the diffraction peak.

For the study of thin films, the grazing incidence X-ray diffraction (GIXRD) technique with a low incoming angle of the incidence X-ray is employed in order to enhance the sensitivity for the diffraction of the thin film and minimize the substrate scattering. The GIXRD was performed on a D5000 Siemens instrument using Cu K\( \alpha_1 \) (\( \lambda = 1.54 \) Å) radiation.

![Figure 6.3. Basic feature of GIXRD](image-url)
6.4.2 Raman spectroscopy

Raman spectroscopy [148] is a powerful spectroscopic technique to study phonons and molecular vibrations in the materials. It is based on inelastic scattering of monochromatic light, usually from a laser beam. Photons of the laser light interact with the sample, resulting in the laser photons frequency being shifted to higher or lower frequency in comparison with the incoming monochromatic frequency, which is called the Raman shift. This shift provides information about vibrational, rotational and other low frequency transitions in molecules which can be further used to identify the chemical structure, phase, strain and impurity of the materials. In a solid material, the vibrational frequencies in the lattice depend on the mass of the atoms and their bonds. The shift in energy from the scattered photons is expressed as the change in frequency:

$$\Delta \nu = \left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right)$$  \hspace{1cm} (6.2)

where $\Delta \nu$ is the wavenumber shift, $\lambda_1$ is the wavelength of the inelastic scattered photons and $\lambda_2$ is the wavelength of the laser source.

In this study, Raman spectroscopy measurements were performed using a Renishaw micro Raman system 2000 with an argon-ion laser of 514 nm line to analyze the phase of crystalline films.

6.4.3 UV-VIS-NIR spectrophotometry

The spectral transmittance and reflectance are measured in the wavelength interval 300 to 2500 nm at different temperatures. A Perkin Elmer Lambda 900 instrument equipped with an integrating sphere was used. A sample of spectralon (a material with highest known diffuse reflectance) is used as reference.
6.4.4 Measurement of electrical resistance

A four-point probe is a simple and widely used technique for measuring the resistivity of samples. Four contacts were made on the thin film surface by painting with silver glue. The two contacts near the edges were connected to the power current supply, and the other two contacts were connected to voltage meter. By passing a current through two outer probes, a voltage between the inner probes is induced and measured. The resistance of the area between two inner probes is $R_{res} = V/I$, and then the resistivity can be obtained as follows:

$$\rho = \frac{R_{res} \cdot d \cdot L_w}{L}$$  \hspace{1cm} (6.3)

where $L$ is the length between two inner probes, $L_w$ is the length of the contacts and $d$ is the thickness of the thin film.

The film sample was glued to a hot plate and connected to a temperature controller. The measurement was performed using a temperature range of $0^\circ$~$130^\circ$C with ramping rate of 3 °C/min. Liquid nitrogen was used for cooling down the sample to ambient temperature.
6.4.5 Scanning electron microscopy

Scanning electron microscopy (SEM) is used to view the morphology of the sample surfaces. An electron beam produced in the electron gun pass through a set of lenses and apertures which result in a focused electron beam. The electron beam interacts with the sample atoms and generates many different types of signals. The signals from the secondary electrons or backscattered electrons can be recorded by different detectors and are used for imaging. The secondary electron signals give more information about surface structure, while the backscattered electron signals give more information about composition contrast in the sample. In this study, the microstructure of the samples was studied using LEO 1550 FEG Gemini scanning electron microscope from Zeiss with secondary electron detector.

An energy dispersive X-ray analysis (EDX) system is attached to the electron microscopy instrument. It can provide both qualitative and quantitative chemical information about the analyzed sample. When the electron beam interacts with the sample, electrons can be knocked out from an inner shell, and X-rays will be generated when the excited atom go back to its stable state. Each element atoms have characteristic X-rays which can be used for chemical composition analysis.

6.4.6 Atomic force microscopy

Electron microscopy can easily generate two dimensional images of a sample surface, but atomic force microscopy (AFM) can provide 3D profile of the surface down to the nanoscale by measuring the force between a sharp probe tip and the sample surface. The tip is placed on a flexible cantilever and the tip gently touches the surface and the force between the tip and sample surface can then be recorded. At very small tip-sample distance, e.g. a few angstroms, repulsive Van der Waals force between the tip and the sample atoms are predominant, the tip and sample are considered to be “in contact”. As the tip moves further away from the surface, attractive Van der Waals force is dominant and the probe will be in a non-contact mode. Usual-
ly the AFM is operated in tapping mode where the tip is oscillated at the resonance frequency and the amplitude of the oscillation is kept constant.

Roughness is one of the important parameters of material surface and it quantifies the average height of the surface features. The root mean square (r.m.s.) surface roughness which is defined as the average r.m.s. deviation from the average surface height is commonly used for describing the surface roughness.

6.4.7 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a widely used tool for investigating the sample surface composition. It can provide information about elemental composition, chemical state of the elements and depth-distribution of chemical species. When an incident X-ray photon hits the sample surface and transfers the energy to a core-level electron, which in turn will be emitted from its initial state with a kinetic energy. The energy and intensity of the ejected photoelectron are then analyzed. XPS spectral lines are identified by the shell from which the electron was ejected. The film surfaces were analyzed using a Physical Systems Quantum 2000 spectrometer with monochromatic Al Kα radiation.

For vanadium oxides, an XPS study of V₂O₅, VO₂, V₂O₃ and VO standards (which were purchased from Alfa Aesar with purity ≥ 99% and packed under argon) [149] showed that all the standards in their as-received states are covered by a layer of vanadium pentoxide V₂O₅ with characteristic peak position at 517 eV regardless of the high chemical purity and storage under argon. Some studies stated that the oxidized surface (vanadium pentoxide) can be removed carefully by argon etching [150]. However, it was found out the argon etching leads to the formation of a mixture of oxidation states. Therefore, in the case of vanadium oxides, the surface can only be analyzed approximately. It is noted that many studies using binding energy of adventitious carbon as energy scale calibration of the XPS instrument. However, in the case of vanadium oxides, the best energy reference is the binding energy (BE) of oxygen O1s level at 530.0 eV because it is not dependent on the valence state of the vanadium in the vanadium oxides [151].

6.5 Accelerated aging tests

From a practical perspective, coatings for spectrally selective windows should have a long-term durability. The most accurate way to test the durability of the coating is to expose the sample to the natural working conditions for very long time, but it is very time consuming and not a viable method to obtain satisfactory results. Instead, many different accelerated aging procedures have been proposed in order to predict and evaluate the stability of
window coatings which are utilized under ambient conditions. Aging tests at elevated temperatures is utilized to bring the aging time scale into practical regime. Hence, the accelerated aging tests are inexpensive and timesaving. The material of the thin coating has to withstand accelerated aging tests in order to be successfully used for practical applications.

One of the critical point of the thermochromic VO\textsubscript{2} coating is that the structure of VO\textsubscript{2} is not permanent with time. From the equilibrium phase diagram of the V-O\textsubscript{2} system, VO\textsubscript{2} is expected to transform to the thermodynamically stable oxide V\textsubscript{2}O\textsubscript{5} ultimately. High temperature and air humidity can cause the coating to be damaged. In this study, thermochromic VO\textsubscript{2} film samples were tested according to two accelerated aging procedures: the accelerated high temperature tests in a Quartz horizontal tube furnace and the accelerated climate aging tests in a climate chamber. The degradation of the coatings was monitored by optical transmission measurements.

Two important goals of the accelerated aging tests are first, predicting the lifetime of the thermochromic VO\textsubscript{2} under various environmental conditions and second, exploiting coatings capable of maintaining the thermochromic state of the VO\textsubscript{2} materials.

6.5.1 Tube furnace

The high temperature aging tests were carried out in a conventional horizontal tube furnace (Heraeus D-6450). A 40-mm-diameter quartz tube is inserted in the center of the furnace. The furnace was initially ramped up to 300 °C and the temperature was stabilized at 300 ± 5 °C, then the samples were placed in a quartz boat and transferred into the center of the furnace quickly. A circulated air flow was introduced through the oven at a flow rate of 100 sccm. The relative humidity in the oven was estimated to be below 0.1 % (referred as “dry air”) and the temperature was kept constant at 300 °C for desired time period of 1 < t\textsubscript{h} < 30 h. After the test, the samples were cooled down to room temperature in a N\textsubscript{2} gas flow atmosphere to ensure no further degradation of the samples.

6.5.2 Climate chamber

In the accelerated air-humidity aging tests, a climate chamber, type Vötsch Industrietechnik VC 4033 MH, was used. In this chamber, the relative humidity (RH) can be regulated between 10 to 95% within the temperature range of 25-90 °C. The samples were subjected to two test conditions. The temperature of the environment was set to 60 °C and the relative humidity was 95% referring to T\textsubscript{h} = 60 °C and RH = 95%, and another test conditions were T\textsubscript{h} = 80 °C and RH = 80%.
7 Results and discussion

This section summarizes the results from the appended papers in the thesis and results that have not yet been published.

7.1 Thermochromic VO₂ in V-SO₂ system

Sulfur exhibits multiple oxidation states and it has both oxidizing ability and reducing ability [152, 153]. It has been shown that it can reduce V₂O₅ as reduction agent [154]. In the work in Paper I, SO₂ is used as oxidation agent.

7.1.1 Thermodynamics in V-SO₂ system

The calculation is based on the thermodynamic rule which states that a system will be in equilibrium when the Gibbs free energy is at a minimum. A computer program EkviCalc [155] is employed which is based on minimization of total free energy of the system and the calculation of equilibrium as a function of temperature and pressure. From the given reactants, first it will identify all the possible chemical species, whether gaseous or condensed phases. And then it will calculate the possible reaction products based on the elements in the reactants.

Ideally, 1 mole V reacts with 1 mole of SO₂ according to the assumed reaction of $\text{V(s)} + \text{SO}_2(g) \rightarrow \text{VO}_2(s) + \text{S(g)}$, but practically it is very difficult to balance exactly the mole ratio between V and SO₂. Therefore, simulation with excess of SO₂ gas is employed. The amounts of reactants used in the calculations can be summarized as following: metal vanadium (solid) – 1 mole, sulfur dioxide (gaseous phase) – 2 mole.

One example of the thermodynamic calculation for the V-SO₂ system is presented in Figure 7.1. At a pressure of 0.5 atm, condensed compounds including both liquid and solid sulfur, VO₂ and V₂O₃ are formed. In particular, it indicates that formation of VO₂ can occur from temperature of 100 °C up to 410 °C. In the low temperature range, the formed sulfur in condensed state is unfavorable for the film purity, but it will be fully evaporated at temperatures above 400 °C. However, at higher temperature, V₂O₃ starts to form. Thus, there is a thermodynamically calculated reaction window for the
growth of pure VO$_2$ in the V-SO$_2$ system which lies in the temperature range of 360 to 410 °C at a system pressure of 0.5 atm as shown in Figure 7.2.

*Figure 7.1.* Amounts of stable compounds in equilibrium at different temperatures. System pressure is 0.5 atm and input reactants are 1 mole V and 2 mole SO$_2$.

*Figure 7.2.* Thermodynamic calculated yields for the formation of stable compounds. System pressure is 0.5 atm and input reactants are 1 mole V and 2 mole SO$_2$. The hatched region indicates reaction windows for VO$_2$ formation.
The phase diagram of V-O system indicates that the amount of oxygen used in the V-O system determines the phase of the vanadium oxide. Based on the chemical reaction, \( V(s) + O_2(g) \rightarrow VO_2(s) \), the molar ratio between vanadium and oxygen has to be 1:1 to precisely oxidize vanadium to \( V^{4+} \). But in reality, the precise molar ratio is difficult to reach. Therefore, the oxygen partial pressure plays a crucial role. To get close to the practical situation, excess of oxygen is input in the simulation. The amounts of reactants used in the simulations for V-O system are: metal vanadium (solid) – 1 mole, oxygen (gaseous phase) – 2 mole. The pressure was set from \( 10^{-7} \) atm to 1 atm in the temperature range of 100 – 700 °C. Same conditions are used in the simulation with \( SO_2 \).

In the V-O\(_2\) system, the thermodynamic calculated formation conditions of \( VO_2 \) are very restricted. \( VO_2 \) can be formed when temperature reaches above 600 °C and the pressure is below \( 10^{-5} \) atm as shown in Figure 7.3(b). These calculated conditions confirm the well-known fact that \( VO_2 \) formation needs high temperature and low \( O_2 \) pressure. In contrast, the thermodynamic calculated diagram of V-SO\(_2\) system indicates that the formation conditions of \( VO_2 \) are at lower temperature range from 100 to 500 °C and at a wider range of pressures from \( 10^{-6} \) to 1 atm. Thus the reaction with \( SO_2 \) proceeds at much less rigorous conditions, at lower temperature than the reaction with \( O_2 \).

![Figure 7.3. Thermodynamic calculated yields of stable VO2 in equilibrium at different temperatures and pressures (a) for V-SO2 system (input reactants are 1 mole V and 2 mole SO2); (b) for V-O2 system (input reactants are 1 mole V and 2 mole O2).](image)

### 7.1.2 Experimental synthesis of \( VO_2 \) thermochromic films in V-SO\(_2\) system

Thermal oxidation of metallic vanadium by \( SO_2 \) at different synthesis temperature (\( T_s \)) was found to form polycrystalline films. The diffraction peaks match the monoclinic \( VO_2 \) phase as shown in Figure 7.4(a). Raman spectrum of the \( VO_2 \) films shown in Figure 7.4(b) confirm that all distinguishable
peaks can be associated with VO$_2$ vibrational modes reported in the literature [156-159].

Figure 7.4. (a) XRD patterns (b) Raman spectra of the VO$_2$ films made at 600 °C and 650 °C. A reference diffractogram for the monoclinic (M1) phase of VO$_2$ according to JCPDS Card No. 00-043-1051 is also shown.

The synthesized VO$_2$ film with a thickness of 90 nm has achieved an optical transmittance switching of 54% at 2500 nm upon phase transition while maintaining an optical transmittance of 40% in the visible region. These data are comparable with other high performance VO$_2$ films prepared by magnetron sputtering [32, 160]. As illustrated in Figure 7.5, the recorded sheet resistance ($R_s$) has changed by about two orders of magnitude with temperature. The width of the heating-cooling hysteresis is determined from the derivatives of log$_{10}R_s(T)$ to be around 12 °C. The phase transition temperature is estimated to be 62 °C, lower than bulk VO$_2$ [51, 161]. SEM image shows that the film surface has a fine nanostructure composed of compact grains with 50-100 nm in diameter.
7.2 Accelerated aging tests of thermochromic VO$_2$ thin films under heating and humidity

The aging behaviors of the VO$_2$-based films were examined in different conditions in Paper II. For all samples, the bottom layers are 80 nm thick VO$_2$; the difference lies in the thickness of the coated alumina on top.

7.2.1 Aging tests in dry air

The uncoated VO$_2$ film degraded rapidly at 300 °C in dry air and no trace of thermochromic switching is shown after a short time of 1 hour. The transmittance of uncoated film is shown in Figure 7.6.

VO$_2$ samples coated with aluminum oxide were subjected to analogous conditions at 300 °C in dry air, but the results are very different. The VO$_2$ films with top coatings have no significant change in transmittance even after aging treatment of 30 hours as shown in Figure 7.7. Clearly the aluminum oxide thin coating prevents degradation of the thermochromism of the underlying VO$_2$. It is evident that a thicker aluminum oxide layer gives better protection whereas the sample with a thinner top coating started to
undergo minor changes in the transmittance for an aging duration time $t_h = 30$ h.

*Figure 7.6.* Transmittance for a VO$_2$ film before and after heating at 300 °C in dry air for one hour.

*Figure 7.7.* Transmittance for VO$_2$ films coated with 10 nm (panels a and b) and 30 nm (panels c and d) of Al oxide top layer, in as-deposited state and after heating at 300 °C in dry air for the shown durations $t_h$. 
7.2.2 Aging tests in humid air

The aging behavior of the VO$_2$-based films was also tested in climate chamber at an aging test temperature $T_h = 60$ °C and RH = 95% as shown in Figure 7.8 and Figure 7.9. For a bare VO$_2$ film, noticeable changes of transmittance have occurred already at $t_h = 24$ h and prolonged heat-treatment further destroyed the thermochromism, which was basically vanished at $t_h = 120$ h. A 10-nm-thick aluminum oxide coating preserves thermochromic properties up to $t_h = 72$ h and a thicker 30-nm-thick aluminum oxide preserves the thermochromic performance to $t_h = 120$ h.

*Figure 7.8.* Transmittance for VO$_2$ films in as-deposited state and after treating at 60 °C with a relative humidity of 95% in a climate chamber for the shown durations $t_h$. 

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Furthermore, analogous tests were performed for a longer time at \( t_h = 80^\circ C \) and RH = 80%. The thermochromism of the VO\(_2\) films with 10 and 30-nm-thick aluminum oxide is almost gone after treatment for one week.

### 7.3 Growth of vanadium oxides on different substrates

It has been reported for many years that the substrates have strong influence for the thermochromic and electrical transport properties of VO\(_2\) films. Different substrates possess tensile or compressive strain on the VO\(_2\) lattice causing a shift of phase transition temperature \([29, 162, 163]\). Furthermore, by varying the surface roughness of the substrate, the transition temperature and the abruptness of the phase transition can also be changed \([97]\). Therefore, the nature of the substrates is of importance to tune the thermochromic properties.

In Paper III, depositions of vanadium oxides on different substrates, ITO coated glass, SnO\(_2\) coated glass and bare glass, were investigated.
The most crucial factor to fabricate thermochromic VO₂ film is precise control of the oxygen amount. Therefore, the oxygen/argon ratio was optimized to obtain VO₂ films with high thermochromic performance. As shown in Figure 7.10, the near-infrared transmittance modulation at 2500 nm of the films varies with different oxygen/argon flow ratios at a fixed target power density of 8.58 W/cm². Deposited films at an oxygen/argon ratio of 5.3% or 6.7% on SnO₂-glass and bare glass do not show optical transmittance modulation. These observations accord with the well-known fact that VO₂ can only be deposited in a very narrow oxygen range. In contrast, the films deposited on ITO-glass show transmittance modulation even under the aforementioned non-optimal conditions.

Diffraction patterns from XRD confirmed the dependence between the optical modulation and the crystallography. Oxygen/argon flow ratio of 5.6% is the optimal for thermochromic VO₂ film fabrication. At this optimal oxygen/argon ratio, diffraction peaks of monoclinic VO₂ were seen for all the films deposited on different substrates. But at lower oxygen/argon ratio of 5.3% or at higher oxygen/argon ratio of 6.7%, monoclinic VO₂ diffraction patterns were observed most intensely from the films on ITO-glass substrates, and very little feature of VO₂ were seen from the films on SnO₂-glass and bare glass substrates.

![Figure 7.10. Transmittance modulation of the deposited films using different oxygen/argon ratio Γ on substrates of ITO/glass, SnO₂/glass, and bare glass at wavelength of 2500 nm.](image)

At optimized oxygen/argon flow ratio of 5.6%, the optical transmittance of the vanadium oxide films deposited on three different substrates is shown in Figure 7.11. All samples have similar thickness of 60 nm and were found to
have good thermochromic performances. The transmittance modulation between the insulating and metallic states at wavelength of 2500 nm are 64%, 37%, and 49% for vanadium oxide films deposited on ITO-glass, SnO$_2$-glass and bare glass, respectively. It is noticed that ITO as a transparent conductor with low transmission in the infrared range partly mask the transition of VO$_2$ in this region. However, the near-infrared transmittance of film deposited on ITO still has highest contrast among the films on different substrates.
Figure 7.11. Transmittance spectra of vanadium oxide films deposited at an oxygen/argon ratio $\Gamma = 5.6\%$ on (a) ITO/glass substrate; (b) SnO$_2$/glass substrate; (c) bare glass substrate below and above the phase transition temperature. Transmittance of bare substrates is also shown in the figures.
From SEM images in Figure 7.12(a) to (c), the vanadium oxide films deposited on all three different substrates at oxygen/argon flow ratio of 5.6% are composed of closely packed grains with typical size of 80–100 nm. It is noted that surface roughness values for the bare substrates are different, the root mean square roughness ($R_{\text{rms}}$) is found to be 1.2, 1.9 and 1.5 nm for ITO-glass, SnO$_2$-glass and bare glass. Therefore, it is assumed that higher initial roughness of the substrate results in higher deposited film roughness. The deposited films on ITO-glass and bare glass have $R_{\text{rms}}$ around 4.0 nm as compared with slightly higher $R_{\text{rms}}$ of 4.7 nm for the film on SnO$_2$-glass.

However, the substrates show an essential influence on the morphologies of the films at an elevated oxygen/argon ratio of 5.9%. As illustrated in Figure 7.12(d) to (f), vanadium oxide deposited on ITO-coated glass possesses micrometer-sized irregular nanoparticles with clear evidence of interspace, whereas vanadium oxide deposited on SnO$_2$-coated glass and bare glass have denser microstructures with rod-like particulates. The deposited film on ITO-glass has larger $R_{\text{rms}}$ of 40 nm, whereas $R_{\text{rms}}$ values are 33 and 29 nm for the film on SnO$_2$-glass and bare glass. Clearly, the vanadium oxide films deposited on ITO look very different and were much more granular compared to the films on SnO$_2$-glass or bare glass under the oxygen rich deposition conditions.

$$\Gamma = 5.6\%$$

a) VO$_2$/ITO/glass  
b) VO$_2$/SnO$_2$/glass  
c) VO$_2$/glass 

$$\Gamma = 5.9\%$$

d) VO$_2$/ITO/glass  
e) VO$_2$/SnO$_2$/glass  
f) VO$_2$/glass 

*Figure 7.12. SEM images for films deposited at oxygen/argon ratios (a-c) $\Gamma=5.6\%$ and (d-f) $\Gamma=5.9\%$ on substrates of ITO/glass, SnO$_2$/glass, and bare glass.*
7.4 Bilayer coating of TiO2 /VO2

One encountered problem for realization of VO2 based thermochromic window is that the visible transmittance is too low. It originates from the strong absorptions in the short-wavelength range for both the metallic and semiconducting states [123, 164].

Antireflection (AR) coatings using a material with a high refractive index is an effective way to enhance the transmittance in the visible region. Such coatings either suppress the reflectance or shift the transmittance peak towards shorter wavelengths. Theoretical study showed that the luminous transmittance can be substantially increased by use of AR coatings which has a high refractive index with suitable thickness on top of VO2 [17]. Among a variety of widely used AR materials, titanium dioxide (TiO2) with refractive index of 2.4 is a most suitable candidate. In addition, TiO2 is a well-known photocatalyst for its excellent photocatalytic degradation ability of organic pollutants. Numerous studies have succeeded in the combination of these two materials of VO2 and TiO2 which could generate multifunctional smart window coatings [165-167].

Generally, luminous transmittance increase with decreasing film thickness due to reduced absorption at the expense of lowered infrared optical switching in VO2. Therefore, a suitable thickness around 50 nm for the VO2 layer was chosen. An earlier optical calculation showed that the luminous transmittance value of 50 nm thick VO2 coated with TO2 exhibits a wave-like change with increasing thickness of TiO2 due to the interference effect [166]. Thus, the thickness of TiO2 antireflection layer is less stringent to obtain good optical properties.

Single layer of VO2, single layer of TiO2 and double layer of TiO2/VO2 deposited on glass substrate by magnetron sputtering were studied in Paper IV. The XRD diffraction pattern and Raman spectra in Figure 7.13 show that VO2 thin film was phase pure monoclinic structure and TiO2 thin film was phase pure anatase structure. For the double layer film of TiO2/VO2, where similar deposition parameters were used, diffraction peaks of monoclinic VO2, anatase TiO2 and additional peaks of rutile TiO2 were detected. The presence of trace amount of rutile TiO2 is not surprising. As the deposition of anatase TiO2 is conducted at a temperature which is above the critical temperature of VO2, it is certain that the monoclinic VO2 has transformed to high temperature rutile structure. The lattice constants of rutile TiO2 and rutile VO2 are rather similar, thus it is expected that a thin layer of rutile TiO2 is formed on top of VO2 layer.
Figure 7.13. (a) XRD patterns and (b) Raman spectra for VO$_2$ film, TiO$_2$ film and TiO$_2$/VO$_2$ film.

Optical characteristics of the films are shown in Figure 7.14. It is obvious that the visible transmittance has been increased by a top layer of TiO$_2$ coating comparing to the transmittance spectra of single layer VO$_2$ film. Although the thick TiO$_2$ layer causes interference in the film, the reflectance in the visible range is partly suppressed. It is noteworthy that absorptance of the TiO$_2$ film is almost negligible except the strong absorptance in the ultraviolet wavelength range. It is seen that the absorptance in the TiO$_2$/VO$_2$ bilayer is much bigger than the single layer TiO$_2$ film which will be important for the photocatalytic properties of the films.

The luminous transmittance of TiO$_2$/VO$_2$ film changes very little below and above critical temperature which demonstrates almost no change in transparency and color to the human eye upon switching. The solar transmittance modulation is increased from 4.3% to 8.8% using the TiO$_2$ coating.
Figure 7.14. (a) Transmittance (b) Reflectance of VO\textsubscript{2} film and TiO\textsubscript{2}/VO\textsubscript{2} bilayer film (c) Absorptance of VO\textsubscript{2} film(53 nm thickness), TiO\textsubscript{2} film(297 nm thickness) and TiO\textsubscript{2}/VO\textsubscript{2} bilayer film(297 nm /53 nm thickness).
The single layer TiO₂ sample and bilayer VO₂/TiO₂ sample were subjected to photocatalytic measurements under two illumination conditions, mimicking the AM 1.5 solar irradiation and enhanced NIR irradiation. Although the thickness of TiO₂ is not optimum for AR purpose, porous and thick TiO₂ are beneficial for high photocatalytic activity.

The photocatalytic properties were evaluated by decomposition of stearic acid on the film surface. The decomposition rate of stearic acid is visualized by the decreased intensity of the C-H group vibration bands with illumination time as shown in Figure 7.15. Under both illumination conditions, it is obvious that the degradation rate by the TiO₂/VO₂ bilayer sample is much faster comparing to the single TiO₂ layer sample. The big difference in degradation rates can be attributed to temperature rise by optical absorption on the TiO₂ films. As noted previously in the optical data, the TiO₂ single layer film barely has absorption except at the shortest wavelength, while the TiO₂/VO₂ bilayer sample has much larger absorption mainly owing to the underlying VO₂ layer. Although TiO₂ layer in these two samples has similar thickness, the bottom VO₂ layer plays an important role in the enhancement of photocatalytic properties in the VO₂/TiO₂ bilayer sample. The detailed photocatalytic measurements are referred to the appended Paper IV.

![Figure 7.15. Absorbance of stearic acid layers for (a) TiO₂ film (b) TiO₂/VO₂ film under mimicking the AM 1.5 solar irradiation; (c) TiO₂ film (d) TiO₂/VO₂ film under enhanced NIR irradiation at different irradiation time points.](image)
7.5 Light scattering from VO\textsubscript{2} films

Many researches have been focused on the enhancement of the optical thermochromic performance of VO\textsubscript{2} films, for instance, to improve the solar energy modulation ability and the luminous transmittance. However, most of the studies investigate the material-light interaction with regard to transmittance, absorption and reflection, and only a few studies have considered the scattering effect between the material and the light [168]. Therefore, a loss of energy associated with scattering has been ignored. The intensity of the light scattering is related to the particle size and refractive index of the particle. In general, if the size of the particle is comparable to the wavelength of the incident radiation, the scattering contribution to the spectral transmittance and reflectance are non-negligible. The Lorenz-Mie theory is employed in Paper V to study the scattering effect of light in the VO\textsubscript{2} films.

From our previous study in Paper III, we know that the ITO substrate promotes the growth of thermochromic vanadium dioxide and can induce a particulate film under certain conditions. It was observed that the deposition of particulate film occurred at oxygen-rich conditions. On the other hand, excessive oxygen/argon ratio will lead to oxygen-rich vanadium oxides which are unfavorable for the thermochromic performance of the films. Therefore, an oxygen/argon flow ratio value of 5.9\% was chosen for deposition of particulate thermochromic films.

It can be observed from SEM in Figure 7.16 that the film consists of polycrystalline grain islands on the order of sub-micrometers in size and there are interspaces among the grain islands which typically are several tens of nanometers to sub-micrometers.

![SEM image of VO\textsubscript{2} film on ITO substrate.](image-url)

Figure 7.16. SEM image of VO\textsubscript{2} film on ITO substrate.
Therefore, the optical transmittance of samples should primarily be attributed to light transmittance from both directly transmitted light and light that is scattered by the VO\textsubscript{2} particles in the forward direction. From the measured diffuse transmittance and diffuse reflectance spectra shown in Figure 7.17, it is confirmed that the film exhibits significant scattering effects, especially in the visible range. The specular reflectance of the film is small, lying consistently below 10\%, whereas the diffuse reflectance of the film is obviously larger. The diffuse reflectance of the film is in general above 10\%, except in the semiconducting state where the film exhibits a diffuse reflectance less than 10\% in the wavelength range longer than 1500 nm.

![Figure 7.17](image)

*Figure 7.17. (a) Total transmittance and reflectance (b) diffuse transmittance and reflectance (c) specular transmittance and reflectance of the particulate VO\textsubscript{2} film in the low temperature semiconducting state and high temperature metallic state.*

A simple modeling of optical cross-sections for a single VO\textsubscript{2} sphere was carried out using Lorenz–Mie theory. Specifically, spectral scattering cross sections $C_{sca}$ were calculated using a computer code from Bohren and Huffman [169]. The complex refractive index of the VO\textsubscript{2} particles were from Mlyuka et al. [170] and the refractive index of surrounding medium of air was set to 1. Particle size radius ranging from 70 nm to 500 nm was used.

The computed spectral scattering cross sections per unit volume ($C_{sca}^{*} = C_{sca} / V_p$) are shown in figure 7.18. It can be seen how the magnitude of $C_{sca}^{*}$
varies with different values of the particle size of VO₂ in the semiconducting state and metallic state, respectively. It is noted that in the infrared wavelength region (λ>700nm) the scattering was dominated by the large particles with radius bigger than 200 nm, while in the visible wavelength region (400 ~700 nm) the scattering was dominated by the particles with radius smaller than 200 nm. Especially, dramatic modulation of the scattered light in the wavelength range between 500 ~1000 nm can be managed by the VO₂ particles with radius ≲200 nm.

Figure 7.18. Spectral scattering cross-section per unit volume calculated from Lorenz–Mie theory for VO₂ spheres of different radii (a) in semiconducting state (b) in metallic state.

The experimental specular and diffuse transmittance and reflectance were converted to extinction coefficient, absorption coefficient and scattering coefficient, respectively. Comparison with theory is referring to the appended Paper V for details.

7.6 Nanocomposite VO₂ based films
7.6.1 Simulated optical properties of VO₂ inclusions in a dielectric matrix

The properties of continuous VO₂ thin films have been extensively studied, but it has been difficult to realize high solar energy modulation and high luminous transmittance simultaneously. However, nanoscaled VO₂ material has dramatically changed the situation to accomplish practical thermochromic glazings. The incorporation of plasmonic VO₂ nanoparticles into dielectric host could significantly enhance the solar energy transmittance modulation and could also be combined with higher luminous transmittance [171].

Based on above facts, optical performance for a composite layer with a dilute VO₂ suspension in a dielectric matrix backed with a glass substrate was simulated based on the Maxwell-Garnett effective medium theory as
described in section 5.3. The detailed method used to calculate optical transmittance is described in section 5.4. The dielectric matrix is assumed to have similar optical properties as glass and the substrate underneath is also glass-like material. Therefore, the dielectric function of the dielectric matrix and the substrate are set to be 2.25. The optical constants of VO$_2$ used in the simulation were experimentally determined by Mlyuka et al. [170] and the particles were assumed to be randomly oriented. The parameters varied in the simulation include the filling factor $f$, the thickness of the layer $d$ and the aspect ratio $m$ of the individual VO$_2$ particle.

First, computed spectral transmittance of continuous VO$_2$ films of different thickness from 10 nm to 100 nm both in semiconducting phase and metallic phase is shown in Figure 7.19. It indicates that the thermochromic properties are strongly related to the film thickness. The transmittance of the VO$_2$ film varies as a function of thickness. In the infrared range, a thinner film has a higher transmittance in the semiconducting state and also has a relatively higher transmittance in the metallic state. On the contrary, a thicker film is more efficient to block the NIR in the metallic state at the cost of lower transmittance in the semiconducting state. The biggest modulation of transmittance occurs at wavelength of 2500 nm.

![Figure 7.19. Simulated spectral transmittance for continuous VO$_2$ films with different thickness $d$ (a) in the semiconducting state and (b) in the metallic state](image)

For a composite film layer with a thickness of 2000 nm, volume fraction $f$ of VO$_2$ particles in the dielectric matrix is varied between 0.01 and 0.05 which corresponding to continuous VO$_2$ films containing equivalent amount VO$_2$ material with thickness between 20 nm and 100 nm. The simulated spectral transmittance is shown in Figure 7.20. In the semiconducting phase, the visible transmittance is quite high, exceeds 60 %. In the metallic phase, the pronounced localized plasmon resonance of VO$_2$ particles has shifted the absorption to shorter wavelength in the near infrared range where the solar intensity is higher. Hence the modulation of solar transmittance throughput has dramatically improved.
Figure 7.20. Simulated spectral transmittance for a layer with a dilute VO$_2$ particle suspension dispersed in a dielectric medium with different filling factors $f$ and film thickness $d=2000$ nm, (a) in the semiconducting state and (b) in the metallic state.

Similarly, transmittance of a film layer of 200 nm thickness with larger volume fractions between 0.10 and 0.15 which can be comparable with continuous VO$_2$ films with thickness between 20 nm and 30 nm were evaluated as shown in Figure 7.21. The shape of the transmittance spectra is quite similar for both the semiconducting and the metallic states as the amount of VO$_2$ material contents are varied very little, although the transmittance variations are a bit bigger in the metallic state.

Figure 7.21. Simulated spectral transmittance for a layer with a dilute VO$_2$ particle suspension dispersed in a dielectric medium with different filling factors $f$ and film thickness $d=200$ nm, (a) in the semiconducting state and (b) in the metallic state.

The transmittance for a layer with randomly oriented VO$_2$ particles in the metallic state with different shapes, referring to aspect ratio $m$ is shown in Figure 7.22. It is noted that spherical VO$_2$ particles ($m=1$) has highest transmittance in the visible range and highest modulation in the NIR range.
Figure 7.22. Simulated spectral transmittance for a layer with a randomly oriented VO$_2$ particle suspension dispersed in a dielectric medium with different aspect ratio $m$ and layer thickness $d=500$ nm and filling factor $f=0.1$ in the metallic state

7.6.2 VO$_2$-SiO$_2$ composite film

The VO$_2$-SiO$_2$ composite film consists of isolated grain islands with typical size of 100-300 nm which are nearly spherical and uniformly distributed as illustrated in Figure 7.23.

Figure 7.23. SEM image of VO$_2$-SiO$_2$ composite film
The elemental distributions of Si, O and V of the VO$_2$-SiO$_2$ composite film were detected by EDX and shown in Figure 7.24. It is evident that the round particles mainly consist of the vanadium element, while the regions between the particles contain much less or is vanadium free. The silicon and oxygen elements are well-dispersed over the entire area.

![Figure 7.24.](image)

*Figure 7.24. (a) SEM photograph of VO$_2$-SiO$_2$ nanocomposite, EDX elemental mapping of (b) vanadium (V), (c)silicon (Si), (d) oxygen (O) corresponding to (a).*

The VO$_2$-SiO$_2$ composite film is consistent with crystalline monoclinic VO$_2$(M) phase from XRD analysis. Due to the very poor crystallinity of SiO$_2$ formed at temperature of 450 °C, a broad diffraction background can be assigned to the SiO$_2$ component and the glass substrate. From the high-resolution XPS spectra of a continuous VO$_2$ film and the VO$_2$-SiO$_2$ composite film in Figure 7.25, the peak at a binding energy (BE) of 105.5 eV signals the presence of SiO$_2$ on the surface of the composite film. The O 1s peak has a shoulder towards low BE and was deconvoluted into two peaks, one is attributed to silicon oxide while the other arises from vanadium oxide; expectedly, the contribution due to vanadium oxide is much smaller. It is noted that at the surface, the binding energy of the V 2p$_{3/2}$ peak, is centered at 517 eV, referring to V$_2$O$_5$ phase. It is expected due to natural aging of VO$_2$. Oxygen from the atmosphere would drive the VO$_2$ material towards the most stable vanadium oxide of V$_2$O$_5$. The presence of vanadium (V) is commonly reported for VO$_2$ samples on the surface [149, 172].
Figure 7.25. XPS core level spectra of (a) V2p and O1s and (b) Si2p for a continuous VO2 film and their curve fittings; (c) V2p and O1s and (d) Si2p for a VO2–SiO2 composite film and their curve fittings.

The optical spectra of the SiO2-VO2 composite film recorded below and above the transition temperature are shown in Figure 7.26. It is clearly visualized that SiO2-VO2 composite film have distinct transmittance contrast in the wavelength range of 700~2000 nm which is very different from pure VO2 film which exhibits the largest transmittance contrast at 2500 nm. The transmittance dip at 1220 nm corresponds to localized surface plasmon resonance (LSPR) wavelength of individual VO2 nanoparticles. Of more interest is that the visible transmittance remains high in both metallic and semiconducting phases. Therefore, the existence of SiO2 as the dielectric environment adjacent to the spherical VO2 grains can be favorable to obtain high NIR switching efficiency and high visible transmittance simultaneously which agree with the optical simulation.
7.7 VO₂ nanoparticles

Hydrolysis of vanadium isopropoxide in a mixture solution of pyridine and acetone leads to the reaction solution turning into cloudy orange color immediately which indicates that amorphous V₂O₅-based colloidal particles (VOPs) are formed. The resulting particles have a composition of V₂O₅∙xPy∙yH₂O where pyridine and water molecules are intercalated between the V₂O₅ layers [146]. The amorphous particles were subsequently heat treated to produce crystalline structures as illustrated in a flow chart in Figure 7.27 where t₁ denotes time period in hydrogen atmosphere, t₂ denotes time period in argon atmosphere and t₃ denotes time period in nitrogen atmosphere. The first thermal treatment was performed in hydrogen. It is important that pure hydrogen gas was used in order to preserve the original shape of the VOPs. Annealing in a mixed flow gas of H₂(10%)/Ar(90%) will cause losing the spherical shape [173]. During the thermal treatment in hydrogen, the hydrogen molecules react with the VOPs to form lower oxidation state vanadium oxides and the water and pyridine molecules intercalated between the V₂O₅ layers were removed along with the simultaneous V₂O₅ reduction reaction. A temperature ≥370 °C is required to remove organic components from the samples [174]. Here we employed a rapid heating treatment: when the furnace temperature reaches the desired temperature, the furnace is slid to the center of the sample tube in order to control the reaction time more precisely.

![Figure 7.27. The flow chart of synthesis route of VO₂(M).](image)
From XRD in Figure 7.28, no clear diffraction peak can be seen for the as-obtained VOP precursor which suggests the formation is amorphous. For a very short reaction time of $t_1=0.1\ h$ in hydrogen, the amorphous precursor crystallized and the diffraction peaks can be assigned to monoclinic VO$_2$(B) phase (Sample A). However, for sample which was thermal treated for longer time at $t_1=0.5\ h$, diffraction pattern corresponding to V$_2$O$_3$ was observed suggesting that the sample was significantly reduced from the original V$^{5+}$ state to V$^{3+}$ state (Sample B). Sample A and sample B were then converted into desired VO$_2$(M) by additional heat treatment.

Conversion of the metastable VO$_2$(B) phase to the more stable and thermochromic VO$_2$(M) phase was realized by annealing under inert argon atmosphere at 450 °C. The argon environment was used due to the instability of VO$_2$ under oxidizing conditions. The diffraction patterns indicate that after 4h treatment at 450 °C under Ar, the VO$_2$(B) phase is completely transformed into the VO$_2$(M) phase (sample A-2).

The resulting V$_2$O$_3$ particles (sample B) were heated in a nitrogen atmosphere at the temperature of 450 °C. After annealing under N$_2$ flow for 2 h at 450°C, VO$_2$(M) is produced due to the re-oxidation of particles by the trace amount of O$_2$ present in the gas flow, the diffraction pattern of sample B-2 is in match with the lattice structure of VO$_2$(M).

Structural transitions between oxides in the V$_2$O$_5$-V$_2$O$_3$ system are complex and the governing mechanism is not well understood at present due to the large span of the available vanadium oxidation states and many intermediate oxides.

**Figure 7.28.** The corresponding XRD patterns of the samples at different stages: (a) precursor VOP, sample A and sample A-2; (b) precursor VOP, sample B and sample B-2.

The SEM micrographs of the vanadium oxide samples at different stages are summarized in Figure 7.29. The as-synthesized VOP precursor has smooth uniform surfaces with spherical shape with dimension of 100 to 200 nm shown in Figure 7.29(a). When the VOPs have been subjected to calcination at 450 °C in hydrogen, the smooth surface becomes coarse, as shown in Fig-
Figure 7.29(b) for sample A and (d) for sample B, which is attributed to the removal of residue pyridine and water molecules from the particles. Further additional annealing process in a nitrogen atmosphere at 450°C, the powders (sample B-2) exhibit a slightly deformed spherical shape as shown in Figure 7.29(e). For the sample obtained after heat treatment for total time of 4 h in argon (sample A-2), the spherical structure has almost disappeared and the particles tend to form large agglomerates as illustrated in Figure 7.29(c). The coalescence of the particles is due to the prolonged annealing at high temperature.

Figure 7.29. SEM images of (a) VOP; (b) sample A; (c) sample A-2; (d) sample B and (e) sample B-2.
Bulk VO₂ sample or VO₂ continuous films have largest optical difference in the NIR around wavelength of 2500 nm where the solar irradiance intensity is low, but VO₂ particles can exhibit unique resonance due to the electronic confinement. For a single spherical VO₂ particle, the localized surface plasmon resonance occurs at a wavelength around 1300 nm as mentioned previously. This plasmon resonance in the nanoparticle will affect the optical properties in two ways. Firstly there will be absorption band in the metallic state located around 1300 nm giving rise to an increased solar transmittance modulation. Secondly the transmittance in the visible range will be enhanced both for the semiconducting state and the metallic state compared to a conventional VO₂ film. The strength of the plasmon resonance depends on the microstructure of the nanoparticles. In order to utilize the improved optical properties benefited from the plasmon resonance, the VO₂ nanoparticles have to be dispersed uniformly on a substrate. Thus incorporation of the VO₂ nanoparticles in a host matrix is necessary. Moreover, the use of a host matrix can also act as a protective barrier for the VO₂ nanoparticles as the thermochromic VO₂ phase is thermodynamic instable and will be converted naturally into non-thermochromic V₃O₅ species. PVP is an optimum polymer matrix as it prevents agglomeration of the VO₂ particles and prohibits deactivation of VO₂ due to oxidation [175].

Depending on the refractive index of the host matrix the plasmon resonance frequency can be slightly tuned. Extinction efficiency for spherical VO₂(\(R\)) nanoparticles ranging in diameter (2\(a\)) from 20 to 220 nm in air (refractive index=1.0) and in a PVP matrix (refractive index≈1.5) [176] were obtained by employing the Mie scattering calculation [177]. The optical constants of VO₂ used are from Mlyuka et al. [170]. The evolution of the resonance as function of the VO₂ particle size is presented in Figure 7.30. It is clearly shown that plasmon resonance peak is red shifted with increasing particle size. The plasmon resonance frequency also shifts towards longer wavelength range for a host matrix with a larger refractive index (PVP) as shown in Figure 7.30(b).
Thin films were made by mixing PVP and a small proportion of VO$_2$ powder. Films involved different VO$_2$(M) samples (sample A-2 and sample B-2) with a similar thickness (~10 µm) were examined over a significant temperature range. As shown in Figure 7.31(a), the film containing sample A-2 exhibits a maximum modulation of transmittance around the wavelength of 2500 nm with 64% and 43% transmittance below and above the transition temperature, respectively. It is clear that the samples of A-2 and B-2 are composed of pure VO$_2$(M) phase from the XRD patterns, but the microstructure are different as demonstrated in the SEM images. In fact, the grain size of the particles has big impact on the phase transition features. While for the film containing sample B-2, the transmittance spectra show different optical characteristics, in Figure 7.31(b). A transmittance dip around 1500 nm was observed in the metallic state, the transmittance then goes up in the longer wavelength range. A maximum modulation of the transmittance around the wavelength of 1500 nm attributed to localized surface plasmon resonance. In the meantime, the maximum visible transmittance remains around 60 % in both semiconducting and metallic phase. It is indicated that VO$_2$ particles are well-dispersed in PVP polymer. In addition, the diffused transmittance of both films is rather low, below 15 %, probably because the polymer film has a smooth surface and the VO$_2$ particles are far away from each other.
Figure 7.31. Optical transmittance spectra of (a) VO$_2$-PVP film with particles from sample A-2 (b) VO$_2$-PVP film with particles from sample B-2 below and above the phase transition temperature.
8 Conclusions and future work

The overall aim of this PhD project was to investigate innovative strategies to improve the performance of VO₂-based materials for thermochromic smart window applications. A number of interesting results have been obtained.

Precise control of oxygen has been a common obsession for VO₂-based material fabrication. In section 7.1, a new approach to fabricate thermochromic VO₂ films via oxidation reaction with V precursor and SO₂ gas has been successfully developed. The thermodynamic analysis, based on minimization of Gibb’s free energy, showed wider reaction window of synthesis conditions between V and SO₂ compared to VO₂ growth conditions in O₂ environment. The thermodynamic prediction was verified experimentally at higher-than-expected synthesis temperatures as the reaction is also governed by kinetic factors. It is believed that under the guidance of the preliminary results, new avenues are opened to do more. For instance, by introducing the SO₂ gas into the sputtering system, direct deposition of VO₂ films will be overwhelmingly likely fulfilled without the stringent process control of oxygen. Furthermore, seeking for a suitable catalyst might accelerate the reaction rate and achieve lower synthesis temperature as in the Haber process for the manufacture of ammonia.

From the perspective of practical implementation, the desirable properties of VO₂ should be maintained for long time. In section 7.2, accelerated aging tests have revealed that by providing a thin top coating of durable and transparent aluminum oxide could prevent oxidation of the underlying VO₂ films both under high temperature dry and humid conditions. The results demonstrate the importance of protective layers for thermochromic coatings and this feature can be extended to other window-related applications as well.

It has been known for a long time that the substrates have big influence for the film growth. In section 7.3, considerable efforts have been made and it has been shown that the substrates have essential influence on the morphologies of the VO₂ films. Furthermore, the study found that thermochromic VO₂ can be deposited in a wider oxygen partial pressure range on ITO-glass substrate compared to SnO₂-glass substrate and bare glass substrate.

In section 7.4, by use of a bilayer system of VO₂/TiO₂, the optical and thermochromic properties of the VO₂ film were improved. In addition, the light absorbed by the VO₂ layer enhanced the photocatalytic properties of
Therefore, TiO$_2$ top-coating is not only increasing the optical performance of the VO$_2$ film but also leading to multifunctional performance of the coating.

Furthermore, scattering of transmitted light is of importance for window coating applications. In section 7.5, from optical measurements of VO$_2$ film deposited on ITO substrate, it is confirmed that the particulate VO$_2$ film exhibit significant scattering effects, especially in the visible range.

In section 7.6, the incorporation of plasmonic VO$_2$ nanoparticles into a dielectric matrix of SiO$_2$ was studied. It shows that composite film of VO$_2$-SiO$_2$ could change the optical performance in comparison with conventional continuous VO$_2$ films which is beneficial for solar transmittance modulation and luminous transmittance.

Sometimes, VO$_2$ in the form of dense films limits the use, for instance, on mechanically flexible substrates. In section 7.7, solution dispersible VO$_2$ particles were synthesized by hydrolysis and subsequent annealing process. Optical properties were of primary interest in this study, thus VO$_2$ particles were involved in PVP in order to facilitate the optical measurement. The optical measurements of the polymeric films show good thermochromic behavior which has the potential to achieve flexible smart window films. One possible extension of the work presented here may involve VO$_2$ particles into electrolyte to achieve multifunctional electrolyte which is potentially useful in many applications. A preliminary attempt was made to involve VO$_2$ particles in PEO-based electrolyte. Transmittance spectra of a VO$_2$:PEO:LiTFSI electrolyte at 25°C and 90°C are shown in Figure 8.1.

![Figure 8.1. Optical transmittance spectra for a suspension of VO$_2$ particles in PEO-based LiTFSI electrolyte at 25°C and 90°C.](image-url)
Although plasmonic VO$_2$-SiO$_2$ thermochromic film with improved luminous properties has been made experimentally, the experimental parameters of repeatability and reproducibility are still under study. Direct fabrication of VO$_2$-SiO$_2$ composite film by magnetron sputtering is cumbersome and challenging. Many trials have been made to deposit composite VO$_2$-SiO$_2$ films; however, most of them are without plasmonic effect. Those composite films also have separated grains but exhibit optical properties similar to those of conventional continuous VO$_2$ films as illustrated in Figure 8.2. On the other hand, these composite films own good anti-oxidation ability. After two years storage in ambient environment, the optical properties almost did not change.

![Figure 8.2](image)

*Figure 8.2.* (a) XRD diffraction pattern (b) transmittance spectra (c) SEM image of a composite VO$_2$-SiO$_2$ film.

Moreover, surface treatment of VO$_2$ film might be a useful way to achieve better thermochromic performance. It is widely reported that grain size and grain boundaries have influence on the MST features of VO$_2$ materials. Mild acid etching may change the morphology and size of the microstructure of VO$_2$ films. SEM images in Figure 8.3 (a)-(d) show the morphology of sputter-deposited VO$_2$ film before and after acid etching treatment for different time. The pristine film consisted of interconnected irregular big particles. After immersed in dilute nitride acid for certain time periods, it is clearly seen that the film becomes more porous and grain size diminishes which can be attributed to the dissolution of VO$_2$ by nitric acid. After acid etching treatment, the film becomes more transparent compared with the pristine film. As shown in Figure 8.3 (f), the transmittance continuously increases.
with prolonged etching time. However, the particle sizes are still too big to exhibit the nano-plasmonic effects. As shown in Figure 8.3 (e), most of the VO$_2$ Raman bands remain and some minute peaks vanished after the acid treatment which can be ascribed to the removal of some impurities on the sample surface by the acid.

![Figure 8.3](image)

*Figure 8.3.* (a)-(d) SEM images of pristine VO$_2$ film and after etching for shown time; (e) the corresponding Raman spectra; (f) the corresponding transmittance spectra at 25°C and 90°C.

We also studied the oxidation of pure metallic vanadium film. A thin vanadium metallic film of 40 nm was fabricated by magnetron sputtering then followed by annealing posttreatment at 450 °C in the presence of little air in a vacuum oven chamber evacuated to 0.1 torr for 1.5 h. The annealing led to a dense rod shaped film shown in Figure 8.4(a). The XRD diffraction pattern in Figure 8.4(b) show the film consists of VO$_2$(M) phase and also impurities.
The film exhibits good thermochromic switching most effectively at 2500 nm as shown in Figure 8.4(c).

Smart thermochromic windows for building fenestration represent a promising green nanotechnology featuring autonomous regulation of solar heat for indoor comfort. The ideal thermochromic coating for use in the building block to cut down the energy consumption would be capable of high visible transmittance, high infrared modulation and could be processed on any type of substrate. In general terms, most of the studies in this PhD project have been proposed to address aforementioned issues in order to make the thermochromic VO₂ window coating market-ready.

The ultimate aim of exploiting scientific research on VO₂ materials is to serve buildings with maximum energy efficiency. For future work, it would be interesting to integrate the thermochromic VO₂ materials into other multi-layer devices (such as electrochromic layer, solar cell layer) which may provide more fruitful multifunctional smart window coatings. Moreover, VO₂ nanoparticles embedded in other functional material matrix, for instance TiO₂, could achieve multifunction coatings with high performance. With much progress in dealing with the limitations of thermochromic VO₂-based materials, VO₂-based smart windows are likely to be realized in the near future.
Det övergripande målet med detta doktorandprojekt har varit att undersöka innovativa strategier för att förbättra prestandan hos termokroma VO₂-baserade material för användning i smarta fönster. Ett antal intressanta resultat har erhållits under projektet.

Exakt kontroll av syrehalten är en nödvändighet för tillverkning av VO₂-baserade material. I avsnitt 7.1 har en ny metod för att framställa termokroma VO₂-filmer via en oxidationsreaktion mellan metalliskt vanadium och SO₂ i gasform framgångsrikt utvecklats. Med utgångspunkt i en termodynamisk analys, baserad på minimering av Gibbs fria energi, påvisades ett större reaktionsfönster för framställning av termokroma VO₂-filmer genom oxidering av vanadium med hjälp av SO₂ jämfört med oxidationsreaktioner där O₂ används. Resultaten från den termodynamiska analysen verifierades experimentellt, vid en högre temperatur än analysen visade, beroende på att reaktionen mellan vanadium och SO₂ också regleras av kinetiska faktorar. Med ledning av dessa preliminära resultat öppnas nya möjligheter för att vidareutveckla metoden och därmed tillverkningen av VO₂-filmer. Genom att till exempel introducera SO₂ direkt under sputtringen av filmen torde det vara möjligt att tillverka VO₂-filmer utan strikt kontroll av syrehalten under deponeringsprocessen. Vidare kan man genom att hitta en lämplig katalysator påskynda reaktionshastigheten och därmed uppnå en lägre temperatur för tillverkningen av de termokroma VO₂-filmerna, på samma sätt som i Haber-processen för tillverkning av ammoniak.

En oro relaterad till VO₂-baserade material är den relativt korta livslängden av de termokroma egenskaperna beroende på att VO₂ inte är den mest termodynamiska stabila varianten av vanadiumoxid. I avsnitt 7.2 har accelererade åldringstester visat att genom att belägga VO₂-filmerna med ett tunnt lager av aluminiumoxid, vilket är både tåligt och transparent, är det möjligt att förhindra oxidation av de underliggande VO₂-filmerna. Försöken gjordes vid höga temperaturer under förhållanden med både torr och fuktig luft. Resultaten visar på vikten av att ha ett skyddande lager ovanpå termokroma beläggningar.

Det har länge varit känt att substratets egenskaper har stor inverkan på filmtilväxten. I avsnitt 7.3 har det visats att olika substrat kan ha en väsentlig inverkan på morfologin hos de tillverkade VO₂-filmerna. Vidare fann man att det är möjligt att tillverka filmer med termokrom VO₂ på ITO-belagda glas i ett större spann av olika partialtryck för syre jämfört med sub-
strat av rent glas och SnO₂ belagt glas. I avsnitt 7.4 förbättrades de optiska och termokroma egenskaperna hos VO₂-filmen genom användningen av ett dubbellager bestående av VO₂ och TiO₂. Dessutom förbättrades även de fotokatalytiska egenskaperna hos TiO₂-filmen på grund av uppvärmningen av densamma genom absorption av ljus i det underliggande VO₂ lagret. Därmed förbättrades inte bara VO₂ filmens optiska prestanda av TiO₂ beläggningen utan den leder också till multifunktionella egenskaper hos beläggningen.

För fönsterapplikationer är spridning av det transmitterade ljuset genom filmen av betydelse. I avsnitt 7.5, visas från optiska mätningar av olika VO₂-filmer belagda på ITO-substrat, att filmer med partikelformiga VO₂-beläggningar uppvisar signifikanta spridningseffekter, särskilt för ljus i det synliga området. I avsnitt 7.6 studerades inblandningen av plasmoniska VO₂ nanopartiklar i en dielektrisk matris av SiO₂. Där visades det att en kompositfilm av VO₂-SiO₂ har andra optiska egenskaper jämfört med konventionella kontinuerliga VO₂-filmer. Detta är fördelaktigt inte bara för moduleringen av solens värmestrålning genom filmen utan även för transmissionen av det synliga ljuset.

Sammantaget kan man säga att smarta termokroma fönster representerar en lovande grön nanoteknik med autonom reglering av instrålningen av solens värme i byggnader för ökad inomhuskomfort och minskad energiförbrukning. Den ideala termokroma beläggningen för användning i byggnader ska ha en hög transmittans av det synliga ljuset, stor modulering av det infraröda ljuset och kunna beläggas på vilken typ av substrat som helst. Generellt sett har de flesta studierna i detta doktorandprojekt företagits för att ta itu med ovan nämnda problem för att göra termokroma fönsterbeläggningar av VO₂ redo för kommersiell användning.

Det slutliga målet är att utnyttja vetenskapliga rön om termokroma VO₂-material för att skapa byggnader med maximal energieffektivitet. För framtida arbeten skulle det därför vara intressant att integrera termokrom VO₂ i andra applikationer så som elektrokroma beläggningar och solceller, vilket kan resultera i multifunktionella smarta beläggningar. Även inkorporering av nanopartiklar av VO₂ i funktionella material som TiO₂ är av intresse för framtida arbeten för att skapa multifunktionsbeläggningar med hög prestanda. Genom ytterligare framsteg när det gäller att hantera begränsningarna hos de termokroma VO₂-baserade materialen kommer VO₂-baserade fönster sannolikt att realiseras inom en snar framtid.
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