Thermally adaptive windows for energy efficient buildings: High performance composite and multilayer vanadium dioxide window coatings

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Impact statement

The latest forecast by the International Energy Agency (IEA) for the CO$_2$ emissions of the built environment is that emissions will reach 15.2 Gt in 2050, double their 2007 levels. Rapid urbanisation and economic development is the driving force behind this growth. Buildings consume 40% of the primary energy in developed countries with heating and cooling alone accounting for 63% of the energy spent indoors. These trends are on an ascending trajectory - the energy demand for air conditioning in the EU has been growing by $\sim 17\%$ per year on average. Counterbalancing actions are urgently required to impede the above trends. Window coatings with dynamic solar transmittance represent an excellent opportunity to reduce the energy consumption of the built environment (by regulating solar heat gain). In particular, inorganic thermochromic coatings, based on the metal-insulator phase-transition of vanadium dioxide, offer long lifetimes (> 30 years) and can be passively integrated into a window system without additional electronics or power requirements. However, the application of vanadium dioxide as a dynamic window coating material has traditionally been hindered by its optical properties (i.e. low visible transparency and limited solar transmittance modulation) and phase-transition properties (i.e. wide phase-change hysteresis and high transition temperatures), along with practical concerns, such as determining optimal transition temperatures for a given location, and finding a production method that is suitable for the window coating industry. This thesis has presented significant progress in addressing both the fundamental and practical issues of vanadium dioxide as a
dynamic window coating material: (1) A simulation method has been developed to investigate how the transition properties of thermochromic coatings affect their energy saving performance in different environments. (2) Scalable fabrication methods and high-throughput characterisation techniques have been optimised to fabricate and characterise high purity vanadium dioxide based composite and multilayer coatings. (3) A method to control coating morphology has been demonstrated to gain control over phase-transition properties. (4) An optically designed multilayer coating has been experimentally demonstrated to improve optical properties (far exceeding previous literature performances). In light of the evidence presented, this thesis concludes that multilayer thin-film vanadium dioxide is the most viable morphology for thermochromic window coatings with high energy saving performances, and has presented a practical route towards achieving a high-performance real-world implementation of such a coating which could deliver a large positive impact on the energy efficiency of the built environment.
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Abstract

As populations increase and cities grow in size, reducing the energy consumption of the built environment is vital for reducing CO₂ emissions and global warming. Heating and cooling loads account for > 40% of energy consumed within the built environment and window coatings with dynamic solar transmittance represent an excellent opportunity to reduce this load (by regulating solar heat gain). In particular, inorganic thermochromic coatings, based on the metal-insulator phase-transition of vanadium dioxide, offer long lifetimes (> 30 years) and can be passively integrated into a window system without additional electronics or power requirements. However, the application of vanadium dioxide as a dynamic window coating material has traditionally been hindered by its optical properties (i.e. low visible transparency and limited solar transmittance modulation) and phase-transition properties (i.e. wide phase-change hysteresis and high transition temperatures), along with practical concerns, such as determining optimal transition temperatures for a given location, and finding a production method that is suitable for the window coating industry. This thesis presents significant progress in addressing both the fundamental and practical issues of vanadium dioxide as a dynamic window coating material: (1) A simulation method is developed to investigate how the transition properties of thermochromic coatings affect their energy saving performance in different environments. (2) Scalable fabrication methods and high-throughput characterisation techniques are optimised to fabricate and characterise high purity vanadium dioxide based com-
posite and multilayer coatings. (3) A method to control coating
morphology is demonstrated to improve phase-transition proper-
ties. (4) An optically designed multilayer coating is experimen-
tally demonstrated to improve optical properties (far exceeding
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sented, this thesis concludes that multilayer thin-film vanadium
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List of abbreviations

- **AFM** - Atomic Force Microscopy
- **ALD** - Atomic Layer Deposition
- **CVD** - Chemical Vapour Deposition
- **EDX** - Energy-Dispersive X-ray Spectroscopy
- **FOM** - Figure of Merit
- **FDTD** - Finite Difference Time Domain
- **FWHM** - Full Width at Half Maximum
- **MCM** - Monte Carlo Method
- **PVD** - Physical Vapour Deposition
- **SEM** - Scanning Electron Microscopy
- **TMM** - Transfer Matrix Method
- **TEM** - Tunneling Electron Microscopy
- **XRD** - X-ray Diffraction Spectroscopy
Reducing energy consumption is vital to reducing CO$_2$ emissions and global warming [27, 28]. The energy consumed in the built environment accounts for one-fifth of the total delivered energy consumed worldwide, with heating and cooling loads accounting for $>40\%$ of this energy consumption [29]. Furthermore, it has been estimated that world energy consumption in buildings will increase by an average of $1.5\%$ per year from 2012 to 2040 [30].

In light of this, the broad aim of the research presented is to improve the energy efficiency of the built environment by modernising one of its oldest and most ubiquitous components: glass windows. Specifically, the aim is to optimise the solar energy flowing through windows depending on ambient conditions. There has been considerable progress in improving the energy efficiency of windows over the last 50 years, however the solutions developed have generally been static in nature, with either high or low amounts of solar energy being transmitted to reduce either
heating or cooling loads. Much of the global population lives in temperate climates with cold winters and warm summers, where these static solutions can, during some months, detrimentally increase the building energy load. It is therefore important in these environments, to employ adaptive and dynamic solutions that can switch their functionality to meet varying conditions.

The adaptive window films in this work are thermochromic in nature. Contrary to actively switched materials (e.g. electrochromic), which require the installation of circuitry and sensors to control the switching properties, thermochromic films switch passively with temperature [31]. Importantly, this means that films can simply be applied to the glass at the point of manufacture or can potentially be retrofitted to existing windows [32,33]. Thermochromic coatings therefore offer a low-cost alternative to active switching devices, though energy saving performances may also be lower [34]. The thermochromic material used throughout this thesis is vanadium dioxide (VO$_2$), which undergoes a semiconductor to metal transition in response to increasing temperature, significantly reducing its transmission of infrared radiation whilst leaving visible light relatively unaffected [35]. The effect of this is that above a certain temperature the relative solar energy entering the building is reduced, whilst below this temperature the relative transmittance of solar energy increases. As such, the vanadium dioxide coating acts to passively regulate solar heat gain in response to seasonal changes in temperature [36].

In this chapter, the relative benefits and limitations of utilising a thermochromic transition will be discussed, as we introduce the range of energy efficient window technologies in the literature. We will then
review VO$_2$ based thermochromic windows from their initial inception to the current state-of-the-art. The conclusions of this review will then be summarised, as the specific motivations and goals of this thesis are outlined.

1.1 Energy efficient windows

1.1.1 Thermal radiation, the solar spectrum, and visible light

When an object’s temperature is above absolute zero, its constituent particles have a source of kinetic energy. This energy causes the particles to move around and collide and as a result, emit radiation due to charge acceleration. The spectral radiance (W.sr$^{-1}$.m$^{-2}$) of the emitted radiation is given by Planck’s law

$$I_{BB}(\tau, \lambda) = \frac{8\pi hc}{\lambda^5} \frac{1}{\exp\left(\frac{hc}{k_B\tau}\right) - 1}$$  \hspace{1cm} (1.1)$$

where $\lambda$ is the wavelength of emission, $h$ is Planck’s constant, $c$ is the speed of light, $k_B$ is Boltzmann’s constant and $\tau$ is the temperature of the body. It can be seen from Planck’s law that as temperatures are increased the radiated power increases whilst the wavelength of emitted light decreases. The total radiated intensity can be determined by integrating the spectral radiance over all emission wavelengths and solid angles over a half sphere, as described by Stefan-Boltzmann law,

$$I(\tau)_{SB} = \tau^4 \sigma_{SB}$$  \hspace{1cm} (1.2)$$

where the Stefan-Boltzmann constant $\sigma_{SB} = 5.6705 \times 10^{-8}$ Wm$^{-2}$K$^{-4}$. 
Figure 1.1: The emission from objects of varying temperatures as described by Planck’s law. The AM1.5 solar spectrum is also shown alongside the luminous efficiency function (LEF) of the human eye.

Figure 1.1 shows Planck distributions for the sun (≈ 5500 K) and a room temperature body (≈ 300 K) along with the luminous efficiency function of the human eye, which describes the wavelength dependency of human vision. We can see that an object at room temperature will emit invisibly in the infrared, whilst a hotter object such as our sun, with a surface temperature of ≈ 5500 K, will emit across all visible wavelengths, appearing as a white light source. Also in figure 1.1 is the AM1.5 solar spectrum, which is the spectral intensity of solar radiation reaching the earth’s surface when the sun is 37° above the horizon, i.e. when air mass between the sun and earth’s surface is 1.5 times greater than when the sun is at normal incidence. It is important to note that solar radiation is restricted to 0.25 < λ < 3 μm and generally does not overlap with thermal radiation from terrestrial objects, meaning that the transmission of each can be controlled independently.
1.1. Energy efficient windows

1.1.2 Transmission of radiation

When radiation is incident on a flat surface such as a window it is either transmitted, reflected or absorbed, satisfying

\[ T(\lambda) + R(\lambda) + A(\lambda) = 1 \]  \hspace{1cm} (1.3)

where \( T(\lambda) \), \( R(\lambda) \) and \( A(\lambda) \) are transmittance, reflectance and absorptance respectively. The question of which wavelengths should be transmitted or rejected depends on the context of the application. Some metrics that will be useful for evaluating the performance of energy efficient windows are the luminous transmission \( T_{\text{lum}} \) (the transmission of light visible to the human eye) and the solar transmission \( T_{\text{sol}} \) (the overall transmission of solar radiation) defined as

\[ T_{\text{lum}} = \frac{\int T(\lambda)f_{\text{lum}}(\lambda) \, d\lambda}{\int f_{\text{lum}}(\lambda) \, d\lambda} \]  \hspace{1cm} (1.4)

\[ T_{\text{sol}} = \frac{\int T(\lambda)f_{\text{sol}}(\lambda) \, d\lambda}{\int f_{\text{sol}}(\lambda) \, d\lambda} \]  \hspace{1cm} (1.5)

where \( f_{\text{sol}}(\lambda) \) is the AM 1.5 solar spectrum [38] and \( f_{\text{lum}}(\lambda) \) is the luminous efficiency of the human eye [39]. It is important to make a distinction between the two ways light can be rejected from a entering a building: absorption and reflection (either specular or diffuse). Rejecting light via reflection is generally preferable since absorbed light will cause the temperature of the film to rise and radiate some of the absorbed energy into the building [40, 41].

1.1.3 Static solutions

Solar-gain refers to the amount of the sun’s energy that is able to enter a building and generate heat, static energy efficient windows generally aim
to minimise or maximise this value depending on the climate [42–45].
To improve energy efficiency in colder climates, low-emittance (low-E) coatings are typically installed on the inner side of the outer pane of a multiple glazed window. Low-E coatings exploit the fact that the solar spectrum does not overlap with the emission spectra from objects < 100°C to achieve a high degree of solar-gain whilst preventing the thermal radiation from indoor sources of heat passing through the window to the outside; in an ideal case

\[
\text{Low-E} \quad T(\lambda) = 1 \quad \text{for} \quad 0.4 < \lambda < 3.0 \mu m \\
R(\lambda) = 1 \quad \text{for} \quad 3.0 < \lambda < 50 \mu m
\]

(1.6)

Alternatively in hot climates, it is desirable to minimise the window solar-gain, so windows are designed to reject as much solar radiation as possible, whilst remaining transmissive to visible light such that

\[
\text{Low Solar Gain} \quad T(\lambda) = 1 \quad \text{for} \quad 0.4 < \lambda < 0.7 \mu m \\
R(\lambda) = 1 \quad \text{for} \quad 0.7 < \lambda < 50 \mu m
\]

(1.7)

Materials used are typically transparent conducting oxides (TCOs) (e.g., \(\text{In}_2\text{O}_3:Sn, \text{SnO}_2:F, \text{ZnO}_2:Al\)) [44] or multilayer sandwich structures comprising dielectric layers and thin layers of noble metals (e.g, Al, Ag) [43].

1.1.4 Dynamic solutions

In brief, the specific energy savings from adaptive windows come from three sources: (i) heating, via high transmittance of solar energy when required (ii) cooling, via low transmission of solar energy when required (iii) lighting, via high transmission of visible light. The relative ability to achieve each of these savings is dependent on both the location and
construction of the building, along with the type of adaptive window technology deployed.

Broadly speaking, dynamic energy efficient windows can be split into two main categories: active and passive. Active systems use sensors to measure ambient conditions, i.e. temperature and lighting, and then use the readings along with programmed rules to determine the point at which to change states. The control available with active systems is attractive, however the complexity of such systems prohibits retrofit to existing windows and increases costs [15]. Alternatively, passive systems have material transitions that respond directly to the relevant ambient conditions so require no control electronics, therefore making installation easier. However this means that the user cannot tailor the transition properties to their needs and must rely on the intrinsic properties of the material.

Performance of a dynamic window can be roughly quantified by two metrics, transmission modulation of solar irradiance $\Delta T_{\text{sol}}$, i.e. the cold state transmission subtracted by the hot state transmission, and transmission of solar luminosity $T_{\text{lum}}$; an ideal window design will maximise both $\Delta T_{\text{sol}}$ and $T_{\text{lum}}$.

### 1.1.4.1 Electrochromics

The most popular commercial implementations of active adaptive windows utilise electrochromic transitions where changes in optical properties occur in response to applied voltages. Modern electrochromic devices generally use a thin-film battery-type configuration, in which a layer of electrochromic material (e.g. metal oxide or conjugated polymer) is
coated on a transparent conducting oxide (TCO) working electrode, and a charge storage layer (e.g. NiO, CeO$_2$) is coated onto a TCO counter electrode (see Fig. 1.2). These two electrodes are joined by a layer serving as an ion-conducting electrolyte and separator [46,47]. The device absorbs significantly more solar radiation when electrons and ions are inserted into the working electrode, and becomes transparent when the charges are extracted to be stored in the counter electrode. These devices exhibit open circuit memory meaning that they can maintain the charge in the working electrode for an extended period of time [46].

**Figure 1.2:** Illustration of the most common design of electrochromic windows. [15]

The technology has been commercialised by a number of companies, including Sage Electrochromics Inc., ChromoGenics AB, View Inc., EControl Glass GmbH, and more. However, a challenge for electrochromic windows has been to increase their lifetime to the minimum 25 years generally required for building components [47]; the lifetime of current designs is typically less than 10000 cycles or 15 years [15]. Another drawback to consider is that a large part of the visible spectrum is absorbed meaning that there is a considerable reduction in visible transmission (though this may be seen as beneficial in some cases for glare reduction).
and also that the devices will heat up considerably when in their absorbing states leading to unwanted indoor heating [40], a point which will be discussed in further detail in Chapter 2.

One example of an electrochromic window design that operates as a reflection based modulator is the use of cholesteric liquid crystals. It has been demonstrated that the reflection bandwidth in the infrared can be tuned from 120 nm to 1100 nm wide, achieving a transmission modulation of 37% (between 8% and 45%) of incident infrared solar radiation [48]. However the relatively short lifetime of the organic molecules under solar irradiation is a significant limiting factor.

1.1.4.2 Photochromics & Thermochromics

Materials for passive adaptive windows are limited to those that switch in response to a relevant ambient property, i.e. irradiance (photochromic) or temperature (thermochromic). Photochromic materials can be seen commonly in certain reactive sunglasses and have potential for energy-saving with respect to indoor cooling costs. However, since the transition is temperature independent, photochromic films will always reduce solar heat gains, even during the cold winter months when solar heat gains could be beneficial. Thermochromic films, which switch passively as a function of temperature, are more attractive for this reason. For thermochromic films it is especially important to consider how light is modulated, since if light is modulated through absorption then the film temperature will have a dependence on the amount solar irradiance, which gives absorbing thermochromic films a pseudo-photochromic property. The effect of this pseudo-photochromic switching is discussed in detail
1. Introduction, Background & Motivation

Figure 1.3: Illustration of the relatively simple design of thermochromic and photochromic windows. [15]

in Chapter 2 of this thesis.

1.2 Vanadium dioxide

The prime candidate material for thermochromic windows is vanadium dioxide (VO$_2$), specifically the M phase\(^1\) [31, 49, 50]. In its low temperature state VO$_2$ exhibits a semiconducting monoclinic distorted-rutile structure (M phase, or cold state); when heated above a critical temperature $T_c$ there is a structural transition to a tetragonal rutile phase (R phase, or hot state) [51]. The phase transition of vanadium dioxide significantly modulates its optical properties, with the high temperature hot state transmitting considerably less infrared radiation than the lower temperature cold state. The cold state VO$_2$(M1) structure demonstrates two alternate V–V intervals of 2.65 and 3.12 Å, whilst the hot state VO$_2$(R) exhibits a regular V–V interval of 2.87 Å. As temperature increases the energy gap between O$_{2p}$ and V$_{3d}$ bands is reduced due to the lowering of the empty V$_{3d}$ band down to the Fermi level (see Fig. 1.4).

\(^1\)There is actually more than one M phase, specifically we are referring to the M1 phase.
calised electrons at the occupied $V_{3d}$ band become untrapped and begin to interact with infrared wavelength of light [52, 53].

**Figure 1.4:** Band structure of vanadium dioxide ($\text{VO}_2$). Above the transition temperature in the metallic state the $V_{3d}$ bands merge at the Fermi level and the bound electrons at the occupied $d$-band become untrapped. The molecular orbital $\pi^*$ also exists at the Fermi level in the metallic state [16].

The precise nature of the phase transition is outside the scope of this research, though it has been investigated by many groups with the transition attributed to the combined effects of a structural Peierls transition driven by instabilities in electron-lattice dynamics and an electronic Mott transition driven by electron-electron correlations [52, 54–63].

A significant advantage of vanadium dioxide as an adaptive window coating material is that, assuming it is protected from oxidation, the material does not degrade during extended cycling representative of the lifespan of a window [64]. However the material has other flaws, specifically there are five key properties that must be optimised for $\text{VO}_2$ based adaptive windows to successfully move from academic research to real world application: (1) Transition temperature, which for pure $\text{VO}_2$ is 68°C, must be brought closer to room temperature. (2) Transition hysteresis width, which results in the films requiring more extreme variations
in temperature to cycle between states, must be minimised. (3) Transition gradient width, i.e. the change in temperature required to fully switch states, must be minimised. (4) Visible transmission, must be kept above an acceptable level for the application (typically > 50%) and have an acceptable colour. (5) Solar modulation depth, must be maximised to provide the greatest degree of seasonal adaptability. The first three properties (1,2,3) will often be referred to collectively in this thesis as the transition properties or transition performance, to distinguish them from the final two properties (4,5), which will be referred to collectively by the term optical performance. Improvements to both optical and transition performance are vital if VO$_2$ based thermochromic window coatings are to be viable in a real world application, however in the following, we will see that improvements in one are often found to come at the detriment of the other.

1.2.1 Transition temperature, hysteresis & gradient

The transition temperature $\tau_c$ is approximately 68°C for bulk VO$_2$ and must be lowered to approach room temperature for application in smart windows. This can be achieved by: elemental doping [49, 65–71], structural stress [72, 73], grain size [74–76] non-stoichiometry [77], or by a combination of these factors. In all cases, the V–V interval in VO$_2$(M1) is reduced, which decreases the structural difference between VO$_2$(M1) and VO$_2$(R), leading to a decrease in the transition activation energy [49, 78].

When replacing a vanadium atom, molybdenum has been used to
reduced $\tau_c$ (15°C per at% Mo) [79], however tungsten is the most efficient dopant with a pronounced reduction in the $\tau_c$ by 23°C per at% W [69, 80–82]. It has been observed that dopants with an ionic radius smaller than $V^{4+}$, or that created $V^{5+}$ defects smaller than $V^{4+}$, increase the transition temperature, whilst dopants with a larger ionic radius than $V^{4+}$ caused a decrease in the $\tau_c$, which is attributed to the effect of these dopants on the V–V interval in VO$_2$(M1) [83].

Alternatively to produce a similar reduction in the structural difference between VO$_2$(M1) and VO$_2$(R), oxygen atoms can be replaced by fluorine to reduce $\tau_c$ by 20°C per at% F. [67]

Hysteresis in the switching of VO$_2$ is seen as a result of cold state nucleation sites being thermally unstable. The effect can be reduced somewhat by increasing the crystal grain size and therefore increase the probability of nucleation sites forming. Other methods to reduce hysteresis have included anisotropic doping, where small regions of the film are left undoped and thus remain in the cold state. When the regions of doped VO$_2$ are cooling down from the hot state the undoped regions act as a stable nucleation site for the cold state [84].

The transition gradient width has been shown to be greater in pure crystals and as dopant concentrations are introduced there is no apparent way to avoid this increase. However, simulations have shown that the negative effects of transition gradients on the overall energy saving performance are reasonably low for gradients above 5% transition width per °C [85].
1.2.2 Visible transmittance & solar modulation

The low visible transmittance and undesirable colour originate from the strong inner-band and inter-band absorptions in the short-wavelength range for both the metallic and semiconductive states [66, 86, 87]. The band-gap between $V_{3d}$ and $O_{2p}$ is 2.5 eV (corresponding to the visible absorption edge of $\sim 500$ nm) therefore VO$_2$ films can absorb visible light at wavelengths below 500 nm which gives the films an undesirable brown-yellow tint along with a decreasing the overall visible transmittance [86]. To achieve a colourless appearance for the VO$_2$ films, the optical absorption edge has to be shifted towards shorter wavelengths in order to sustain the blue part of visible light.

It has been shown previously that there is a relation between the optical band-gap energy of metal-nonmetallic compounds and the difference in electronegativity of the composite elements [88], where a larger difference in electronegativity results in a larger optical band-gap energy. Vanadium has an electronegativity of 1.63 and oxygen has an electronegativity of 3.44. Therefore, substituting vanadium atoms with elements with an electronegativity value lower than 1.63 or substituting oxygen atoms with elements with higher electronegativity than 3.44 increases the optical band-gap energy and reduces the extinction of short wavelength visible light. For example, it has been shown that substituting magnesium for vanadium in VO$_2$ raises the conduction band and increase the bandgap between the $V_{3d}$ and $O_{2p}$ since the electronegativity value of magnesium (1.31) is lower than that of vanadium [89]. Other elements with low electronegativity that have been investigated similarly as dopants for VO$_2$ are calcium (1.00), strontium (0.95) and barium
The colour of the VO₂ films can also be altered using nanostructures, for example through the use of monolayer photonic crystal comprised of SiO₂ coated with VO₂ [91], whereby specific wavelength bands of visible light can be reflected to vary the transmission colour of the films; the wavelength band can be tuned by varying the size of the spheres. A downside to this is that it will reduce the overall visible transmission, however this may be seen as an acceptable trade-off from an aesthetic perspective.

Increases in modulation depth can generally be achieved by increasing the thickness of VO₂ films however this results in reduced visible transmission. The solar modulation depth is typically reduced as dopant concentrations are increased, so dopants that have the largest intended effect per wt% are preferable. For example, tungsten is generally the preferred dopant for reducing the transition temperature since it results in a 20 °C decrease in transition temperature per %wt. [49]

### 1.2.3 Thin film deposition

Methods for preparing VO₂(M1) thin films can be split into three groups: sol-gel methods [92–97], physical vapour deposition [53,71,98–100], and chemical vapor deposition (CVD) [49,82,101–106]. In all cases of VO₂(M1) synthesis, the final oxidation state of the thin film is determined by the oxidation state of the source material and the environmental conditions during crystal formation.
1.2.3.1 Physical vapour deposition

Physical vapour deposition (PVD) uses physical process (such as heating or sputtering) to produce a vapour of material, which is then deposited onto the substrate. Many solar-control and low emittance coatings for windows are made by PVD, specifically by DC magnetron sputtering using multicathode in-line deposition systems [107]. First the coating materials are placed on a magnetron in a solid form. The chamber is evacuated to remove contaminants from the chamber and then backfilled with a process gas. The gas selected depends on the type of material to be deposited; gases (e.g. nitrogen or oxygen) which are normally stable and inert under normal circumstances can become ionized and reactive in the plasma environment as a result of the high energy collisions such that the gas can react chemically with the target material and create a molecular compound which then becomes the thin film coating. For example, a vanadium target reactively sputtered with oxygen gas can produce a vanadium oxide film. If the amount of oxygen is controlled then various oxides with different oxidation states can be formed, including \( \text{VO}_2(M1) \) [53, 71, 98–100].

1.2.3.2 Solution based methods

Sol-gel based methods involve conversion of precursor gels from solution to form solid films. Once a sol-gel is prepared it can be deposited on a substrate to form a film by dip coating, spin coating, or spray coating. A subsequent thermal treatment is often necessary in order to induce the desired crystal structure. In the literature \( \text{VO}_2(M1) \) has been formed from vanadium solutions with a variety of oxidation states (e.g. \( 3^+ \), \( 4^+ \),
5\textsuperscript{+}), with either highly oxidising or highly reducing environments used for source materials in the 3\textsuperscript{+} and 5\textsuperscript{+} respectively [92–97]. VO\textsubscript{2} thin films prepared by sol-gel methods have been cycled 10\textsuperscript{8} times without any degradation in electrical resistance contrast [108].

1.2.3.3 Chemical vapour deposition

Chemical vapour deposition (CVD) is another method well suited for in-line production in industry. In the case of CVD the substrate is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit [49, 82, 101–106]. In this case the substrate could be fed through a critical temperature region where the film formation at the interface can be initiated at a well controlled rate.

1.2.4 Multilayers & nanostructures

Since vanadium dioxide is highly reflective in the visible region of the spectrum, much of the optics based work on VO\textsubscript{2} thermochromic windows has focused on reducing the reflections from thin film VO\textsubscript{2} using multilayer and graded index structures. Multilayer structures can improve performance by creating resonant cavities in which constructive and destructive interference bands are tuned to enhance $T_{\text{lum}}$ and $\Delta T_{\text{sol}}$. These type of anti-reflection layers have been formed using a number of materials including silica, titania [96, 109–111].

An early example of a multilayer coating was a five-layer system of TiO\textsubscript{2}/VO\textsubscript{2}/TiO\textsubscript{2}/VO\textsubscript{2}/TiO\textsubscript{2} [109], this coating was demonstrated to have a solar modulation $\Delta T_{\text{sol}} = 11.8\%$ and visible transmittance $T_{\text{lum}} = \ldots$
45.3% in the low-temperature state. The best optical performance of a multilayer design in the literature at the time of writing was demonstrated by a three layer structure of Cr$_2$O$_3$/VO$_2$/SiO$_2$ fabricated via magnetron sputtering, which was shown to provide a significant improvement on the optical performance of single layer VO$_2$ with $\Delta T_{\text{sol}} = 16.1\%$ and $T_{\text{lum}} = 54.0\%$ [111]. Whilst this study demonstrates a significant improvement in visible transmittance and solar modulation over simple thin films the transition temperature is at 68 °C so doping is required to make it viable for real world application.

Previous work within our group has aimed to achieve broadband wide-angle polarization insensitive anti-reflection through the use of nanostructures inspired by the eyes of moths, these moth-eye type structures are densely packed, tapered cones that form a highly efficient optical impedance matching anti-reflection layer. Simulations have predicted possible solar energy modulation 23.1% whilst maintaining a high visible transmittance of 70.3% [112]. A conceptually similar design was demonstrated experimentally [113] however the measured performance was considerably lower with a solar modulation of 7.5% and a luminous transmittance of 45%. To achieve a performance close to the simulated structure it would require a well controlled conformal coating of VO$_2$ to the nanostructure. This could be achieved with a CVD process known as atomic layer deposition (ALD) where precursors react with the surface of a material one at a time in sequential self-limiting steps allowing for atomically specified control of the conformal film thickness.
1.2.5 Nanoparticle composites

Theoretical calculations have predicted that VO$_2$ nanoparticle composites can significantly outperform single and multilayer vanadium dioxide films, according to simulations VO$_2$ based nanocomposite could theoretically achieve $\Delta T_{\text{sol}}$ of above 20% with visible transmission above 60% [114]. The relative refractive index of the effective medium depends on both VO$_2$ and composite indexes, with properties intermediate between VO$_2$ and the dielectric host. Size and volume fraction of VO$_2$ particles are important factors in determining the optical properties of the composite coating [115]. Additionally in comparison to VO$_2$ thin films and multilayers, VO$_2$ polymer-nanoparticle films could be retrofitted to existing windows, which is important since it is generally not cost effective to replace existing window with energy efficient windows unless they are at the end of their life-cycle.

Early methods for the production of vanadium dioxide nanoparticles have included: ion implantation followed by annealing [116–118], ion beam lithography and pulsed laser deposition [119,120], ultrasonic spray and laser pyrolysis [121], molten salt synthesis [122], however these methods are not scalable enough for practical application.

Aqueous chemical methods are more scalable however obtaining control over particle size and agglomeration is challenging [123–125]. Hydrothermal synthesis, whereby crystals are grown under high temperature and high pressure water conditions from substances which are insoluble in ordinary temperature and pressure (< 100°C, <1 atm) has been successfully demonstrated for fabricating small quantities of VO$_2$ nanoparticles with well controlled size distributions [126]. The method
has since been scaled up to a continuous hydrothermal flow process (CHFS) as would be required for industrial scale production of the nanoparticles [127] and further developed for improved crystallinity and reduced synthesis time via a microwave-assisted hydrothermal process. [128]

Once particles have been produced direct embedding of VO$_2$ particles in polymer composites is an efficient method for obtaining thermochromic coatings provided particles do not agglomerate [129, 130]. In solution particle agglomeration can be prevented via functionalisation with long chain molecules. Subsequently when removing particles from solution agglomeration can be reduced though the use of lyophilisation (freeze-drying), where since there is no liquid-to-gas phase transformation, particles are not subjected to capillary force and therefore are less likely to agglomerate [25].

The best optical performance results for nanoparticles at the time of writing have been produced by Chen and co-workers [131], who employed highly dispersed VO$_2$ nanoparticles in polyurethane (PU) host after surface adjustment by poly-vinylpyrrolidone (PVP). The result showed superior thermochromic properties ($T_{\text{lum}}$ 45.6%, $\Delta T_{\text{sol}}$ 22.3%) for VO$_2$/PU nanocomposite derived from nanoparticles prepared using a ”heating-up” technique at 330°C, whereby a burst of particle nucleation is induced by precursor decomposition at a critical temperature. The high optical performance has been attributed to the nanoparticles being highly crystalline and well distributed in the host matrix. However, due to the small domain sizes of VO$_2$ in this composite the hysteresis and gradient width are both large ($\sim$ 40 °C and $\sim$ 30 °C respectively).
1.2.6 Overall energy saving performance

Previous works have aimed to model the overall energy saving performance of thermochromic coatings [40, 132, 133]. Warwick and co-workers used a modified EnergyPlus building simulation to demonstrate the effect of switching temperature, gradient width, and hysteresis width on the overall energy saving performance [132], their work focused on an idealised case, where films modulate solar transmittance solely via changes in reflectance, such that they are non-absorbing and do not re-radiate thermal energy into the building [132, 134]. The study was conducted for several locations and found that the greatest potential energy benefit was >50% compared to the a clear glazing, however since this particular value was for a high temperature climate (Cairo), they acknowledged that this benefit could have been achieved similarly with a static coating rejecting solar radiation. They concluded that the best performance is achieved with the transition temperature at room temperature for all values of the transition hysteresis and gradient width. The effect of absorption in thermochromic coatings was investigated separately by Ye and co-workers [40, 133], who found that absorption was highly detrimental to the overall energy saving performance due to the absorbed energy being thermally re-radiated into the building. As a result they concluded that an ideal thermochromic coating should have no solar absorption and instead engineer coatings that can vary solar transmittance though changes in solar reflectance, rather than changes in solar absorptivity. However their theoretical investigation only studied binary switching thermochromic films, i.e. those that exhibit no hysteresis or gradient in their transition.
1.3 Motivations of this thesis

To summarise the review of the literature, the two most promising methods for improving the optical performance of vanadium dioxide based adaptive window coatings appear to be multilayer structures and nanoparticle composites, however each of these methods brings with it new challenges. Multilayer films require careful control of each layer thickness to achieve beneficial optical interference conditions [135], whilst composites typically exhibit significant transition hysteresis and gradient widths [131]. The effects of transition gradient and hysteresis width have been shown theoretically to be highly detrimental to the overall performance however these studies did not account for absorption. The motivations of this thesis are therefore to:

- Create a model and an appropriate metric to evaluate and compare the overall performance of thermochromic films with different optical and transition performances.
- Develop methods to synthesise both VO$_2$ thin films and nanocomposites and characterise both their optical and transition performances.
- Design and fabricate multilayered VO$_2$ coatings that improve optical performance.
- Design and fabricate nanocomposite VO$_2$ coatings that improve optical performance whilst maintaining narrow transition hysteresis and gradient widths.
1.3. Motivations of this thesis

The progress in achieving each of these objectives will be detailed in the following four chapters respectively. A final chapter will then draw conclusions, evaluate the progress made, and suggest future directions for the research.
2.1 Introduction

This chapter describes the development of a theoretical model to compare the overall performance of thermochromic coatings (taking into account both the optical and transition performances); the key results have been published in ref [3]. Specifically in this chapter the model is used to demonstrate how the the effects of the transition characteristics differ between absorbing and non-absorbing thermochromic coatings.

Previous works have aimed to model the energy saving performance of thermochromic coatings [40,132,133] and others have presented idealised parameters for optimal performances [41]. Critical parameters that have been cited as key to improving performance are the switching temperature, transition gradient width, and hysteresis width [132].
Investigations into the effects of transition gradient width and hysteresis width on the overall energy saving performance of thermochromic coatings have previously been carried out by Warwick and co-workers using a modified EnergyPlus building simulation [132, 134]. Their work focused on an idealised case, where films modulate solar transmittance solely via changes in reflectance, such that they are non-absorbing and do not re- radiate thermal energy into the building. In these cases it has been found that the switching temperature should be at room temperature, transition gradient sharp, and hysteresis width narrow. However, the performance of state-of-the-art thermochromic coatings depends largely on the use of anti-reflective structures [8, 111, 112, 136] or nanoparticles [114, 125, 137–139] where modulation of solar transmittance is achieved primarily through changes in absorption rather than reflection, and specifically in the case of nanoparticles, where coatings exhibit significant hysteresis and gradient widths due to the small non-uniform domain sizes of the phase change components [125, 137]. The effect of absorption in thermochromic coatings was investigated separately by Ye and co-workers [40, 133], who found that absorption was highly detrimental to the overall energy saving performance due to the absorbed energy being thermally re-radiated into the building. As a result they concluded that an ideal thermochromic coating should have no solar absorption and instead engineer coatings that can vary solar transmittance through changes in solar reflectance, rather than changes in solar absorptivity. However their theoretical investigation only studied binary switching thermochromic films, i.e. those that exhibit no hysteresis or gradient in their transition. In light of these factors, this chapter demonstrates
for the first time, how the effects of transition gradient and hysteresis differ between absorbing and non-absorbing thermochromic coatings.

### 2.2 Energy transfer model

The first step in developing the model is to determine what the equilibrium temperature of absorbing coatings would be under solar illumination and also how much of the absorbed energy would be transferred through a window as heat, this is of significant interest since it would be detrimental to the overall energy saving performance. To do this the temperature \( \tau \) at which the net energy flux \( P_{\text{net}} \) into the window coating was equal to zero must be determined; the net energy flux is given by,

\[
P_{\text{net}} = P_{\text{abs}} - P_{\text{rad}} - P_{\text{conv}} - P_{\text{cond}}
\]

(2.1)

where \( P_{\text{abs}} \) is the solar power absorbed by the film, \( P_{\text{rad}} \) is the radiation emitted from the film, \( P_{\text{conv}} \) is the power transferred to the ambient air by convection, and \( P_{\text{cond}} \) is the power transferred into the building through the window via conduction.

The components \( P_{\text{abs}}, P_{\text{rad}}, P_{\text{conv}}, \) and \( P_{\text{cond}} \) are given by:

\[
P_{\text{abs}} = I_{\text{sol}}A_{\text{sol}}(\tau)
\]

(2.2)

\[
P_{\text{rad}} = I_{\text{BB}}(\tau)\epsilon
\]

(2.3)

\[
P_{\text{cond}} = U(\tau - T_{\text{in}})
\]

(2.4)

\[
P_{\text{conv}} = h(\tau - T_{\text{out}})
\]

(2.5)

where \( I_{\text{sol}} \) is the solar irradiance at the window surface, \( A_{\text{sol}} \) is absorption of the film integrated over the AM1.5 solar spectrum, \( I_{\text{BB}}(\tau) \) is the
spectral emission from a black body at temperature $\tau$, and $\epsilon$ defines the thermal energy that is emitted from the film, where $\tau$ is the temperature of the film and $\tau_{\text{in}}$ and $\tau_{\text{out}}$ are the internal and outside temperatures respectively. The parameter $U$ is the overall heat transfer coefficient of the window in W/m$^2$.K, and we assume throughout that $U = 2$ W/m$^2$.K, which is equivalent to a simple double glazed window with a low thermal emissivity inner coating; more advanced designs with insulating gas fillings can achieve $U$-values of below 1 W/m$^2$.K [42]. Finally, the parameter $h$ is the convective heat transfer coefficient, which is given commonly for building applications as a function of wind speed by [140],

$$h = \begin{cases} 4.0v_\infty + 5.6 & v_\infty < 5\text{ms}^{-1} \\ 7.1v_\infty^{0.78} & v_\infty \geq 5\text{ms}^{-1} \end{cases}$$

where $v_\infty$ is the free stream wind speed. After calculating the equilibrium film temperature we are then able to determine how much of the absorbed energy is transferred into the building as heat and thermal radiation, defined as $P_{\text{build}}$,

$$P_{\text{build}} = P_{\text{cond}}$$

assuming that contributions from $P_{\text{rad}}$ are negligible when a low-e coating is installed. To determine the overall energy saving performance we need to consider how performance varies annually as a function of time. The change in temperature of the coating $\Delta\tau$ in a given time interval is given by

$$\Delta\tau = \int [P_{\text{net}}(t)/C] \, dt = \int [(P_{\text{abs}}(t) - P_{\text{conv}}(t) - P_{\text{build}}(t) - P_{\text{rad}}(t))/C] \, dt,$$

$$ (2.8)$$
where \( C = 1000 \text{ J/K} \) is the assumed heat capacity of the coating [141]. The heat capacity is inversly proportional to the time required for the coating to reach an equilibrium temperature. It is worth noting that since the rate at which conditions change in the built environment is relatively slow it was found that assuming a heat capacity of 10000 J/K (equivalent to a 5 mm thick pane of glass) had a negligible effect on the overall performance metric introduced later in this chapter.

With this model we are then able to calculate the varying energy flux through the window over the course of a year, with inputs for varying solar irradiance, air temperature, and wind speed either calculated or taken directly from the EnergyPlus\(^1\) database [142].

In the following, the annual and diurnal variations in solar irradiance and air temperature for different locations were derived following ref [17]. The terrestrial solar irradiance arriving at the surface of the earth is given relative to the extraterrestrial solar irradiance by

\[
I_t = \alpha I_{et}
\]

where \( \alpha \) an empirically derived coefficient representing solar attenuation in different climates [143]. The value of \( \alpha \) for a given location was determined by fitting calculated peak values to measured peak solar irradiance found from ref [142]. The hourly variation in extraterrestrial solar irradiance over a year is given in W/m\(^2\) by [17]

\[
I_{et} = 1370\epsilon_0 \sin(\beta)
\]

where the empirical coefficient of annual variation \( \epsilon_0 \) is given by,

\[
\epsilon_0 = 1 + 0.033 \left[ 2\pi (t_d - 10) / 365 \right]
\]

\(^1\)EnergyPlus is a widely used open source software for building energy simulations.
and the hourly variation, i.e. the elevation of the sun relative to the surface of the earth, is given by

\[
\beta = \arcsin(a + b \cos(\tau))
\]

where \(\tau\) is the solar hour, given as a function of the hour of the day \(t_h\) by

\[
\tau = \frac{\pi}{12} (t_h - 12)
\]

and where \(a\) and \(b\) are given by,

\[
a = \sin(\lambda) \sin(\delta)
\]

\[
b = \cos(\lambda) \cos(\delta)
\]

where \(\lambda\) is the latitude of the observer and \(\delta\) is the solar declination given by,

\[
\delta = -0.4093 \cos \left[ 2\pi (t_d + 10)/365 \right]
\]

where \(t_d\) is the day of the year.

![Diagram of solar position with respect to the Earth. Np and Sp are the North Pole and South Pole respectively.](image)

**Figure 2.1:** Solar position with respect to the Earth. Np and Sp are the North Pole and South Pole respectively. [17]

The diurnal variation of temperature can be split into three sections and is defined in relation to the time of sunrise and sunset along with
2.2. Energy transfer model

![Figure 2.2: The three stages of diurnal temperature variation. [17]](image)

values for the minimum and maximum temperatures reached taken from ref [142]. The sunset and sunrise times are given by

\[
t_{ss} = 12 + \frac{12}{\pi} \arccos \left( -\frac{a}{b} \right) \\
t_{sr} = 12 - \frac{12}{\pi} \arccos \left( -\frac{a}{b} \right)
\]

whilst the outside air temperature is then given by,

\[
\tau_{set} + \frac{(\tau_{min} - \tau_{set})(24 + t_{h} - t_{ss})}{(t_{sr} + 1.5) + (24 - t_{ss})} \quad \text{for stage I}
\]

\[
\tau_{min} + (\tau_{max} - \tau_{min} \sin \left[ \frac{\pi(t_{h} - t_{sr} - 1.5)}{t_{ss} - t_{sr}} \right]) \quad \text{for stage II}
\]

\[
\tau_{set} + \frac{(\tau_{min} - \tau_{set})(t_{h} - t_{ss})}{(t_{sr} + 1.5) + (24 - t_{ss})} \quad \text{for stage III}
\]

where \(\tau_{set}\) is the outside temperature at sunset for the previous day.

The initial value for this parameter is predetermined by a preliminary simulation of the solar irradiance and outside temperature over the year.

At the start of a simulation it is set at the predetermined initial value, after which it is be updated daily at \(t_{h} = t_{ss}\).

To quantify and compare the performance of films with different transition characteristics we calculate the varying net energy flux through the
window over the course of a year, including thermal energy re-radiated into the building from the film. When the outside air temperature is below room temperature (constant 21 °C), we consider a high net energy flux to be beneficial, whereas when the outside air temperature is above room temperature a low net energy flux is considered beneficial. In both cases the beneficial net energy flux $\Phi_B$ is calculated in relation to a common reference taken to be non-absorbing with a static transmission set as the average of the high and low transmitting states $T_{avg}$. The above is summarised in the equations below:

$$
\Phi_B = \begin{cases} 
I_{sol}(T - T_{avg}) + P_{\text{build},s} - P_{\text{build},r} & \text{for } t_{\text{air}} < 21^\circ C \\
I_{sol}(T_{avg} - T) + P_{\text{build},r} - P_{\text{build},s} & \text{for } t_{\text{air}} > 21^\circ C 
\end{cases}
$$

(2.9)

where the subscripts $s$ and $r$ denote the study and reference values respectively. Integrated over the course of a year, equation (2.9) gives the total beneficial energy per unit area which we use as our metric to compare the performance of different films. Whilst this metric cannot be said to quantify the actual energy cost benefit of installing a thermochromic coating like in other studies [40,132], it provides us with insights into the impact that the transition characteristics can have on the solar regulating ability of absorbing or non-absorbing thermochromic films.

### 2.3 Results & Discussion

The absorbing and non-absorbing coatings investigated are both assumed to have a solar transmittance modulation of 20% ($T_{max} = 0.8; T_{min} = 0.6$) which is within theoretical performance limits for thermochromic window coatings [112,114]. In the non-absorbing case, as in
previous work [132,134], this modulation is assumed to occur by changes in reflectance, where the solar absorption is 0% in both high and low solar transmitting states. In the absorbing case, it is assumed that in the low-temperature state 20% of incident solar radiation is absorbed whilst in the high temperature state 40% of incident solar radiation is absorbed, which is representative of optimised nanoparticle composites [114].

Since the key benefit of a thermochromic window is that it can vary its properties in response to changing conditions it is important to compare annual performances. To do this we must determine the temperature and transmittance of the window coating as a function of time over the year. A schematic of the system investigated is shown in Figure 2.3a. In all cases the thermochromic coating is assumed to be on the exterior surface of the window such that there is the greatest amount of thermal insulation between the coating and the inside of the building. The effect of this is to reduce thermal re-radiation from the film into the building, as is discussed later in the text. In the following, the transition characteristics i.e. switching temperature $S$, transition gradient width $G$, hysteresis width $H$, and modulation depth $D$, are defined as shown in Figure 2.3b. A simplified model of the hysteretic dependence of film transmittance on temperature allows for a clear separation of the effects of hysteresis and transition gradient in our results.

In Figure 2.4 the annual performance as described in equation (2.9) is given as a function of switching temperature and hysteresis width for both reflecting (Figure 2.4a) and absorbing (Figure 2.4b) coatings with equal modulation depths and binary switching ($G = 0^\circ\text{C}$). The environmental parameters were chosen to represent New York City. As
2. **Energy modelling of non-ideal thermochromic coatings**

![Diagram](image)

**Figure 2.3**: (a) Schematic of window energy fluxes with an absorbing coating on the outer surface of the window. (b) Schematic heating (red line) and cooling (blue line) hysteresis loop of a thermochromic film, including definitions of the transition gradient width $G$, hysteresis width $H$, switching temperature $S$, and modulation depth $D$.

expected from previous literature [132], in Figure 2.4a we see that for the case of reflective films the optimum performance occurs when the switching temperature is at room temperature and that the performance rapidly diminishes with increasing hysteresis width. In contrast, for the case of absorbing films an immediate observation from Figure 2.4c is that the optimum switching temperature is higher than for reflecting films, which can be expected since the equilibrium temperature under solar illumination will be significantly higher with increased solar absorption (see Figure 2.4e). With regards to the increased optimum switching temperature it is important to note that the switching temperature of pure vanadium dioxide is around $68^\circ C$, making it impractical for building temperature regulating applications. The switching temperature can be reduced with elemental doping (e.g W, Mo, Nb) however this comes at a cost of solar modulation depth [49]. This result suggests that absorbing films would require less elemental doping than those which are purely re-
2.3. Results & Discussion

Figure 2.4: (a-b) Annually integrated performance metric from equation (2.9) of binary switching films (G = 0°C) as a function of switching temperature and hysteresis width for (a) reflecting films and (b) absorbing films. We note that the large areas of uniform performance outlined in red towards the top left and right of figures a and b indicate the parameters for which the coatings are entirely in low [i] or high [ii] solar transmitting states. (c) Optimum transition temperature as a function of hysteresis width for absorbing and reflecting coatings. (d) Performance at the optimum transition temperature as a function of hysteresis width for absorbing and reflecting coatings. (e,f) Diurnal variation in (e) film temperature, and (f) film transmittance for absorbing and reflecting coatings at their respective optimum switching temperatures when H = 10°C.

Reflective and thus preserve more of the solar modulation depth achievable with undoped vanadium dioxide. As described in previous works [41], we note that the optimum performance for the absorbing case for hysteresis widths of 0°C is lower than the reflecting case since some of the absorbed energy is transferred into the building as thermal energy rather than being reflected outwards. However, in Figure 2.4d, we see that the rapid decline in performance with increasing hysteresis is mitigated for absorbing films, with high performances still seen for hysteresis widths greater
than 15°C. In Figure 2.4d we compare the performances absorbing and reflecting films when both are at their respective optimum switching temperatures as a function of hysteresis width. It can be seen from Figure 2.4d that for moderate hysteresis widths of 15°C, the performance of the non-absorbing case drops to \( \sim 60\% \) of its initial value whilst the performance of the absorbing film only drops to \( \sim 95\% \). As a result we find that the absorbing case outperforms the non-absorbing case when hysteresis widths are greater than 8°C. The reason for this can be appreciated from Figure 2.4e where we see that the absorbing film reaches a significantly wider range of temperatures due to the additional dependence of film temperature on solar irradiance. The increased range of temperatures allows for the absorbing film to remain responsive throughout more of the year despite moderately large hysteresis widths. This can be seen in Figure 2.4e where film transmittance is plotted over a period of two days. We see that due to the wider range of temperatures reached, the absorbing film remains responsive despite the hysteresis width of 10°C. In contrast, during the same period, the non-absorbing film is prevented from switching and loses its functionality as a result of hysteresis.

The difference in performance between the two types of modulation is made more significant by the introduction of a gradient in the transition. In Figure 2.5 the performance metric is given as a function of switching temperature and gradient width for both absorbing and reflecting coatings (\( H = 0^\circ\text{C} \)). For the reflecting film in Figure 2.5a, as reported previously \([132]\), the increase in transition gradient results in a rapid loss of performance. Specifically in our case, as shown in Figure 2.5d, there is loss in performance of \( \sim 50\% \) for gradient widths greater
2.3. Results & Discussion

Figure 2.5: (a-b) Annually integrated performance metric from equation (2.9) of graded films (H = 0°C) as a function of switching temperature and gradient width for (a) reflecting films and (b) absorbing films. (c) Optimum transition temperature as a function of gradient width for absorbing and reflecting coatings. (d) Performance at the optimum transition temperatures as a function of gradient width for absorbing and reflecting coatings. (e,f) Diurnal variation in (e) film temperature, and (f) film transmittance for absorbing and reflecting coatings at their respective optimum switching temperatures when G = 10°C.

than 20°C. In the case of the absorbing film in Figure 2.5b the loss of performance for gradient widths of 20°C is less than 25% of its original performance. As a result of this, we see that when gradient widths are greater than 10°C, the performances of absorbing films are higher than that of reflecting films when both are at their respective optimum switching temperatures. The reasoning for this can be seen in Figure 2.5f where in the non-absorbing case, the increase in gradient results in films only partially switching between high and low temperature states and a loss in performance. The introduction of a gradient in the transition is less detrimental for absorbing films due to the interdependence of coating temperature and absorption, which results in a feedback loop that drives
the transition further towards the extremes, resulting in a much sharper transition than in the reflecting case.

When comparing the performance of thermochromic coatings in different locations we find that in the case of more extreme climates where temperatures are almost always above (see Cairo) or almost always below (see London) room temperature during daylight hours thermochromic window coatings are much less beneficial since the peak performance is actually very similar to the static none switching cases. In the low temperatures of London it would be almost equally beneficial to have a static high solar transmitting window whereas in the high temperatures of Cairo it would be similarly beneficial to have a static low solar transmitting window. In spite of this, as described in the main text, we do still see that the decreased susceptibility to the effects of hysteresis and gradient, and increased optimal transition temperatures are maintained in each location when comparing absorbing and non-absorbing films.
Figure 2.6: London study; (a-b) Annual performance of binary films ($G = 0^\circ C$) as a function of switching temperature and hysteresis width for (a) reflecting films and (b) absorbing films; $T_{\text{max}} = 0.8; T_{\text{min}} = 0.6$. (c-d) Annual performance of graded films ($H = 0^\circ C$) as a function of switching temperature and gradient width for (d) reflecting films and (e) absorbing films; $T_{\text{max}} = 0.8; T_{\text{min}} = 0.6$. 
2. Energy modelling of non-ideal thermochromic coatings

Figure 2.7: Cairo study; (a-c) Annual performance of binary films (G = 0°C) as a function of switching temperature and hysteresis width for (a) reflecting films (b) absorbing films and (c) difference of absorbing subtracted by reflecting films; $T_{\text{max}} = 0.8$; $T_{\text{min}} = 0.6$. (d-f) Annual performance of graded films (H = 0°C) as a function of switching temperature and gradient width for (d) reflecting films (e) absorbing films and (f) difference of absorbing subtracted by reflecting films; $T_{\text{max}} = 0.8$; $T_{\text{min}} = 0.6$.
2.4 Conclusions

In summary, the detrimental effects of phase transition hysteresis on performance that are apparent in non-absorbing thermochromic coatings are greatly mitigated in absorbing coatings due to an additional dependence of transition state on the intensity of incident solar radiation. This pseudo-photochromic effect is further enhanced in coatings with graded transitions between high and low temperature states, as commonly seen in nanoparticulate vanadium dioxide films. The results of this chapter can be seen as encouraging to those pursuing vanadium dioxide window coatings for passive solar control applications. Specifically, the detrimental effects of increased hysteresis and transition gradient widths have been shown to be significantly mitigated in the case of absorbing thermochromic films. Additionally, absorbing thermochromic coatings are found to have higher optimal transition temperatures compared with purely reflective coatings, such that significantly less doping may be required to give an optimal switching temperature. However, solar absorption itself is detrimental to the overall performance since it leads to thermal re-radiation from the coating into the building. Therefore, assuming that it is impossible to achieve a VO$_2$ coating with hysteresis and gradient widths of zero or without solar absorption, the realistic ideal thermochromic coating would have a hysteresis and gradient width as narrow as possible with an optimal amount of solar absorption so as to mitigate the effects of hysteresis and gradient whilst not resulting in excessive thermal re-radiation. The coated windows must also have sufficiently high insulation values to prevent absorbed solar radiation being
2. Energy modelling of non-ideal thermochromic coatings

transmitted into the building.

Although the majority of the discussion in this work has focused specifically on vanadium dioxide, these key results can be generalised to any smart window coatings that make use of absorbing thermochromic materials. Whilst these results demonstrate the significant differences between the switching dynamics of absorbing and non-absorbing films with varying degrees of transition hysteresis and gradient, it would be interesting in the future to investigate the effect of these differences on the overall reduction of heating and cooling costs within the built environment by employing a full building energy simulation, as this has so far been overlooked in the literature.
3.1 Introduction

This chapter serves to detail the methods developed to reproducibly synthesise vanadium dioxide and characterise its properties. The first section details the optimisation of the sol-gel fabrication process, the second section covers the characterisation of both the optical and transition performance, whilst the third section details the development of an optical material model for vanadium dioxide via ellipsometry.
3. Synthesis and characterisation of vanadium dioxide

3.2 Sol-gel thin film fabrication

3.2.1 Precursor synthesis

As mentioned previously there are many routes to synthesis VO$_2$. In the case of this thesis a sol-gel spin coating process was used initially since the relevant equipment was readily available. The method was found to be effective at producing high performance prototype coatings with good control over thickness as we will see in Chapter 4. Plans to scale up production are described in Chapter 6. The VO$_2$ precursor used throughout this thesis is vanadium oxalate, which we obtain by reducing vanadium pentoxide (V$_2$O$_5$) with oxalic acid dihydrate at a 1:3 molar ratio in solution anhydrous ethanol, such that

$$V_2O_5 + 3[C_2H_2O_4.2(H_2O)] \rightarrow 2[VO(C_2O_4)_2.x(H_2O)] + 2CO_2 + (6-2x)(H_2O)$$

The solution is left to react for 12 hours at 80 °C under magnetic stirring. Whilst being heated the solution container is connected to a condenser, such that evaporated solvent is returned to the solution and the solution concentration is maintained. Afterwards, the blue coloured solution is filtered and diluted to the desired concentration with anhydrous ethanol.

3.2.2 Coating formation and annealing

3.2.2.1 Process overview

The fused silica wafer substrate is exposed to an oxygen plasma for 1 min and then moved immediately to the spin coater. The precursor solution is then deposited on to the substrate using a pipette until the substrate is completely wetted. The spin coater is then ramped up to set speed
3.2. Sol-gel thin film fabrication

at 2000 RPM/s and remains at set speed for 40 s. After coating the substrated is moved immediately to a hot plate at 100 °C for 15 min. The coated sample is then moved into a glass vacuum tube (1 atm) inside a tube furnace at 150 °C for 15 min. The glass vacuum tube is then exposed to vacuum to lower the pressure to ~ 10 mbar. Once the pressure is stable at ~ 10 mbar the tube furnace temperature is ramped up by 20 °C/min to 550 °C and held at the set temperature for 1 hour. A schematic of the annealing setup is shown in Fig. 3.1 and further detail of each step, including the reasoning behind each process step, is given in the following.

![Figure 3.1](image)

**Figure 3.1**: Schematic of vacuum exposed tube-furnace setup used for synthesis of VO₂.

### 3.2.2.2 Spin coating

The coating is initially formed on the substrate via spin coating. To ensure that the coating adheres well to the surface, all substrates are exposed to an oxygen plasma for 1 min before coating to form hydrophilic groups at the surface. The thickness of the coating is defined by the spin
speed. The relation between thickness and spin speed is given by [144]

\[ t = \frac{A}{\sqrt{\omega}} \]  

(3.1)

where \( \omega \) is the spin speed, and \( A \) is a solution specific constant that depends on physical properties such as concentration of solutes and viscosity. For a given solution, the constant \( A \) can be determined empirically by coating with a certain spin speed and measuring the film thickness obtained (after all subsequent process steps are complete). Once \( A \) is known the spin speed can then be adjusted appropriately to obtain a thin film coating of desired thickness; the accuracy of this thickness optimisation method is demonstrated in Chapter 4.

### 3.2.2.3 Baking

After spin coating the sol-gel is immediately dried in air at 100 °C on a hot plate to remove excess solvent from the coating before it is subsequently annealed. This drying step was found to be critical to the final coating quality since if the film was not fully dried before being exposed to vacuum, the resulting surface of the film would roughen and the coating would exhibit cracks due to the rapid evaporation of moisture from the film. Additionally, it was noted that this would also happen if the film was left for a short time (1-2 minutes) between being dried and put into the furnace. It appears that the dried sol-gel is hygroscopic and re-absorbs moisture from the atmosphere, which has also been reported in other vanadium oxide sol-gels [145]. The re-absorption of moisture in the films was minimised by preheating the furnace to 120 °C and leaving the samples inside to once again dry in air for 15 minutes before applying
3.2. Sol-gel thin film fabrication

vacuum.

3.2.2.4 Annealing

The formation of high purity vanadium dioxide relies on precise control of the oxygen content during annealing. To control the oxygen content in our vacuum tube, the vacuum was partially opened to ambient air (see Fig. 3.1). It was found that VO$_2$ was formed when the pressure near the inlet was measured at around 10 mbar, whilst at higher or lower pressures, V$_2$O$_5$ or amorphous VO$_x$ would be obtained respectively. This system generally worked well but we found that the results were not always consistent, with the optimal pressure drifting over time.

![Figure 3.2: Raman microscope images and measured Raman spectra across a single VO$_2$ film. The peaks at $\sim$ 140, 192, 223, 260, 308, 338, 387, 395, 440, 482, 497, 588, 613, 661 and 823 cm$^{-1}$ are assigned to the VO$_2$(M1) phase [18-20]. The broad peak at $\sim$ 613 cm$^{-1}$ is a convolution of the peaks at 588, 613 and 661 cm$^{-1}$. The low frequency phonons at 192 and 223 cm$^{-1}$ correspond to lattice motion involving V-V bonds [21], whilst the peak at 140 cm$^{-1}$ has previously been attributed to soft-phonon vibrations [19, 22]. The rest of the peaks are assigned to vibrational modes of V-O bonds [21, 23]. From left to right, pure VO$_2$ is oxidised with increasing oxygen content along the length of the furnace. The Raman peaks for VO$_2$ become less well defined as the sample is oxidised.](image-url)
A potential inconsistency identified was the humidity of the ambient air. Any increase in humidity in the air intake would mean that the partial pressure of oxygen inside the vacuum was lower than expected. To avoid this inconsistency the vacuum air intake was passed through a highly hygroscopic material, however the resultant increase in the partial pressure of oxygen inside the vacuum tube meant that the pressure had to be decreased significantly. In fact, after flushing through with dry air and fully sealing the vacuum, it was found that the films would still oxidise to $\text{V}_2\text{O}_5$. However, since there is a gradient in pressure across the vacuum tube with the lowest pressure point closest to the vacuum inlet, a further degree of oxygen content control is available by moving the samples within the furnace closer to the vacuum pump (previously all samples were placed in the center of the furnace).

### 3.2.2.5 Raman microscope analysis

To determine the crystalline phase of the fabricated samples, Raman spectroscopy was performed using a Renishaw inVia confocal Raman microscope. It was found, as can be expected, that the first signs of oxidation to $\text{V}_2\text{O}_5$ are observed at the surface of the films. Figure 3.2 shows several Raman microscope images taken along the length of a VO$_2$ sample annealed at the critical point in the furnace where oxidation to $\text{V}_2\text{O}_5$ starts to occur. From this we can see how the oxidation of VO$_2$ in these conditions is far from uniform, instead separate fractal-like crystallites of $\text{V}_2\text{O}_5$ are formed in the low oxygen environment, as evidenced from the additional weak Raman signal for $\text{V}_2\text{O}_5$ when focusing the Raman excitation on the dark fractal-like regions. This visual method of identifying
oxidation was very useful for quickly determining the region of highest purity VO\textsubscript{2} which could then be confirmed with Raman spectroscopy and XRD (shown in Chapters 4 and 5). When performing Raman analysis on VO\textsubscript{2} it is critical to limit the laser power used, since excessive laser power may result in the sample heating up and transitioning into the metallic rutile state; 1\% laser power was found to be sufficiently low to not cause significant heating of the sample.

### 3.3 Characterising performance

#### 3.3.1 Optical performance

To characterise the optical performance we must determine the transmittance, reflectance and absorption of the sample in both the monoclinic semiconducting state and rutile metallic state across the full solar spectrum (300 - 2500 nm). The set up used is quite simple, but not entirely standard, so it is worth discussing the verification of its accuracy. For transmittance measurements the samples are placed onto a proportional-integral-derivative (PID) controlled heat stage positioned between two optical fibres (source and probe). The probe fibre is moved as close as possible to the back of the sample to limit any loss of light due to scattering (see Figure 3.3), however this was generally found to be minimal for the samples examined. To verify that all transmitted light was being captured, measurements of a VO\textsubscript{2} film taken with this scheme were compared to measurements taken using an integrating sphere in the short wavelength range (300 - 1000 nm) and were found to be equivalent, as can be seen in Figure 3.4. The transmittance is calculated from the
3. Synthesis and characterisation of vanadium dioxide

Figure 3.3: Temperature controlled set-up used for characterising optical and transition performances: source fibre (A), probe fibre (B), thermocouple on stage (C), thermocouple on sample (D).

Figure 3.4: Comparison of measurements made using the optical fibre and integrating sphere set-ups.

measured intensity by

\[
T = \frac{I - I_d}{I_0 - I_d}
\]

(3.2)

where \(I\) is the measured intensity though the sample \(I_d\) is a dark intensity measurement taken without the source and \(I_0\) is a reference transmitted intensity measured for an uncoated glass substrate.

Reflectance measurements were taken with a different set-up with a combined two-channel source-probe fibre (see Fig. 3.3). To determine the reference reflectance spectra, we need to use a reference sample with a
known reflectance (a plain silicon wafer was used). The reference spectra \( I_0 \) from equation 3.2 is instead given by

\[
I_0 = \frac{I_r - I_d}{R_r}
\]  

(3.3)

where \( I_r \) is the measured reference intensity and \( R_r \) is the known absolute reflectance of the reference sample. The absolute reflectance of the sample is then given by

\[
R = \frac{I - I_d}{I_0}.
\]  

(3.4)

3.3.2 Transition performance

In brief, the transition temperature, hysteresis width and gradient are calculated by monitoring the infrared transmittance through the film (\( \lambda = 1800 \text{ nm} \)) as a function of time whilst the sample is heated up and cooled down. The temperature of the sample is also monitored during this time and both time series data sets are then used to construct a full hysteresis loop.

To measure temperature we use a thermocouple attached to the heat stage (separate from the one used with the PID controller). Since the sample is mounted on an area of the heat stage where there is a hole, there is a significant difference between the measured temperature and the sample surface that must be accounted for. To account for this the temperature difference between these two points was measured as a function of time using two thermocouples (see Fig. 3.3). Figure 3.5 shows this temperature difference as a function of the measured stage temperature, along with derived fitting functions for heating and cooling steps. To ensure that the calibration curves can be fit with simple functions
within the extremes of the transition, the set temperature of the stage was set at 120 °C, well above the transition temperature of undoped VO$_2$ (68 °C), the effect of this is that the heat stage was constantly heating until the VO$_2$ was fully switched. This was done to avoid fluctuations in the calibration introduced by the PID controller, which can be seen above 80 °C due to the power supplied to the heat stage starting to switch on and off so that it does not overshoot the set temperature. A

![Figure 3.5](image)

**Figure 3.5:** The temperature difference between sample and stage as function of stage temperature.

test of the empirically derived calibration functions is shown in Figure 3.6. The point at which the temperature difference still deviates is well above the transition temperature so will not effect the accuracy of the calibration. A comparison between measured hysteresis loops before and after calibration of the heat stage can be seen in Figure 3.7, which shows the importance of performing such calibrations. To calculate the metrics of transition performance we take the first derivative of the heating and cooling portions of the hysteresis loop. The maximum point of the resulting peaks defines the transition temperature for heating and cooling respectively, with the difference between these two values defining the
3.3. Characterising performance

**Figure 3.6**: Temperature difference between stage and sample as a function of time before and after calibration.

**Figure 3.7**: Comparison between hysteresis loops before (solid lines) and after calibration (dashed lines).

hysteresis width. The transition gradient width for heating and cooling steps is then defined as the full width of half maximum (FWHM) of the peaks (see Fig. 3.8). When discussing transition temperature or gradient width without specifying heating or cooling, we are referring to the average of the values calculated for the heating and cooling steps.
3. Synthesis and characterisation of vanadium dioxide

Figure 3.8: Analysis of hysteresis loops before (solid lines) and after calibration (dashed lines).

3.4 Determining the optical constants of vanadium dioxide

3.4.1 Optical constants

Before introducing the concept of optical constants it is important to introduce the concept of dielectric polarisation in response to an electric field. The electric susceptibility $\chi$ is a dimensionless proportionality constant that indicates the degree of polarization of a dielectric material in response to an applied electric field $E$. The greater the electric susceptibility, the greater the ability of a material to be polarised in response to the field, and thereby reduce the total electric field inside the material. It is in this way that the electric susceptibility influences the electric permittivity of the material and thus influences many other phenomena in that medium e.g., the capacitance of capacitors and the speed of light.

The polarisation density $P$ within a material is given by [37]

$$P = \epsilon_0 \chi E.$$  

(3.5)
3.4. Determining the optical constants of vanadium dioxide

where \( \epsilon_0 \) is the permittivity of free space.

Electric susceptibility is related to two dimensionless optical constants which will be referred to frequently in the following: the complex relative permittivity \( \epsilon \) and the complex refractive index \( \tilde{n} \) defined as

\[
\epsilon = \epsilon_1 + i \epsilon_2 = \tilde{n}^2 = (n + i \kappa)^2 = \chi + 1,
\]

with their components related by

\[
\epsilon_1 = n^2 + \kappa^2 \quad (3.7)
\]

and,

\[
\epsilon_2 = 2n\kappa
\]

and,

\[
n = \sqrt{\frac{|\epsilon| + \epsilon_1}{2}}
\]

\[
\kappa = \sqrt{\frac{|\epsilon| - \epsilon_1}{2}}
\]

where \( |\epsilon| = \sqrt{\epsilon_1^2 + \epsilon_2^2} \).

The optical responses of non-magnetic materials can be fully described provided that these constants are known for the wavelength range of interest [37]. For non-absorbing materials where \( \kappa = 0 \), the electric field amplitude of a plane wave propagating through a medium with refractive index \( n \) in the \( z \)-direction at time \( t \) is given by

\[
E(z, t) = E_0 e^{i \frac{2\pi}{\lambda} (nz - ct)}
\]

where \( E \) and \( E_0 \) are the electric field amplitudes in the medium and free-space respectively and \( \lambda \) and \( \omega \) are the wavelength the angular frequency of the wave respectively. If \( \kappa > 0 \) the equation then becomes,

\[
E(z, t) = e^{-\frac{2\pi}{\lambda} \kappa z} E_0 e^{i \frac{2\pi}{\lambda} (nz - ct)}.
\]

\[
(3.10)
\]
where it can be seen that $E$ is exponentially attenuated with distance. Since intensity is proportional to the square of the amplitude we can also write,

$$I(z) = I_0 e^{-\alpha z} \quad (3.11)$$

where $I_0$ is the intensity at the interface ($z = 0$) and $\alpha = 4\pi\kappa/\lambda$ is the attenuation coefficient.

The complex dielectric constant of a material can be considered as a sum of contributions due to optical response from different microscopic parts, with potential contributions from permanent dipoles, displacement of charged ions or electrons, inter-band transitions of valence electrons, or molecular vibrations. Essentially, the optical response of a material results motion of charges in response to the electromagnetic field of the light, and can therefore be well represented by a summation of different oscillators.

$$\epsilon_1 = \epsilon_\infty + \sum_i \epsilon_{1,i} \quad \epsilon_2 = \sum_i \epsilon_{2,i} \quad (3.12)$$

where $\epsilon_{1,i}$ and $\epsilon_{2,i}$ are real and imaginary parts of dielectric function of the $i$th oscillator respectively and $\epsilon_\infty$, often referred to as the background permittivity, is the permittivity as wavelengths tend to 0. The oscillators used to define the optical properties of materials in this thesis are introduced here.

3.4.1.1 Lorentz model

The motion of a bound electron can be considered equivalent to the classical equation of motion for mass on a spring with damping and driving forces and is appropriate for semiconductors and insulators to
account for dispersion arising from bound charges, the equation of motion of a charge $-e$ with mass $m$ bound by a harmonic force and acted on by an electric field $\mathbf{E}$ is given by \[m \left( \frac{d^2 z}{dt^2} + \gamma \frac{dz}{dt} + \omega_0^2 z \right) = -e \mathbf{E} \tag{3.13}\]

where $\gamma$ is a damping force and $\omega_0$ is the resonant frequency and $z$ is the displacement of the charge. The dipole moment $p$ of a single charge is given by

$$p = -ez = \frac{e^2 \mathbf{E}}{m} \frac{1}{\omega_0^2 - \omega^2 - i\omega \gamma}. \tag{3.14}$$

Assuming a charge density $n_e$ and taking a sum of the dipole moments, the polarisation density is given by

$$P = n_e p = \frac{n_e e^2 \mathbf{E}}{m} \frac{1}{\omega_0^2 - \omega^2 - i\omega \gamma}. \tag{3.15}$$

which we can relate back to equation 3.5 & 3.6 to recover the Lorentz model for $\epsilon(\omega)$,

$$\epsilon(\omega) = 1 + \frac{\omega_p^2}{(\omega_0^2 - \omega^2 - i\omega \gamma)^2} \tag{3.16}$$

where $\omega_p$ is the plasma frequency i.e. the natural oscillation frequency of electrons in a material in response to a small charge separation, which is given by,

$$\omega_p = \sqrt{\frac{n_e e^2}{\epsilon_0 m}}. \tag{3.17}$$

The real and imaginary components of equation 1.18 are given by

$$\epsilon_1(\omega) = 1 + \frac{\omega_p^2 (\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \omega^2 \gamma^2}$$

$$\epsilon_2(\omega) = \frac{\omega_p^2 \omega \gamma}{(\omega_0^2 - \omega^2)^2 + \omega^2 \gamma^2}. \tag{3.18}$$
3.4.1.2 Drude model

The Drude model assumes a free electron gas oscillating in the electromagnetic field. The Drude model can therefore be used to describe the movement of free electrons in metals or charge carriers in semiconductors. Since the electrons in this case are not bound, the restoring force in the Lorentz model is absent and there is no resonant frequency ($\omega_0 = 0$) such that

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{(\omega^2 + i\omega\gamma)}$$  \hspace{1cm} (3.19)

where the damping parameter $\gamma$ in this case is related to the scattering time in the material $\tau_{SC} = 1/\gamma$. The real and imaginary parts of equation 1.21 are given by,

$$\epsilon_1(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \gamma^2}$$

$$\epsilon_2(\omega) = \frac{\omega_p^2\gamma}{\omega^3 + \omega\gamma^2}$$  \hspace{1cm} (3.20)

3.4.2 Light in layered media

3.4.2.1 A single interface

The kinematic properties of light at an interface, i.e. the angles of refraction and reflection, follow directly from the wave nature of light and the fact that boundary conditions must be satisfied, they do not depend on the specific properties of the field. The magnitude of the wave numbers $k$ of incident, refracted and reflected fields illustrated in figure 3.9 are given by,

$$|k_i| = |k_r| = k_i = \frac{2\pi c}{\lambda} \sqrt{\epsilon_i}$$

$$|k_t| = k_t = \frac{2\pi c}{\lambda} \sqrt{\epsilon_t}$$  \hspace{1cm} (3.21)

The existence of boundary conditions requires that the spatial and time
3.4. Determining the optical constants of vanadium dioxide

![Diagram showing transmission and reflection of light at a single incidence]

**Figure 3.9:** Transmission and reflection of light at a single incidence, split into components parallel (p) and perpendicular (s) to the plane of incidence.

The variation of all fields must be the same at \( z = 0 \), such that,

\[
(k_i \cdot z)_{z=0} = (k_t \cdot z)_{z=0} = (k_r \cdot z)_{z=0}
\]  

(3.22)

and,

\[
k_i \sin \theta_i = k_t \sin \theta_t = k_r \sin \theta_r
\]

(3.23)

since \( k_i = k_r \) we can see that the angle of incidence \( \theta_i \) is equal to the angle of reflection \( \theta_r \). The angle of refraction \( \theta_t \) can be described by Snell’s law,

\[
\frac{\sin \theta_i}{\sin \theta_t} = \frac{k_r}{k_i} = \sqrt{\epsilon_t} = \frac{n_t}{n_i}
\]

(3.24)

The dynamic properties, i.e. the intensities of reflected and refracted radiation and the changes in phase and polarisation, depend on the specific properties of the field at the interface and the associated boundary conditions. The boundary conditions at the interface state that the normal components of \( \mathbf{D} \) and \( \mathbf{B} \) and the tangential components of \( \mathbf{E} \) and \( \mathbf{H} \) are continuous at the interface. By applying the boundary conditions to Maxwell equations, the amplitude transmittance \( t \) and reflectance \( r \) of the fields at the interface can be recovered, as given by the Fresnel
3. Synthesis and characterisation of vanadium dioxide

equations [135],

\[
\begin{align*}
    r_s &= \frac{n_1 \cos \theta_i - n_2 \cos \theta_t}{n_1 \cos \theta_i + n_2 \cos \theta_t} \\
    t_s &= \frac{2n_1 \cos \theta_i}{n_1 \cos \theta_i + n_2 \cos \theta_t} \\
    r_p &= \frac{n_2 \cos \theta_i - n_1 \cos \theta_t}{n_1 \cos \theta_i + n_2 \cos \theta_t} \\
    t_p &= \frac{2n_1 \cos \theta_i}{n_1 \cos \theta_i + n_2 \cos \theta_t}
\end{align*}
\] (3.25)

The subscripts \( s \) and \( p \) define the polarisation of the light relative to the plane of incidence, \( s \)-polarised is perpendicular to the plane containing the incident, reflected and refracted waves\(^1\), whilst \( p \)-polarised is parallel to the plane of incidence; these definitions are also illustrated in Figure 3.9. Any elliptical polarisation of light can be represented as a combination of the \( s \)- and \( p \)-polarised components.

The transmittance and reflectance intensities of the \( s \) and \( p \) components are given by,

\[
\begin{align*}
    T_{s,p} &= \frac{n_2 \cos \theta_i}{n_1 \cos \theta_i} |t_{s,p}|^2 \\
    R_{s,p} &= |r_{s,p}|^2
\end{align*}
\] (3.26)

3.4.2.2 Coherent layers

The phase of the wave becomes very important when considering interference arising from multiple reflections in a coherent layer. When describing light refracted through a material of thickness \( d \) and complex refractive index \( \tilde{n} \), it is useful to define a parameter \( \phi \) to encompass both phase change and attenuation,

\[
\phi = \frac{2\pi \tilde{n}d \cos \theta_t}{\lambda}
\] (3.27)

\(^1\)The label \( s \)-polarised derives the German, *senkrecht*, meaning perpendicular.
The overall *coherent* reflection amplitude resulting from the internal reflections shown in 3.10 can be given by the Airy summation \[135\],

\[
r = r_{12} + t_{12} r_{23} e^{-2i\delta} + t_{12} t_{21} r_{23} r_{21} e^{-4i\delta} + \cdots = \frac{r_{12} + r_{23} e^{-2i\delta}}{1 - r_{21} r_{23} e^{-2i\delta}}
\] (3.28)

Similarly, the coherent transmission amplitude is given by,

\[
t = t_{12} t_{23} e^{-2i\delta} \left[ 1 + r_{23} r_{21} e^{-2i\delta} + (r_{23} r_{21} e^{-2i\delta})^2 + \cdots \right] = \frac{t_{12} t_{23} e^{-i\delta}}{1 - r_{21} r_{23} e^{-2i\delta}}
\] (3.29)

### 3.4.2.3 Incoherent layers

When light passes through an incoherent layer where phase coherence is not preserved, transmittance and reflectance amplitudes are undefined and instead the transmittance and reflectance intensities are calculated \[135\], as given by

\[
R = R_{12} + \frac{T_{12}^2 R_{23} e^{-2\alpha d}}{1 - R_{21} R_{23} e^{-2\alpha d}}
\]

\[
T = \frac{T_{12} R_{23} e^{-\alpha d}}{1 - R_{21} R_{23} e^{-2\alpha d}}
\] (3.30)

where \(d\) is the layer thickness and \(\alpha = 4\pi \kappa /\lambda\) is the attenuation coefficient. When modelling real layered materials a combination of coherent and incoherent contributions is often required.
3.4.3 Principle of ellipsometry

In brief, ellipsometry uses the theory described in the previous section to relate measured changes in phase and polarisation of light reflected from a material, to the optical constants and thickness of that material. The changes in polarisation and phase are parametrised by the amplitude component $\Psi$ and the phase difference $\Delta$ respectively. Importantly, both $\Psi$ and $\Delta$ can be fully described using the Fresnel equations, provided that we know the refractive index ($n$), the extinction coefficient ($k$), and the thickness ($t$) of the film. $\Psi$ and $\Delta$ are related to the amplitudes of the $s$ and $p$ components of the reflected light by [146]

\[
\frac{r_p}{r_s} = \tan(\Psi)e^{i\Delta} \quad (3.31)
\]

If the thickness was the only unknown variable then we would only need to measure one wavelength at one angle. However when fitting with all unknown ($n, k, t$) values there may actually end up being multiple sets of variables that give the same result for a single wavelength and angle, and only one of these sets of $n, k, t$ is the correct physical result. If a material is transparent (i.e. $k = 0$) it is enough to measure at a single wavelength and vary the angle to determine $n$ and $t$, since if we change the angle of incidence then the measured / calculated $\Psi$ and $\Delta$ will also change. The correct physical values for $n$ and $t$ would then be those that match for all angles of incidence. The situation becomes more complicated if the material is absorbing (i.e $k > 0$) in this case a spectroscopic measurement can be used to determine if the fit is the correct physical result, since the complex dielectric function must also
satisfy the Kramers–Kronig relations [146].

**Figure 3.11:** Ellipsometric analysis of (a-c) VO\(_2\)(M) and (d-f) VO\(_2\)(R). (a,d) Derived optical constants. (b,e) Measured and theoretically derived (dashed lines) \(\Delta\) for multiple angles of incidence (50\(^\circ\), 60\(^\circ\), 70\(^\circ\)). (c,f) Measured and theoretically derived (dashed lines) \(\Phi\) for multiple angles of incidence (50\(^\circ\), 60\(^\circ\), 70\(^\circ\)).

A Semilabs SE-2000 ellipsometer was used to determine the optical constants of vanadium dioxide thin films in the 250-1650 nm wavelength range. The dielectric function of the low temperature monoclinic state was modelled using six Lorentz oscillators which aptly describe light-matter interaction with the tightly bound electrons of the semiconducting state, whilst the high temperature rutile state was modelled using six Lorentz oscillators and three additional Drude oscillators to describe the motion of free electrons in the metallic state. The fitting of both states had a high degree of fitting accuracy \((R^2 > 0.995)\). The film thickness was determined to be 87 nm with a 7 nm roughness defined as a gradient layer with material fill fractions varying linearly between VO\(_2\) and air. The effective refractive index of the gradient structure was defined as a function of depth using Bruggeman effective medium theory [147].
The film thickness calculated from ellipsometry is in good agreement with electron microscopy observations (see Figure 3.12) and the optical constants are similar to those found from the literature [109, 148]. The optical constants derived here will be used in the next chapter to design multilayer thin film coatings with optimal optical performances.

**Figure 3.12:** Electron microscopy image of vanadium dioxide thin film. Scale bars corrected for a 45° observation angle.
4.1 Introduction

There are many advantages to using thin film vanadium dioxide instead of nanoparticulate vanadium dioxide in smart window coatings. Specifically, with regards to those factors found to be critical to the overall energy saving performance in Chapter 2, thin film vanadium dioxide typically exhibits reduced hysteresis and gradient widths compared to nanoparticulate coatings. Furthermore, thin films do not absorb as much solar radiation so thermal re-radiation from the window into the building is reduced. The fabrication methods for thin films are also more applicable for industrial scales, with PVD, CVD and spray-coating methods all well suited to an in-line fabrication process at the point of glass manufacture.
However, despite many efforts to design high performance coatings based on thin film vanadium dioxide [8, 35, 109, 149–151] none of these efforts has been able to achieve optical performances (i.e. solar modulation and visible transmittance) comparable to that of the best nanoparticle composites. In this chapter, the optical constants for vanadium dioxide derived in Chapter 3 are used to derive an optical performance limit for thin film vanadium dioxide coatings, which we find to be far beyond current literature achievements. A multilayer coating is then designed to approach the optical performance limit, after which the optimised coating design is fabricated and characterised using the methods described in Chapter 3.

The reason for the poor performance of thin film vanadium dioxide as a dynamic window coating material can be appreciated from its optical constants. In Figure 4.1a we see that as a result of the transition from low-temperature VO$_2$(M) to high temperature VO$_2$(R), the extinction coefficient increases across all solar wavelengths; conversely, for the refractive index, increases are seen only at longer wavelengths (> 2000 nm) whilst decreases are seen below this wavelength. These opposing changes in extinction coefficient and refractive index mean that changes in absorption and reflectance are typically found to oppose each other in thin films [152], which dramatically reduces solar transmittance modulation. To this end, this chapter introduces an alternative approach based on optical impedance matching in thin films, where the opposing changes in optical constants are no longer detrimental to solar modulation but rather taken advantage of in the optical design of the coating.

In this chapter, x-ray diffraction measurements were performed by
4.2 Thin film performance limit

In the idealised design, a thin film of vanadium dioxide is sandwiched between two transparent impedance matching layers (see Fig. 4.1b), with the surrounding layers designed to optically impedance match between the low-temperature VO$_2$(M) state and the surrounding environment. In this case, when in the low temperature VO$_2$(M) state, reflections are minimised across the entire solar spectrum and solar transmittance is maximised. When the thermochromic transition occurs, the impedance matching condition is broken and broadband increases in reflectance are

**FIGURE 4.1:** Deriving solar control limits of thin film vanadium dioxide dynamic window coatings: (a) Thermochromic response of vanadium dioxide. Low temperature optical constants subtracted from high temperature optical constants. (b) Schematic of idealised design for maximum solar control. (c) Simulated reflectance and transmittance of idealised structure for 100 nm thick vanadium dioxide in high-temperature (red) and low-temperature (blue) states. (d) Derived solar control performance limit at normal incidence compared with previous literature and the experimentally demonstrated coating in this work.

GKL, the electron microscopy images were provided by TL, and haze characterisations were performed by MP.
achieved (see Fig. 4.1c); by matching optical impedance into and out-of the thin film in its low-temperature VO\(_2\)(M) state, the thermochromic response is utilised beneficially for solar control regardless of whether the change in refractive index is positive or negative, therefore maximising solar modulation. Figure 4.1d shows this derived theoretical limit for thin film vanadium dioxide in comparison with current literature and also this work. A design approaching the perfect index matching limit could conceivably be achieved using a graded-index nanostructure or many ultra-thin layers to form a graded-index composite. However, until ultra-thin-film coating technologies and large scale nanofabrication methods mature, simpler solutions that are viable in the window coating industry must be considered.

### 4.3 Impedance matching layers

Alternatively, if we restrict our impedance matching condition to shorter wavelengths where solar irradiance is highest (400-1000 nm), it can largely be achieved using thin film interference effects with only a few layers and, as we demonstrate here, provide great improvements to solar modulation. The materials used are silica, amorphous titania, and anatase titania. These materials are chosen both for their optical properties (see Fig. 4.2) and because of their well established viability in the window coating industry, for example in hydrophilic self-cleaning coatings [42]. The top two silica and titania layers have refractive indices (\(n_D = 1.41\) and 1.89 respectively) ranging between that of air and VO\(_2\)(M) so are able to effectively impedance match between air and VO\(_2\)(M), provided
4.3. Impedance matching layers

that appropriate thicknesses are chosen. The bottom layer is a crystalline anatase titania layer (see Fig. 4.3) with a refractive index \( n_D = 2.08 \) between that of the fused silica substrate \( n_D = 1.43 \) and VO\(_2\)(M), with the layer thickness also chosen such that optical impedance is matched between VO\(_2\)(M) and the silica substrate.

![Graph showing optical constants of impedance matching layers]

**Figure 4.2**: Optical constants of impedance matching layers as derived from ellipsometry.

### 4.3.1 Synthesis of silica sol.

A mixture of hydrochloric acid (37%, extra pure, Fisher Chemical), H\(_2\)O and half of the prescribed amount of anhydrous ethanol was slowly added at room temperature to a solution of tetraethyl orthosilicate ([Si(OEt)\(_4\)], TEOS, 98%, Acros Organics) in the other half of the anhydrous ethanol. The clear solution was stirred for 1 d in a sealed glass vial and was used without further purification. The molar ratios of the reactants were as follows: (TEOS : H\(_2\)O : HCl : ethanol = 1:4:0.01:20).
4.3.2 Synthesis of titania sol.

A solution of titanium(IV) isopropoxide (TTIP) (Sigma-Aldrich, > 97%), anhydrous isopropanol (IPA) and acetic acid (CH$_3$COOH) (Sigma-Aldrich, > 99.5%) was kept stirring for 0.5 h and used soon after. The volume ratios of the reactants were as follows: (TTIP : IPA : CH$_3$COOH = 1:5:0.4).

4.3.3 Fabrication of thin films.

The spin solutions were uniformly cast onto fused silica substrates by spin-coating at a range of spin speeds for 30 s (SCS G3 Spin Coater). All the spin-cast films were aged in a box furnace at 100 °C for 10 min to remove any remaining solvent. The subsequent heat treatments varied for each desired material. Amorphous titania TiO$_2$(a) and silica SiO$_2$ were obtained by heating in a box furnace at 150 °C for a further 1 h, anatase titania TiO$_2$(A) were obtained by annealing in tube furnace at 550 °C in air for 1 h. Raman and x-ray diffraction (XRD) analysis showing the crystal phases within the sample are shown in Figure 4.3. The XRD measurements were performed using a Bruker-Axs D8 (GADDS) diffractometer.

4.4 Multilayer optimisation

When calculating the transmission and reflection from multilayer films, the previously discussed methods quickly become tedious and complicated as layers increase in number. The amplitudes of forward and back-
Figure 4.3: Identification of crystalline material phases within the sample. (a) Raman spectrum of the multilayer sample. The peaks at \( \sim 140, 192, 223, 260, 308, 338, 387, 395, 440, 482, 497, 588, 613, 661 \) and 823 cm\(^{-1}\) are assigned to the VO\(_2\)(M1) phase \([18–20]\). The broad peak at \( \sim 613 \) cm\(^{-1}\) is a convolution of the peaks at 588, 613 and 661 cm\(^{-1}\). The low frequency phonons at 192 and 223 cm\(^{-1}\) correspond to lattice motion involving V-V bonds \([21]\), whilst the peak at 140 cm\(^{-1}\) has previously been attributed to soft-phonon vibrations \([19, 22]\). The rest of the peaks are assigned to vibrational modes of V-O bonds \([21, 23]\). (b) X-ray diffraction spectrum of sample showing peaks for both TiO\(_2\)(A) (101) \([24]\) and VO\(_2\)(M1) (011, 220) \([25, 26]\).

ward propagating light at each interface (see figure 4.4) can instead be calculated via a transfer matrix method \([135]\).

In the transfer matrix method, the amplitudes of light waves are related between each interface by a dynamic matrix \(D\) defined as,

\[
\begin{pmatrix}
A_1 \\
B_1
\end{pmatrix} = D_{12} \begin{pmatrix}
A'_2 \\
B'_2
\end{pmatrix} \quad (4.1)
\]

where

\[
D_{12} = \begin{pmatrix}
\frac{1}{2} \left( 1 + \frac{k_2}{k_1} \right) & \frac{1}{2} \left( 1 - \frac{k_2}{k_1} \right) \\
\frac{1}{2} \left( 1 - \frac{k_2}{k_1} \right) & \frac{1}{2} \left( 1 + \frac{k_2}{k_1} \right)
\end{pmatrix} \quad \text{for s-component} \quad (4.2)
\]
4. Multilayer thin film vanadium dioxide coatings

Figure 4.4: Amplitudes of forward and backward propagating light in the transfer matrix method.

\[ D_{12} = \begin{pmatrix} \frac{1}{2} \left(1 + \frac{n_1^2 k_1}{n_2^2 k_2}\right) & \frac{1}{2} \left(1 - \frac{n_1^2 k_1}{n_2^2 k_2}\right) \\ \frac{1}{2} \left(1 - \frac{n_1^2 k_1}{n_2^2 k_2}\right) & \frac{1}{2} \left(1 + \frac{n_1^2 k_1}{n_2^2 k_2}\right) \end{pmatrix} \text{ for } p\text{-component.} \quad (4.3) \]

Within each layer a propagation matrix \( P \) accounts for the attenuation and phase change of the light as it propagates within each layer, given by

\[
\begin{pmatrix} A'_2 \\ B'_2 \end{pmatrix} = P_2 \begin{pmatrix} A_2 \\ B_2 \end{pmatrix} = \begin{pmatrix} e^{i\delta_2} & 0 \\ 0 & e^{-i\delta_2} \end{pmatrix} \begin{pmatrix} A_2 \\ B_2 \end{pmatrix} \quad (4.4)
\]

The amplitudes at the outer interfaces of a multilayer stack with \( N \) layers are thus given by

\[
\begin{pmatrix} A_0 \\ B_0 \end{pmatrix} = D_{01} P_1 D_{12} P_2 D_{23} \ldots D_{(N-1)N} P_N D_{Ns} \begin{pmatrix} A'_s \\ B'_s \end{pmatrix} \quad (4.5)
\]

where the subscripts 0 and \( s \) denote the incident medium and substrate respectively. The transmission and reflection coefficients are then given by,

\[
r = \frac{B_0}{A_0} \quad t = \frac{A'_s}{A_0} \quad (4.6)
\]

from which the transmittance, reflectance and absorption can be calculated.
When optimising the structure, the vanadium dioxide layer thickness was held constant at 100 nm since this was expected to transmit >50% visible light; for greater visible transmittance the thickness can be reduced at the cost of solar modulation as shown in Figure 4.1d. The surrounding impedance matching layers were varied in thickness between 20 and 300 nm. The maximum $\Delta T_{\text{sol, max}}$ and $T_{\text{lum, max}}$ from the parameter sweep were found to be 22.4% and 59.7% respectively, however these respective optimum values occur for different thickness structures so a compromise is required. A figure of merit ($FOM$) is calculated to find structures that are able compromise between the two performance metrics as defined by

$$FOM = \left( \frac{\Delta T_{\text{sol}}}{\Delta T_{\text{sol, max}}} + \frac{T_{\text{lum}}}{T_{\text{lum, max}}} \right) / 2. \quad (4.7)$$

The figure of merit is shown as a function of TiO$_2$(A) layer thickness in Figure 4.5a and as function of silica and titania top layers in Figure 4.5b.

### 4.5 Performance characterisation

In Figure 4.6a a schematic of our optimised design is shown alongside an electron microscopy (Zeiss XB1540 Crossbeam FIB-SEM Microscope) image of the fabricated structure. Figure 4.6b shows the London skyline unobstructed (left) and also as seen through the sample in its low-temperature state (right). The view has a golden tint that is characteristic of the optical absorption band of VO$_2$ ($\sim$ 500 nm). However previous works have shown that the optical absorption band can be raised via
4. Multilayer thin film vanadium dioxide coatings

Figure 4.5: Selection of layer thicknesses: (a) Selection of TiO$_2$(A) layer thickness. Peak figure of merit found from full sweep of titania and silica top layer thicknesses (20 - 300 nm) as a function of TiO$_2$(A) layer thickness. First maximum (60 nm) was chosen since thicker films (> 150 nm) at the second maximum were found to show cracks after annealing. (b) Selection of top silica and titania layers. Normalised figure of merit is plotted as a function of titania and silica top layer thickness whilst TiO$_2$(A) thickness is constant at 60 nm. Peak FOM is found for 100 nm titania thickness and 110 nm silica thickness with TiO$_2$(A) thickness of 60 nm.

doping to achieve a more neutral colour [153]. The skyline image was taken using a Samsung Galaxy S7, with exposure and focus values set automatically without the presence of the sample and held constant for the subsequent measurement through the sample. When developing window coatings an important parameter to consider is optical haze, which should be minimal for most commercial applications. The scattering behaviour of the films was measured in transmission using a Radiant-Zemax Imaging Sphere for Scatter and Appearance Measurement (IS-SA) where samples were illuminated at a normal angle of incidence at 50 nm wavelength intervals between 400 nm and 700 nm wavelengths. The light transmitted is measured as a function of transmittance angle using a detector mounted on a moving arm and the haze value is then defined as the portion of light beyond 2° from normal (see Fig. 4.7).

Figures 3c and 3d show that the measured reflectance and transmit-
4.5. Performance characterisation

**Figure 4.6**: Solution processed multilayer with record performance: (a) Electron-microscopy image of fabricated structure alongside schematic design. (b) Clear view of London skyline (left) and same view through sample in the low-temperature state (right). (c) Spectral reflectance of fabricated structure compared with simulation. (d) Spectral transmittance of fabricated structure compared with simulation. (e) Relative transmittance as a function temperature during heating and cooling. (f) First derivative of relative transmittance as a function of temperature.

**Figure 4.7**: Characterisation of visible haze. Fraction of the transmitted light that is outside 2° from normal is below 0.5% across the full visible range.

Transmittance spectra of the fabricated multilayer stack match well with simulation for both low-temperature and high-temperature states. The solar transmittance modulation of the measured spectra is 21.8% and the visible transmittance is 48.9% (see Fig. 1d for comparison with literature). Additionally, the hysteresis width and gradient width (see Fig. 3f) of the fabricated structure are both narrow (12.9 and 10.1 °C respectively)
which is critical to the overall energy saving performance [3, 85, 132] as was demonstrated in chapter 2. The transition temperature of the coating is 69.3 °C, which is typical for undoped VO$_2$; since titanium doping has been widely reported to raise the transition temperature of VO$_2$ we can infer that there was no significant diffusion of titanium ions into the VO$_2$ layer during the fabrication process.

4.6 Conclusions

In summary, this chapter has shown that the optical performance limits of thin film vanadium dioxide window coatings are significantly higher than previously reported. The theoretical observations have subsequently been used to experimentally demonstrate a simple multilayer structure that has a solar modulation far greater than any inorganic thin film thermochromic coating (> 30% greater than the previous state-of-the-art [150]) whilst maintaining a high degree of visible transparency (48.9%), and a narrow hysteresis (12.9 °C) and gradient width (10.1 °C). The additional materials used are common within the glass coating industry and the fabrication methods are scalable. Therefore, once combined with metal ion doping to optimise the transition temperature [49], we anticipate that this thin film design methodology will yield an optimal dynamic window coating highly viable for real-world application.
The effect of morphology on the transition properties of composite vanadium dioxide coatings

5

5.1 Introduction

Chapter 4, along with work in the literature, shows that improvements to luminous transmittance can be achieved by suppressing reflection of visible light with anti-reflective thin film systems [4, 8, 109, 150, 154–156]. Alternatively the optical performance can be improved through the use of composite films comprised of vanadium dioxide nanoparticles embedded in a dielectric matrix [114, 125, 126, 137, 157]. The low density and sub-wavelength dimensions of vanadium dioxide domains means that visible reflectance is minimal. Additionally vanadium dioxide nanoparticles have the benefit of exhibiting a plasmon resonance in their metallic
state which greatly improves the solar modulating performance around 1000 nm where solar irradiance is high [114]. However, most composite coatings with high solar modulations exhibit a broad hysteresis and transition gradient. The reason for this is that the probability of phase transition in vanadium dioxide depends on the density of suitable heterogeneous nucleating sites such as surface defects, dislocations and grain boundaries [158–161]. Consequently, the onset temperature of the phase transition increases (decreases) during heating (cooling) as the sizes of the nanocrystals are reduced. Chapter 2 highlighted the importance of reducing the hysteresis width of thermochromic films to improve their overall energy saving performance, as wide hysteresis loops mean that coatings are less responsive to changing climate conditions. Several previous works have shown that the hysteresis width can be reduced significantly by doping vanadium dioxide with metal ions [49, 137], however this generally results in an increase in transition gradient [49] which was also shown to be detrimental to the overall energy saving performance in Chapter 2.

So, whilst the previous chapter demonstrated ways to improve the optical performance using thin film interference effects, the additional focus of this chapter is on controlling the transition performance. Specifically, this chapter aims to demonstrate the influence of the nanostructure of composite films on both the hysteresis and gradient width of a thermochromic coating. Silica was chosen as the added composite material for its relative stability, low refractive index, and established use within the glass coating industry. Nanocomposite films of silica and vanadium dioxide with different composition were prepared by sol-gel
methods. We compare two different composite morphologies: VO$_2$ sol with SiO$_2$ nanoparticles dispersed within (samples A1-A4), and VO$_2$ sol mixed with SiO$_2$ sol (samples B1-B4). The performance of both composite types is contrasted with a plain VO$_2$ reference sample (sample V).

We demonstrate that by dispersing SiO$_2$ nanoparticles within the VO$_2$ sol, the optical performance can be improved whilst the hysteresis and gradient width remain minimal. The key results from this chapter have been accepted for publication in ref [2].

All samples discussed in this chapter were fabricated by JS. Atomic force microscopy images were provided by TL. MP provided imaging sphere measurements to determine the scattering properties of the coatings. Transmission electron microscopy (TEM) images were provided by TM. X-ray diffraction measurements were performed by DM.

### 5.1.1 Simulation of performance limits for composite films

The performance metrics $\Delta T_{\text{sol}}$ and $T_{\text{lum}}$ of vanadium dioxide composite films were simulated via a transfer matrix method [135]. The optical constants of composite films with varying compositions were calculated via the Bruggeman effective medium theory, which is well suited to modelling composite materials with both high and low fill fractions and non-spatially separated domains [162,163]. Figure 5.1 shows $\Delta T_{\text{sol}}$ and $T_{\text{lum}}$ plotted together for coating of varying thickness and compositions.

It can be seen from Figures 5.1a & 5.1b that as the silica fill fraction ($FF$) is increased, the optical performance range increases due to
5. THE EFFECT OF MORPHOLOGY ON THE TRANSITION PROPERTIES OF COMPOSITE VANADIUM DIOXIDE COATINGS

Figure 5.1: (a) Performance limits of vanadium dioxide composite coatings with different silica fill fractions (\(FF\)) with the target performance shown as a gold star. (b) Luminous reflectance as a function of film thickness for coatings with different silica fill fractions.

The suppressed visible reflectance of the silica-VO\(_2\) composite, which is a result of silica having a lower refractive index (\(\sim 1.45\)) than that of VO\(_2\). Figure 5.1b shows that the thickness of these coatings is also key to maximizing luminous transmittance since the peaks observed in Figure 5.1b are the result of thickness dependent optical interference in the thin films. Whilst optimisation of the composite thickness was outside of the scope of this study, this shows the potential optical improvements that can be achieved via the formation of such composites with precise thicknesses. These simulations, however, give no indication of the hysteresis and gradient properties of the films, both of which are key to the overall energy saving performances. This is particularly important to determine for nanocomposites, since as the size of vanadium dioxide domains decreases, the hysteresis width increases due to a decrease in suitable phase change nucleation sites [158–161]. Additionally many composite materials exhibit significant polydispersity in their components which in the case of vanadium dioxide can lead to large gradients in the phase
transition since the different sized grains have different hysteretic behaviour [158].

5.2 Fabrication of composites

Figure 5.2: TEM images of SiO$_2$ nanoparticles. Inset shows the size distribution of the nanoparticles determined by measuring the size of particles in the TEM image. Figure produced by JS.

5.2.1 Synthesis of silica nanoparticles

SiO$_2$ nanoparticle dispersions were prepared by JS according to a previously described, slightly modified procedure [164]. In short, a mixture of 50 mL of absolute ethanol, 1 ml of deionized water and 1 mL of ammonia (25%, Fisher Chemical) was heated to 40 °C. Afterward, 3 mL of TEOS were added drop-wise to the reaction mixture under vigorous stirring. After 2 h additional 2 mL of TEOS were added. This step was repeated in 2 h intervals (4x) amounting to 11 mL of TEOS in total. The nanoparticles dispersion was used as obtained without any further
5. THE EFFECT OF MORPHOLOGY ON THE TRANSITION PROPERTIES OF COMPOSITE VANADIUM DIOXIDE COATINGS

purification steps. The synthesised particles were fairly monodisperse with a mean diameter of \(~14\text{ nm (SD 1.6 nm)}\) (see Fig. 5.2).

5.2.2 Synthesis of composite coatings

Spin solutions for the nanocomposite films were synthesised by mixing the vanadium(IV) sol with the silica nanoparticle dispersion (samples A1-A4) or with the silica sol described in the previous chapter (samples B1-B4). The molar concentration of vanadium was kept constant at 1 M.

5.3 Performance characterisation

The optical properties of all samples: plain VO\(_2\) (sample V), VO\(_2\) sol with SiO\(_2\) nanoparticles dispersed within (samples A1-A4), and VO\(_2\) sol mixed with SiO\(_2\) sol (samples B1-B4), were evaluated by measuring the transmittance and reflectance at room temperature and 90 °C. All coatings showed a large reduction in transmittance in the infrared part of the spectrum at temperatures of 90 °C due to the transition from the insulating to the metallic phase (Figure 5.3). The metrics \(\Delta T_{\text{sol}}\) and \(T_{\text{lum}}\) of all coatings are detailed in Table 5.1.
5.3. Performance characterisation

Figure 5.3: (a) Spectral transmittance in hot and cold states for samples A1-A4 and plain VO$_2$ film (V). (b) Spectral transmittance in hot and cold states for samples B1-B4 and plain VO$_2$ film (V).

Figure 5.4: Reflectance spectra of plain VO$_2$ (V) and (a) silica nanoparticle nanocomposite films A1-A4 and (b) mixed sol-gel nanocomposite films B1-B4.

All nanocomposite films show a higher solar modulation than plain VO$_2$ with comparable visible transmittance. The highest solar modulation of the mixed sol-gel films was 16.1% compared to the 6.79% solar modulation of the plain VO$_2$ sample, whilst the highest solar modulation of the nanoparticle containing films was 12.8%. The composites are able to achieve a higher solar modulation with comparable visible transmittance since they are less reflective in the visible region than the pure VO$_2$ film. Reflectance spectra showed a drop in reflectance with increasing
5. The effect of morphology on the transition properties of composite vanadium dioxide coatings

Table 5.1: Luminous and solar transmittance of plain VO$_2$ and nanocomposite films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si:V</th>
<th>FF</th>
<th>$T_{\text{Lum, c}}$ (%)</th>
<th>$T_{\text{Lum, h}}$ (%)</th>
<th>$\Delta T_{\text{Lum}}$ (%)</th>
<th>$T_{\text{Sol, c}}$ (%)</th>
<th>$T_{\text{Sol, h}}$ (%)</th>
<th>$\Delta T_{\text{Sol}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>0.00</td>
<td>0</td>
<td>52.2</td>
<td>52.5</td>
<td>0.3</td>
<td>51.1</td>
<td>44.3</td>
<td>6.69</td>
</tr>
<tr>
<td>A1</td>
<td>0.25</td>
<td>0.24</td>
<td>42.3</td>
<td>45.9</td>
<td>3.6</td>
<td>47.9</td>
<td>39.3</td>
<td>8.60</td>
</tr>
<tr>
<td>A2</td>
<td>0.50</td>
<td>0.38</td>
<td>48.1</td>
<td>48.9</td>
<td>0.8</td>
<td>54.6</td>
<td>44.6</td>
<td>10.0</td>
</tr>
<tr>
<td>A3</td>
<td>0.75</td>
<td>0.48</td>
<td>48.9</td>
<td>49.2</td>
<td>0.3</td>
<td>55.6</td>
<td>42.8</td>
<td>12.8</td>
</tr>
<tr>
<td>A4</td>
<td>1.00</td>
<td>0.56</td>
<td>52.7</td>
<td>52.4</td>
<td>-0.3</td>
<td>57.4</td>
<td>46.1</td>
<td>11.3</td>
</tr>
<tr>
<td>B1</td>
<td>0.25</td>
<td>0.24</td>
<td>49.1</td>
<td>47.7</td>
<td>1.4</td>
<td>49.0</td>
<td>39.5</td>
<td>9.58</td>
</tr>
<tr>
<td>B2</td>
<td>0.50</td>
<td>0.38</td>
<td>43.1</td>
<td>45.5</td>
<td>-2.4</td>
<td>51.1</td>
<td>39.7</td>
<td>11.4</td>
</tr>
<tr>
<td>B3</td>
<td>0.75</td>
<td>0.48</td>
<td>44.5</td>
<td>44.7</td>
<td>0.2</td>
<td>52.3</td>
<td>38.7</td>
<td>13.6</td>
</tr>
<tr>
<td>B4</td>
<td>1.00</td>
<td>0.56</td>
<td>46.1</td>
<td>43.7</td>
<td>2.4</td>
<td>53.6</td>
<td>37.5</td>
<td>16.1</td>
</tr>
</tbody>
</table>

amount of Si for both nanocomposite films (see Fig. 5.4).

The phase transition of plain VO$_2$ and the nanocomposite films A3 and B3, were investigated by temperature dependent transmittance measurements. The samples were heated up in small temperature steps to above the transition temperature and were cooled down slowly. As can be seen from the hysteresis loops in Figure 5.5 and as detailed in Table 5.2 the hysteresis width of plain VO$_2$ is much narrower than the one for the sol-gel film B3. In contrast, the nanoparticle-based film showed a loop width similar to plain VO$_2$. Hysteresis width and transition temperatures $T_t$ were obtained by plotting the first derivative $d(T_r)/d(T)$ against $T$ and determining the position of the minimum (Table 5.2). The average transition temperature $T_t$ of A3 (61.3 °C) is similar to the one of plain VO$_2$ (64.6 °C) whereas the sol-gel film exhibit a higher $T_c$ of ca. 68 °C. The hysteresis width is following a similar trend, with $\Delta T_c$ of B3 (17.7 °C) more than double the size as the one for plain VO$_2$ and A3. The transition gradient width was determined by the FWHM of the transition peaks in Figure 5.5. A sharp phase transition was observed for plain VO$_2$ and A3, with gradient widths of 5.6 °C & 2.6 °C respectively, whereas the larger hysteresis width in B3 is accompanied by a
5.3. Performance characterisation

Figure 5.5: Measured hysteresis loops used to calculate transition hysteresis and gradient width of samples V, A3, B3. The first derivative $d(T_r)/d(T)$ against $T$ is given for both heating (red) and cooling (blue) of samples V, A3, and B3.

Table 5.2: Transition temperature, hysteresis width and transition gradient width for plain VO$_2$ films and nanocomposite films.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$T_{t,c}$ (°C)</th>
<th>$T_{t,h}$ (°C)</th>
<th>$T_t$ (°C)</th>
<th>$\Delta T_t$ (°C)</th>
<th>$w_{1/2}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>60.6</td>
<td>68.6</td>
<td>64.4</td>
<td>8.0</td>
<td>5.6</td>
</tr>
<tr>
<td>A3</td>
<td>56.6</td>
<td>66.0</td>
<td>61.3</td>
<td>9.4</td>
<td>2.9</td>
</tr>
<tr>
<td>B3</td>
<td>58.1</td>
<td>75.8</td>
<td>67.0</td>
<td>17.7</td>
<td>11.1</td>
</tr>
</tbody>
</table>

more gradual transition with a gradient width of 11.1 °C.

In the following, atomic force microscopy (AFM) studies were performed using a Bruker Dimension-Icon, whilst transmission electron microscopy (TEM) images were obtained using a JEOL 2100 microscope with a LaB6 cathode operating at an acceleration voltage of 200 kV. TEM samples were prepared by drop-casting a nanoparticle dispersion onto a holey carbon film on 300 mesh copper grid (Agar Scientific). In brief, the differences in phase transition performance can be correlated to the different domain size of VO$_2$ in the nanocomposite films. Specifically,
5. The effect of morphology on the transition properties of composite vanadium dioxide coatings

Figure 5.6: Top view SEM images (left), 45° view SEM images (center) and AFM images (right) of VO$_2$-SiO$_2$-nanocomposite SiO$_2$ nanoparticles containing A3 (top) and mixed sol-gels B3 (bottom).

The narrower transition hysteresis and gradient in A3 can be explained by the larger and more uniform grain size of VO$_2$ which gives rise to more simultaneous nucleation within a small temperature window. SEM and AFM analysis of the sol-gel and nanoparticle nanocomposite films showed clear differences in film structure and morphology (Figure 5.6). The mixed VO$_2$-SiO$_2$ sol-gel films (B1-B4) exhibit a smooth surface texture with small particles of $\sim$ 13 nm diameter on the film surface. All of the composite films containing silica nanoparticles show a higher surface roughness with a granular structure of the films clearly visible in the SEM images (see Fig. 5.6 & 5.7). The size of the individual grains measured by AFM ($d = 25$ nm, $SD = 4$ nm) is larger than the average diameter of the silica nanoparticles (14 nm).

The influence of the silica nanoparticles on the film structures can be
5.3. Performance characterisation

Figure 5.7: Electron microscopy images of (a) silica nanoparticle nanocomposite films A1-A4 and (b) mixed sol-gel nanocomposite films B1-B4. Scale bar represent 500 nm.

Figure 5.8: Raman spectra of samples A3 and B3. The peaks at ~140, 192, 223, 260, 308, 338, 387, 395, 440, 482, 497, 588, 613, 661 and 823 cm\(^{-1}\) are all assigned to the VO\(_2\)(M1) phase [18–20]. The broad peak at ~613 cm\(^{-1}\) is a convolution of the peaks at 588, 613 and 661 cm\(^{-1}\). The low frequency phonons at 192 and 223 cm\(^{-1}\) correspond to lattice motion involving V-V bonds [21], whilst the peak at 140 cm\(^{-1}\) has previously been attributed to soft-phonon vibrations [19,22]. The rest of the peaks are assigned to vibrational modes of V-O bonds [21,23].

clearly seen in Figure 5.6. In the composite formed by sol-gel mixing, the silica sol acts to encapsulate the in-situ formed VO\(_2\) and prevents further growth of the crystallites, resulting in the formation of relatively small, polydisperse particles embedded in a silica matrix. Conversely in
the composite containing silica nanoparticles, the silica particles allow for
the formation of much larger crystalline domains of VO$_2$ in the film which
can have a pronounced effect on the phase transition properties of the
films as shown in Table 5.2. It has been shown that the hysteresis width
is strongly correlated with grain size because of the increased probability
of nucleation [158, 165, 166]. The controlled size of the domains means
that grain sizes are large enough such that hysteresis width is narrow and
grain sizes are small enough such that the composite is non-scattering.
Additionally, the uniformity in domain size means that the transition
gradient is in fact sharper than for our plain VO$_2$ sample (2.9 °C vs 5.6
°C).

Raman analysis (Fig. 5.8) of the two key samples shows similar
intensities and no peaks other than those expected for VO$_2$(M1) which
provides some indication that the large difference in performance between
the two samples is not a result of differences in purity of the VO$_2$(M1)
phase. Furthermore, the XRD pattern of all fabricated films showed
exclusively diffraction peaks for the monoclinic VO$_2$(M) phases (011,
211, 220) [25, 26], though the patterns for sample type A are slightly
more defined, with the FWHM of the main peak narrower than for type
B (Figure 5.9 & 5.10) indicating that the crystallites are larger in type
A than type B since the FWHM of XRD peaks can be related to the
crystalite size via the Scherrer equation:

$$\tau = \frac{0.9\lambda}{\beta \cos(\theta)}$$  \hspace{1cm} (5.1)

where $\tau$ is the crystallite size, $\lambda$ is the x-ray wavelength, $\beta$ is the FWHM
of the diffraction peak and $\theta$ is the incident angle. It is important to note
that the Scherrer equation only provides a lower bound on the particle size. This is because a variety of factors can contribute to the width of a diffraction peak aside from instrumental effects and crystallite size; the most significant effects being crystal lattice imperfections and inhomogeneous strain [167].

![Figure 5.9: XRD of samples showing peaks indicative of monoclinic VO₂ (011, 211, 220). Figure produced by JS.](image)

Additionally, the structure of the coatings were investigated further by TEM. Parts of the films were de-laminated with a scalpel and were transferred on a TEM grid coated with a holey carbon film. In the case of
5. The effect of morphology on the transition properties of composite vanadium dioxide coatings

Figure 5.10: Lorentzian fitting of XRD peak (011) with calculated FWHM; X is the lower bound of crystallite size as calculated by the Scherrer equation from the FWHM of the 011 diffraction peak (size parameter = 0.9).

Sample A3 shown in Figure 5.11 the coexistence of two nanoscale structures can be identified by their diffraction pattern from selected area electron diffraction (SAED). Crystalline domains with a sizes ~ 50 nm were observed and identified as monoclinic VO₂(M) phases (011, 211,
5.3. Performance characterisation

Figure 5.11: TEM image of sample A3. SAED analysis shows VO$_2$(M) phases (011, 211, 220). Figure produced by TM.

The spacing of the lattice fringes of 3.19 Å is in good agreement with the d-spacing of the (011) planes in monoclinic VO$_2$. The amorphous phase is formed by the silica nanoparticles. The particles form a network of aggregated, spherical nanoparticles with a mean diameter of around 22 nm which is in good agreement with the particle size measured by AFM. For the case of sample B3 shown in Figure 5.12 the amorphous phase is more polydisperse and the crystalline VO$_2$(M) domains observed are generally smaller than in sample A3 which is in agreement with the calculated crystallite size from XRD. In terms of elemental composition the two key films A3 and B3 appear fairly similar from energy-dispersive x-ray analysis as shown in Figure 5.13, this provides further evidence that the difference in transition performance between samples A3 and B3 is a direct result of the differing morphologies.

Transparent coatings for glazing applications are subject to tight limits on visible haze. Diffuse scattering of light is correlated to the structure
5. The effect of morphology on the transition properties of composite vanadium dioxide coatings

Figure 5.12: TEM image of sample B3. SAED analysis shows VO$_2$(M) phases (011, 211, 220). Figure produced by TM.

Figure 5.13: Energy-dispersive X-ray spectra showing elemental composition of samples A3 and B3.

size in the film and the optical properties of the materials. Agglomeration of particles in composite films can introduce scattering sites due to the larger structure size of the agglomerates compared to the single nanoparticles. The scattering behaviour of both nanocomposites (A3 and B3) was measured in transmission. Both samples were illuminated at a normal angle of incidence with blue light (450 nm) and only a small amount of transmitted light was detected outside of the 2° haze cone.
surrounding the incident path of light (see Fig. 5.14); samples A3 and B3 had $98 \pm 0.5\%$ and $99 \pm 0.5\%$ of transmitted light within the $2.5^\circ$ cone respectively. The slightly increased scattering in A3 can be explained by the larger grain sizes observed from SEM and AFM. Overall, the low degree of diffuse scattering in both samples shows that the VO$_2$ domains are evenly distributed within in the film and no larger agglomerates of the vanadium oxide or silica nanoparticles are formed.

![Proportion of light transmittance within haze cone as a function of polar angle for samples A3 and B3.](image)

**Figure 5.14**: Proportion of light transmittance within haze cone as a function of polar angle for samples A3 and B3.

### 5.4 Conclusions

In summary, this chapter has demonstrated the synthesis and improved transition properties of a nanocomposite thermochromic coating based on a VO$_2$ sol with SiO$_2$ nanoparticles dispersed within. The composite can be considered as an effective medium between VO$_2$ and SiO$_2$ which reduces visible reflectivity. When deposited onto the substrate, the silica particles act as a matrix within which uniform sized domains of VO$_2$ form, the uniformity in domain size means that the transition gradient is sharper than for the plain VO$_2$ film (2.6 °C vs 5.6 °C). Additionally, the SiO$_2$ particles allow for the in-situ formation of larger VO$_2$ domains in
5. **The effect of morphology on the transition properties of composite vanadium dioxide coatings**

the nanocomposite which reduces the hysteresis width compared to the mixed sol-gel films (9.4 °C vs 17.7 °C). All films exhibit a good luminous transmittance of around 50% combined with a competitive solar modulation of up to 16.1% for the mixed sol-gel films (B1-B4) and up to 12.8% for the composites containing silica nanoparticles (A1-A4). The composite coatings could be incorporated into a multilayer structure similar to that described in the previous chapter, however the roughness of the silica nanoparticle composites may reduce the effectiveness of the coherent impedance matching layers since they appear to cause a small amount of scattering.
To summarise, in Chapter 2 a theoretical model for evaluating the overall performance of thermochromic coatings was demonstrated. This model was then used to investigate how the effects of hysteresis and gradient width differ between absorbing and non-absorbing coatings. It was found, contrary to previous literature, that solar absorption is not always detrimental to the overall performance of thermochromic coatings. In the case of non-ideal coatings where hysteresis and gradient widths are significantly wide, the effect of solar absorption was found to be beneficial in mitigating the negative impact of the wide transition hysteresis and gradient widths. Specifically, in the case investigated, it was found that for hysteresis widths $> 15 \, ^\circ\text{C}$, the performance of the non-absorbing case dropped to $\sim 60\%$ of its initial value whilst the performance of the absorbing film only drops to $\sim 95\%$. As a result we find that the absorbing case outperformed the non-absorbing case when hysteresis widths were greater than $8 \, ^\circ\text{C}$. 
In Chapter 3, the methods developed to synthesis and characterise thermochromic vanadium dioxide coatings were detailed. Interestingly, it was found that the highest purity vanadium dioxide region could be identified using only a microscope, since the initial oxidation of VO$_2$ to V$_2$O$_5$ during annealing formed large (>2µm) fractal-like patterns.

The optical constants for high purity vanadium dioxide were obtained using ellipsometry and in Chapter 4, the optical constants were used to derive an optical performance limit for thin film vanadium dioxide, which was found to be far beyond current literature achievements. A multilayer coating was then designed to approach the theoretical limit, and subsequently fabricated to yield a coating that significantly surpassed previous performance records for thin film vanadium dioxide. The fabricated coating has a solar modulation of 21.8% and a visible transmittance of 48.9% along with a hysteresis and gradient width of 12.1 ºC and 10.1 ºC respectively.

In Chapter 5, the effect of nanocomposite morphology was investigated. It was found that when silica nanoparticles were dispersed within a vanadium(IV) sol-gel, the final coating formed after annealing exhibited significantly reduced hysteresis and gradient width compared with composites formed by mixing silica and vanadium(IV) sol-gels. In fact, the vanadium(IV) sol-gel that had silica nanoparticles dispersed within was found to have a transition gradient width narrower than the pure vanadium dioxide thin film control sample. Evidence collected from SEM, TEM, and XRD, suggests that the reduced hysteresis is due to the the silica nanoparticles acting as a matrix for vanadium dioxide domain growth, leading to larger and more uniform crystalline domain sizes.
In the literature, it has been shown theoretically that nanoparticulate coatings have the greatest potential optical performance due to their reduced reflectivity and their increased solar modulation, arising from a plasmon resonance in the metallic state around 1000 nm wavelengths \[114\]. This has been supported by experimental demonstrations of many high performing nanoparticle composite coatings (see Fig. 6.1a). However, as shown in Chapter 2, the overall performance of thermochromic coatings is significantly diminished with increasing hysteresis and gradient width, both of which are greater for nanoparticulate coatings (see Fig. 6.1b). Furthermore, whilst solar absorption can mitigate the effects of hysteresis and gradient width, solar absorption itself is detrimental to the overall performance since it leads to thermal re-radiation from the coating into the building. Therefore, assuming that it is impossible to achieve a VO\(_2\) coating with hysteresis and gradient widths of zero or without solar absorption, the realistic ideal thermochromic coating would have a hysteresis and gradient width as narrow as possible with an optimal amount of solar absorption so as to mitigate the effects of hysteresis and gradient whilst not resulting in excessive thermal re-radiation. From reviewing reported literature, this ideal seems impractical for nanoparticulate coatings, which rely on strongly absorbing resonances and small domain sizes so as to be non-scattering. Alternatively, based on the results of Chapters 3 and 4, thin film vanadium dioxide appears to be capable of meeting these conditions whilst still achieving solar modulation and visible transmittance values comparable to that of the best nanoparticulate coatings in the literature (see Fig. 6.1a). Additionally, the fabrication methods for thin films are more ap-
Applicable for industrial scales, with PVD, CVD and solution spray-coating methods all having the potential to be performed in-line at the point of glass manufacture.

![Figure 6.1: Comparison of the optical performance (a) and hysteresis (b) nanoparticulate and thin film vanadium dioxide based coatings in the literature. The performance of the multilayer coating demonstrated in Chapter 4 is indicated by the green marker.](image)

When scaling up the solution based synthesis described in Chapter 3 several alterations would likely need to be made to the process. For example, controlling the oxygen content via vacuum during VO$_2$ synthesis would be unsuitable, since the solution would immediately evaporate when exposed to vacuum. Instead, the oxygen content during VO$_2$ formation step could be controlled by flowing a mixture of oxygen and inert gas (e.g. argon, nitrogen). However, the resulting film may be denser than those formed using the vacuum process as a result of the higher pressure. Any increased film density would adversely effect the impedance matching conditions relied upon in Chapter 4, since the vanadium dioxide layer will have a higher optical impedance. In this case the surrounding layers may need to be replaced with materials with higher optical impedance to better match that of the dense VO$_2$. Alternatively,
instead of changing the surrounding layers, the optical impedance of the fabricated vanadium dioxide layer could be reduced using the methods described in Chapter 5, however further optimisation of the annealing conditions would be required to limit surface roughness and scattering, as this would result in a loss of coherence and thus limit the impedance matching arising from coherent interference. This optimisation would involve reducing the annealing time and temperature to reduce the size of the crystallites, whilst ensuring that the films obtained were still high purity VO$_2$ and that the transition performance was not adversely affected.

Alongside these efforts, the VO$_2$ layer must be doped, preferably with tungsten, such that the transition is brought nearer to room temperature. The specific optimum temperature will depend heavily on the solar power absorbed by the coating and therefore the geographical location of the film, as shown in Chapter 2. Additionally, the results of Chapter 2 show the importance of including the absorption, transition gradient, and transition hysteresis in any analysis of the overall energy saving performance, however the model presented would require further development to provide a quantitative analysis of the overall energy saving performance of the building. Once a fully comprehensive model was developed a year long outdoor study would be required for experimental verification. A prototype unit resembling a small room should be built and tested under outdoors conditions. The prototype may consist of a box with five insulating walls. A window would be installed on the sixth surface covered by a thermochromic film. Inside the unit heating and cooling elements would work to maintain the temperature inside at a
constant value. The electric power consumption can then be monitored over the year and compared with the simulated result. Such a model could then be used to determine optimal film properties for various locations around the world.
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