THE EFFECT OF SMART COATINGS ON THE RADIATION PASSING THROUGH GLAZING

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Abstract

Windows provide us with natural light and fine-looking connections to the outdoors. However, a huge amount of energy is lost through these building envelopes. This study reviews the most common and contemporary coatings of the glass surface with thin films. Through this review the various types of intelligent coatings are compared in terms of their performance in saving air-conditioning and electrical lighting energy. Having completed the review, it is determined that electrochromic and thermochromic windows consume less than around 40 kWh/m^2 for electric lighting energy and around 10 kWh/m^2 for cooling energy.Therefore,these two types feature better performance compared to other smart windows.The thermochromic effect of vanadium dioxide (VO_2) thin films has inspired many research teams to apply this type of smart thin films as a promising coating for windows leading to drastic reductions in lighting and ventilation energy. In this study vanadium dioxide thin films have been deposited on clear glass by RF magnetron sputtering. Different film thicknesses (20 nm, 50 nm, 80 nm and 120 nm) were deposited by altering the sputtering duration. The films were characterized for their crystal structure and surface morphology by means of X-Ray Diffractometer (XRD) and Field Emission Scanning Electron Microscope (FESEM). The reflectance and transmittance of samples were measured before and after transition temperature using a UV-Vis-NIR spectrophotometer. Finally, the thermochromic behavior of the samples is compared.The 50 nm sample exhibited better reflective behavior at room temperature, greater reflectance difference (-5.6 %) in the visible range and highest thermochromic efficiency (η (2200 nm) = 54.3%). By the same token, the 80 nm sample performed the best in increasing the reflectance (6.7 %) in near-IR range. However, the thickness should be selected according to the glazing requirements and the priority of visible or near-IR optical properties.

Abstrak

Tingkap menyediakan kami dengan cahaya semulajadi dan denda-cari sambungan ke luar. Walau bagaimanapun,sejumlah besar tenaga hilang melalui sampul surat bangunan. Kajian ini mengkaji lapisan yang paling biasa dan kontemporari permukaan kaca dengan filem nipis. Melalui kajian ini pelbagai jenis lapisan pinta rdibandingkan dari segi prestasi mereka dalam penjimatan penghawa dingin dan tenaga pencahayaan elektrik. Setelah selesai kajian, ia ditentukan bahawa elektrokromik dan tingkap thermochromic mengambil kurang daripada sekitar 40 kWh/m2 untuk tenaga lampu elektrik dan sekitar 10 kWh/m2 untuk tenaga penyejukan. Oleh itu, kedua-dua jenis mempunyai prestasi yang lebih baik berbanding dengan lain-lain tingkap pintar. Kesan thermochromic vanadium dioksida (VO_2) filem nipis telah memberi inspirasi kepada banyak pasukan penyelidikan untuk memohon jenis ini filem pintar nipis sebagai lapisan yang menjanjikan untuk tingkap yang membawa kepada pengurangan drastik dalam lampu dan tenaga pengudaraan. Vanadium dioksida kajian ini filem nipis telah didepositkan di kaca jelas oleh RF magnetron sputtering. Filem ketebalan yang berbeza (20 nm, 50nm, 80nm dan 120nm) telah didepositkan dengan mengubah tempoh sputtering. Filem-filem yang telah dicirikan untuk struktur kristal mereka dan morfologi permukaan oleh cara XRD dan FESEM. Pantulan dan pemindahan sampel telah diukur sebelum dan selepas suhu peralihan menggunakan spektrofotometer UV-Vis-NIR. Akhirnya, tingkah laku thermochromic sampel dibandingkan. Sampel 50 nm mempamerkan tingkah laku yang lebih baik mencerminkan pada suhu bilik, lebih besar perbezaan pantulan (-5.6%) dalam julat nampak dan kecekapan thermochromic tertinggi (η (2200 nm) = 54.3%). Dengan cara yang sama, sampel 80 nm dilakukan yang terbaik dalam meningkatkan pantulan (6.7%) dalam pelbagai hampir-IR.Walau bagaimanapun, ketebalan perlu dipilih mengikut kepada keperluan kaca dan keutamaan hartanah dilihat atau berhampiran-IR optik.

Acknowledgement

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List of Symbols and Abbreviations

AACVD	Aerosol assisted chemical vapor deposition
APCVD	Atmospheric pressure chemical vapor deposition
AR	Anti-reflective
CVD	Chemical vapor deposition
D/M/D	Dielectric/Metal/Dielectric
EC	Electrochromic
ECW	Electrochromic window
FESEM	Field EmissionScanning Electron Microscopy
IR	Infrared
low-E	Low emissivity
MST	Metal to semiconductor transition
PDLC	Polymer dispersed liquid crystals
PVD	Physical vapor deposition
R	Reflectance
RF	Radio Frequency
R_h	Reflectance at hot state
R_c	Reflectance at cold state
SPD	Suspended-particle devices
T	Transmission

TC	Thermochromic
TCW	Thermochromic windows
T_R	Room temperature
T_h	Transmittance at hot state
T_c	Transmittance at cold state
T_t	Transition temperature
UV	Ultraviolet
XRD	X-ray diffractometer
ΔR	Reflectance change
$\Delta R\%$	Transition efficiency in terms of reflectance
ΔT	Transmittance change
$\Delta T\%$	Transition efficiency in terms of transmittance

1 Introduction

A significant amount of energy is consumed for maintaining thermal comfort in buildings. This energy is mostly burnt off to keep vapor compression cycles and air conditioning devices running. The building energy consumption is noticeably high in hot and humid regions, contributing to one third to half of the electricity produced in some countries (Al-Rabghi and Hittle, 2001; Kwak et al., 2010; Wilde and Voorden, 2004). Therefore, energy saving procedures should be implemented in order to decrease energy losses (Sadineni et al., 2011). It is highlighted as a major responsibility of designers of new buildings not only to cut down on electricity consumption in lighting and HVAC systems but also to choose building materials wisely (Mekhilef et al., 2012; Thormark, 2006).

The energy received from the sun on the earth's surface in one hour equals to the amount of approximately one year energy needs of earth. Sun acts like a black body radiator with the surface temperature of 5800 K, which leads to a 1367 w/m^2 energy density over the atmosphere (Chen et al., 2008; Goetzberger et al., 2003; Gueymard, 2004). This is also important to have a profound knowledge of the sun spectrum. This importance lies on the fact that this knowledge can help designersunderstanding the effects of atmosphere on the radiation and guide themto select the best material and methods for glazing (Gottschalg et al., 2003).

1.1 Windows and glazing

Windows provide us with natural light and fine-looking connections to the outdoors. However, a huge amount of energy is lost through these building envelopes. Specifically, windows as the most energy-inefficient component of buildings are the major contributor to these energy losses (Baetens et al., 2010).

Cooling and heating energy is noticeably wasted via windows. Particularly in commercial buildings, which are excessively exposed to solar radiation due to large area fenestration leading to thermal discomfort (Arpino et al., 2008; Zinzi, 2006). According to the National Renewable Energy Laboratory report (2009), windows are culpable of about 30 percent of building heating and cooling electrical loads and applying high-tech fenestration techniques can potentially save approximately 6 percent of the energy consumption nationwide.

Consequently, if researcherscurtail these losses by improving the windows thermal performance, less electricity costs and greenhouse gas emissions will be resulted. Therefore, controlling solar gain and loss by means of fenestration should be emphasized in building design. While reducing radiation transmitted, the window materials should be capable of sufficient transmission of visible light through windows (Correa and Almanza, 2004). Modern architecture lends a lot to the concept of residents' comfort (de Wilde et al.). From the aesthetic standpoint, these transparent facades are essential building elements that provide a comfortable indoor environment by creating eye-catching views as well as illuminating the interior space by inviting light inside (Hassouneh et al., 2010). There is quite a vast number of parameters influencing the heat transfer through windows such as outdoor conditions, shading, building orientation, type and area of window, glass properties and glazing characteristics (Hassouneh et al., 2010). Improving glazing characteristics of windows such as thermal transmittance and solar parameters is the most important criterion to be considered in building windows standards (Tarantini et al., 2011). Moreover, there are some goals, which cannot be achieved by conventional materials such as metals and plastics, whereas glass will be suitable (Axinte, 2011).

1.2 Smart windows

The emerging technology of smart coatings has contributed a lot to various applications. Smart windows, refers to a type of glass coated with thin films which change their optical and thermal properties in response to an external stimulus. This external trigger can either be an environmental and climate change such as temperature or light for passive devices or it can be human defined preference such as applied current or voltage for active devices. By dynamically controlling the performance of smart windows, peak electric loads and lighting requirements will be reduced. This can lead to enhanced thermal comfort and improved productivity in buildings.

There are two major types of smart windows, passive devices such as thermochromics and photochromics; and active devices such as liquid crystal, electrochromics and suspended particle devices.

1.3 Scope of the study

The study focuses on the intelligent coatings on glazing that improve the efficiency of windows. The different types of smart coatings are reviewed and compared. Moreover, thin films of vanadium dioxide with different thicknesses are sputtered on glass surface. The coated thin films are characterized and the effect of film thickness on the thermochromic transition of the films is discussed.

1.4 Significance of the study

Although, there have been many works on VO_2 thin films, there has been merely a little number of reports in which clear glass is coated by means of radio frequency (RF) magnetron sputtering to investigate the thermochromic transition of the films. In this study clear glass is coated with VO_2 films of different thickness (20 -120 nm) and the effect of the film thickness on the optical properties of the films before and after the thermochromic transition temperature is determined. The change in optical properties can potentially reduce energy losses.

1.5 Objective of the study

To review the various types of smart coatings for glazing purposes

To compare the smart coatings in terms of their energy saving performance

To coat glass surface with vanadium dioxide thin films of different thicknesses using RF magnetron sputtering

To evaluate the thermochromic performance of the coated samples and find the most appropriate thickness of the film

1.6 Organization of the study

Chapter 1 of this study explains the concept and importance of smart coatings. The importance of taking the measures to reduce energy loss through windows is also highlighted. Chapter 2 contains a review of literature and relevant research associated with the various types of smart coatings. It also reviews the technologies used for coating glass with thermochromic vanadium oxide thin films focusing on previous sputtering coatings and the associated parameters used in their experiments. Chapter 3 offers the details of sputtering and the chosen parameters to conduct the experiment. In addition, it elaborates the characterization tests performed on the samples. Chapter 4 presents and discusses the achieved results containing the resulted coated samples, the results of thin film characterization and the graphs of UV-Vis-NIR measurements. Chapter 5 presents the concluding remarks of the study and suggests the potential future studies in this field.

2 Literature review

There are two approaches in building energy saving strategies, the active strategies and the passive ones. Improving HVAC systems and building lighting can actively increase the building’s energy efficiency, whereas measures amending building envelopes are the passive methods for the above mentioned purpose. Any building element, such as wall, roof and fenestration which separates the indoor from outdoor is called building envelope (Sadineni et al., 2011).

Using cool coatings on roofs, adding thermal insulation to walls and coated window glazing are among the effective envelope-based passive techniques that meliorate energy efficiency (Bojic et al., 2001; Cheung et al., 2005; Synnefa et al., 2007).

2.1 Modern glazing and smart coating

In recent years, glazing technologies and materials have been the major focus of many studies. Aerogel glazing, vacuum glazing, switchable reflective glazing, suspended particle devices film, holographic optical elements (Bahaj et al., 2008; Sullivan, Beck, et al., 1996), low-e coatings, all-solid-state switchable mirror glass (Tajima et al., 2010; Yamada et al., 2007), gas cavity fills and improvements in frame and spacer designs (Robinson, 1994) are among the most common glazing technologies in terms of controlling solar heat gain, insulation and lighting. Electrochromic (EC), thermochromic (TC) and photochromic materials are employed in glass industry for different, sometimes odd, applications. The two most recent developments in the industry, “self-cleaning glass” and “smart glass”, offer excellent energy efficient and environmentally friendly features in various applications (Axinte, 2011).

In the following sections, the contemporary technologies most recently employed in glazing industry are be reviewed and elaborated.

2.1.1 Low-E coatings

Low emissivity (low-E) coatings are spectrally selective films that are aimed to let the visible light pass through and block the IR and UV wavelengths which generally create heat(Sadineni et al., 2011). Because of its high IR-reflectance, this type of glazing has been developed greatly, and many have studied their different properties during the last two decades (Huang et al., 2008; Ren et al., 2011; Rosencrantz et al., 2005; Schaefer et al., 1997). Typically, there are two types of low-e coatings, the tin oxide based hard coating and the silver based soft coating with higher IR reflectance and lower transmittance than the other one. However, the visible transmittance of hard coatings can boost up with anti-reflectingproperty of silicon dioxide(Hammarberg and Roos, 2003).

2.1.2 Dielectric/Metal/Dielectric films (D/M/D)

D/M/D films on glass exhibit great energy saving effects by reflecting the IR radiation by their reflective metal film and transmitting visible and near IR radiation through the two antireflective dielectric coatings (Leftheriotis et al., 1997). Design, fabrication and properties of D/M/D films have been studied thoroughly by many researchers focusing on the optimization (Al-Shukri, 2007; Cheng and Ting, 2007; Dima et al., 1991; Durrani et al., 2004; Lee et al., 1996; Leftheriotis and Yianoulis, 1999). Beside the optimized performance, cost of these films in terms of their material and the fabrication technique is also important (Leftheriotis et al., 1997).

2.1.3 Switchable reflective glazing (intelligent glazing)

This type of glass – also named “smart window” – is generally based on optical switching along with modulation in glass properties. These dynamic tintable windows are categorized in to passive and active systems.

In passive devices, the switching process is activated automatically in accordance with the environmental conditions. This environmental factor can be light in case of photochromic windows; or temperature and heat in thermochromic windows (TCW). Alternatively, the active systems require an external triggering mechanism to perform the modulation. For instance, electricity is the actuating signal in electrochromic windows (ECW). The active switchable glazing systems offer supplementary options compared to the passive systems whereas their dependency on power supply and wiring should be reckoned with as a drawback. Chromic materials, liquid crystals, and suspended particle windows are the three most common active-controlled intelligent windows (Baetens et al., 2010). The latter two share the disadvantage of their dependency on an electric field to be maintained when a transparent mode is desired; resulting in excessive electricity consumption. This is not the case in EC glazing that wants electricity only for transition (Lampert, 1998). However, chromic materials are classified into four types: electrochromic (EC), gasochromic, photochromic and thermochromic (TC). The first two belong to active glazing, responding to electricity and hydrogen gas respectively as a function of solar irradiation (Baetens et al., 2010; Bahaj et al., 2008). Smart windows are apt to glazing the cooling load demanding buildings with large solar gain (Sullivan, Beck, et al., 1996), though providing a see-through mode is a must in any application.

The decisive factors, based on which the performance of intelligent windows can be evaluated, are ordered below with respect to their importance (Baetens et al., 2010).(a)Transmission modulation in the visible and outer visible spectrum, (b)Anticipated life time and the number of cycles without degradation, (c)Response time, (d)The time required to switch between colored and bleached states, which depends on the size of the window, (e)The resulted window size, (f)Overall energy consumption and (g) Operating voltage and temperature. The different classes of switchable glazing are presented in the following sections.

2.1.3.1 Electrochromic windows (ECW)

The EC effect which was first explained in 1969 is a characteristic of a device which varies its optical properties when an external voltage triggers the EC material. The EC device modulates its transmittance in visible and near IR when a low DC potential is applied (Granqvist, 1995; Syrrakou et al., 2006).

It is usually consisted of several layers deposited on glass. The glass substrates are usually coated with transparent conducting films with natural colors-mostly tin oxide doped with either indium (ITO) or fluorine (FTO). The three major deposited layers cover the coated glass substrate as follows: *The Electrochromic film* (cathodic electro-active layer with reversible transmittance modulation characteristic) which gets a darker color when the external circuit transfers electrons into the EC lattice to compensate for the positive ions injected from the adjacent ion storage layer; *Ion conductor* (ion conducting electrolyte); and *Ion storage layer* (anodic electro-active layer) that becomes darker while releasing positive ions (Granqvist, 1995; Papaefthimiou et al., 1999, 2001a, 2001b; Zinzi, 2006).

The electro-active layers (also named electrochromics) switch between their oxidized and reduced forms causing variations in their optical properties and colors as well. Ideally, it is desired that electrochromics act more reflective rather than absorptive in their colored state compared with their bleached mode (Syrrakou et al., 2006).

EC windows should provide daylight while acting as a barrier to heat. Obviously, this type of window is not capable of providing both effects simultaneously (Lee and DiBartolomeo, 2002). The EC function can be controlled by thermal load, temperature and sunlight. The latter is stated to be the best governing parameter, especially from the comfort point of view (Karlsson et al., 2000; Sullivan et al., 1994; Sullivan, Lee, et al., 1996; Sullivan, Rubin, et al., 1996). All the more, self-powered EC windows are also developed using semitransparent PV cells, which provide the required activating electricity (Bechinger and Gregg, 1998; Benson et al., 1995; Deb, 2008; Deb et al., 2001; Gao et al., 1999; Gao et al., 2000; Hauch et al., 2001; Huang et al., 2011; Pichot et al., 1999). Figure 2.1: demonstrates the structure and function of EC windows.

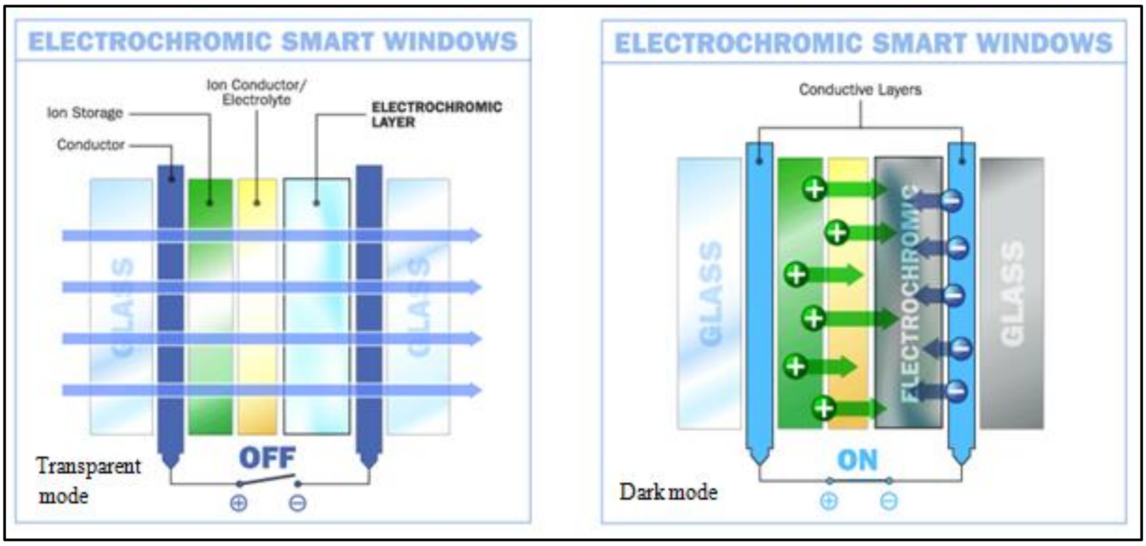

Figure 2.1: Electrochromic windows in bleached or transparent mode at left and in colored or dark mode at right(HowStuffWorks)(HowStuffWorks, 2009)

2.1.3.2 Gasochromic windows

The function of gasochromic devices is also based on electrochromism in EC windows. The main difference is that instead of DC voltage, a hydrogen gas (H_2) is applied to switch between colored and bleached states. Compared to their counterpart, gasochromic devices are cheaper and simpler because only one EC layer is enough and the ion conductor and storage layers are not needed anymore. Although, gasochromic devices exhibit some merits such as better transmittance modulation, lower required voltage, staying lucid in the swap period, and adjustability of any middle state between transparent and entirely opaque; only a few numbers of EC materials can be darkened by hydrogen. Furthermore, strict control of the gas exchange process is another issue (Georg et al., 1998).

2.1.3.3 Liquid crystals (LC)

Commonly used in wrist watches, LC technology is getting more popular as a means of protecting privacy in some interior applications such as bathrooms, conference halls and fitting rooms in stores. As it can be seen in Figure 2.2:, two transparent conductor layers, on plastic films squeeze a thin liquid crystal layer, and the whole set is pressed between two layers of glass. Normally, the liquid crystal molecules are situated in random and unaligned orientations scattering light and cloaking the view to provide the interior space with privacy. When the power is switched on the two conductive layers provide an electric field via their electrodes. The field causes the crystal molecules to be positioned in an aligned direction causing a change in transmittance (Doane et al., 1987; Fergason, 1992). The LC technology suffers from the disadvantage of high power demand in transparent mode, resulting in an electricity usage of 5-20 W/m^2. These devices have problems, in long term UV stability and high cost disadvantages as well (Baetens et al., 2010). The technology using liquid crystals in intelligent windows is called Polymer dispersed liquid crystals (PDLC) which is illustrated in Figure 2.2:.

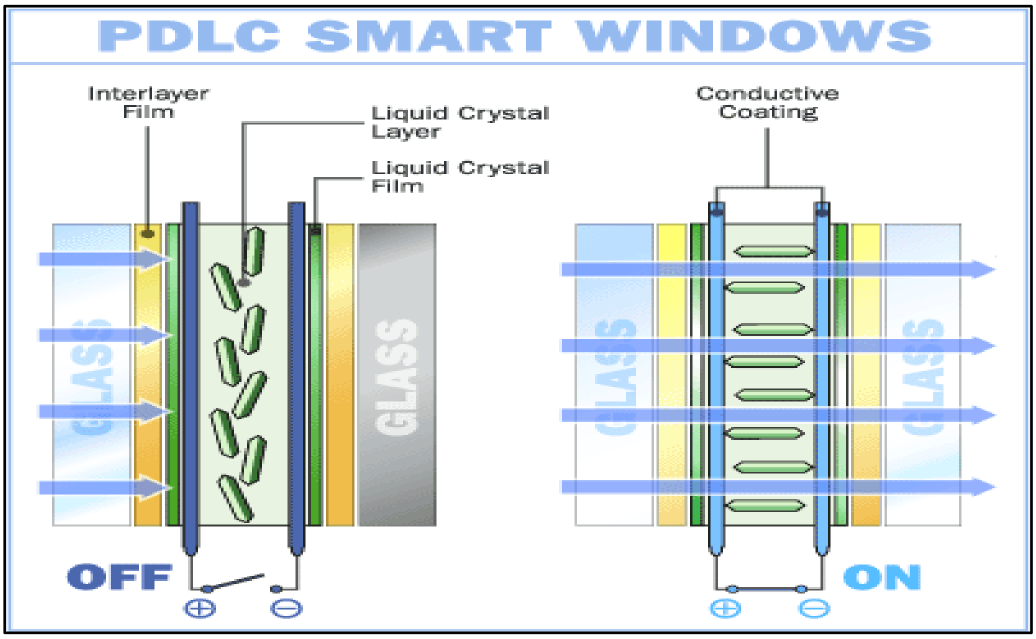

Figure 2.2: PDLC technology used in smart windows

2.1.3.4 Electrophoretic or suspended-particle devices (SPD)

SPDs have many things in common with LC devices: they are both fast in switching between phases, high electricity consumptive and dependent on an electric field. Figure 2.3: shows the construction and operation of SP windows. According to the figure, they consist of the liquid like active layer formed by adsorbing dipole needle-shaped or spherical particles (molecular particles), i.e. mostly polyhalide, suspended in an organic fluid or gel sandwiched between two sheets of glass coated with transparent conductive films. Normally, the device is in the dark reflective state because of the random pattern of the active layer’s light absorbing particles. When the electric field is applied, the particles will align resulting in the clear transmissive state. As soon as the power turns off the device switches to its dark state. Typically, the transmission of SPDs varies between 0.79-0.49 and 0.50-0.04, with 100 to 200 ms switching time and 65 to 220 V AC requirements (Baetens et al., 2010).

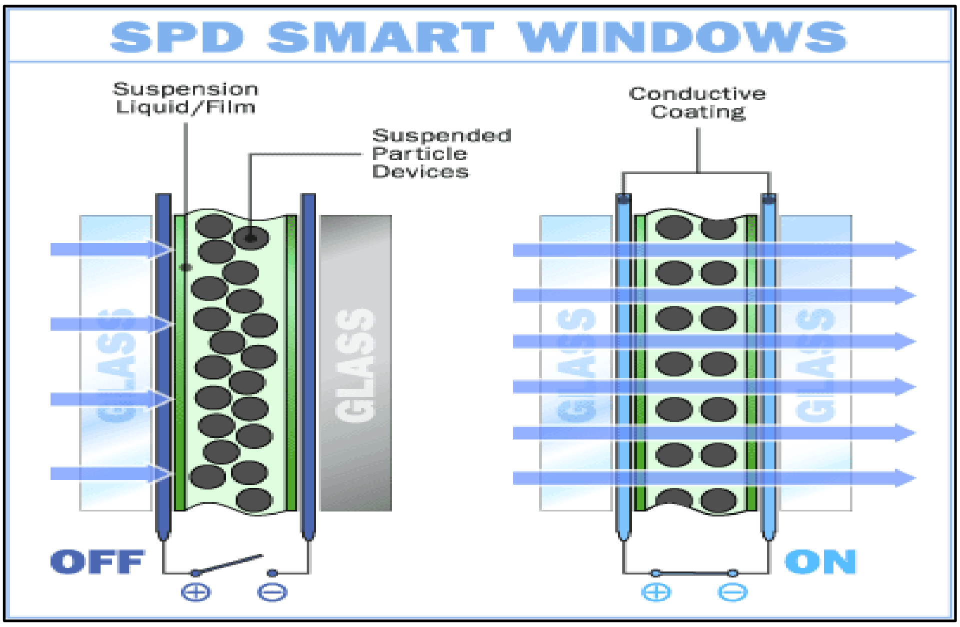

Figure 2.3: Suspended particle device in smart windows

2.1.3.5 Thermochromic windows (TCW)

In the first glance, the word “Thermochromic” might seem strange. But the word originates from the Greek roots: “Thermos” meaning warm or hot; and “Chroma” which means color. A thermochromic material changes color as the temperature changes (Ritter, 2007). TCW is a device on which a thin film of TC materials is deposited. This can reduce the energy demand of buildings by changing the device’s reflectance and transmission properties, reducing the solar energy gain (Greenberg, 1983; Parkin and Manning, 2006). The TC thin film is initially in its monoclinic state at lower temperatures (usually room temperature). Monoclinic materials behave as semiconductors, less reflective, especially in near IR radiation. As the temperature rises, the TC material changes its nature from monoclinic to the rutile state. This effect is called metal to semiconductor transition (MST). In the rutile state, the material acts like a semi-metal, reflecting a wide range of the solar spectrum (Blackman et al., 2009). In high temperatures, it blocks near-IR (800-1200 nm) the wavelengths from which most of the heat is originated and far-IR (1200-2500 nm) while in low temperatures it allows those parts of the spectrum to pass (Lee and Cho, 2000).

The MST is fully reversible, co-occurred with large variations in electrical and optical properties in near infra-red (Morin, 1959). For more illumination Figure 2.4: is presented. In order to make this type of glazing feasible, the MST temperature (T_t) should decrease to near the ambient temperature. Doping metal ions into the lattice of TC materials can alter T_t(Béteille et al., 1997; T. Phillips et al., 1987). The size and charge (MacChesney and Guggenheim, 1969; Nag and Haglund Jr, 2008; Phillips et al., 1987)of dopant ion, film's strain (Binions, Hyett, et al., 2007; Xu et al., 2005) as well as the variations in electron carrier density are the determinant factors prevailing on the fall or rise of T_t(Pierce and Goodenough, 1972).

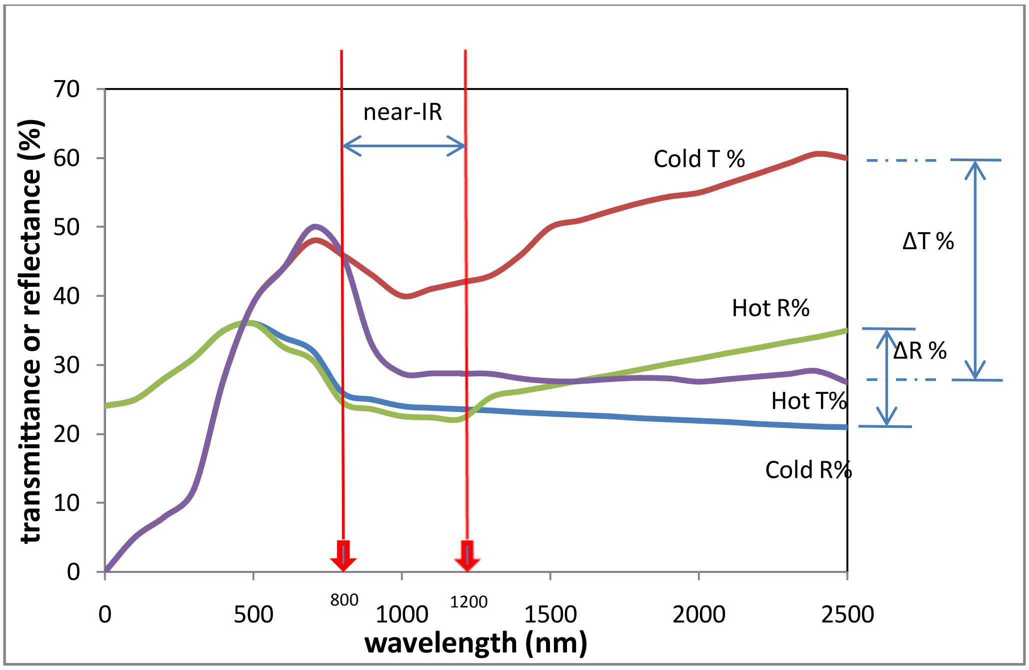

Figure 2.4: Typical transmittance change (ΔT) and reflectance change (ΔR) of thermochromic films through MST (adapted from (Saeli et al., 2010))

2.2 Thermochromic thin film

The TC materials for glazing purposes, their properties and fabrication are not new in glazing industry, having been studied by the early 1970's (MacChesney et al., 1968; Ryabova et al., 1972).

The most promising TC material for windows is vanadium dioxide (VO_2). It is known to be in four polymorphic forms: monoclinic VO_2(M) and rutile VO_2(R) and two meta stable forms VO_2(A) and VO_2(B) by monoclinic to rutile transition temperature of 68^o C (Leroux et al., 1998). VO_2 TCWs suffer from low luminous transmittance, the drawback which could be solved by fluorination (Gutarra et al., 1994) or applying SiO_2 anti-reflective (AR) coating (Babulanam et al., 1987; Lee and Cho, 2000). Using ZrO_2 coating with its appropriate refractive index is reported to enhance the luminous transmittance while maintaining the TC switching (Xu et al., 2004). The most popular materials used in TC coatings, and their corresponding effects are presented in Table 2-1. Fluorine and tungsten-doped VO_2 are good choices for energy-saving windows (Burkhardt et al., 2002; Shi et al., 2007).However, tungsten (W) by reducing the T_t of VO_2 to the ideal temperature of 25^o C at 2 at% (lowering the T_t by 25 ^oC per dopant atomic percent incorporated) is the most effective dopant ion for VO_2 (Blackman et al., 2009; Manning et al., 2004). In another experiment, it is shown that a 2.7 mol % content of WO_3 has also made the film's T_t drop to room temperature (Cho et al.).

Gold nanoparticles have been used as dopant in recent studies. It gives a pleasant green/blue color to the films and affects the MST and T_t. However, because of its high price, gold doping cannot be prevalent (Binions et al., 2008; Saeli et al., 2010).

Fluorine doping of VO_2 films have been done by PVD techniques (Burkhardt et al., 2002; Burkhardt et al., 1999a; Khan et al., 1988). Incorporation of fluorine in the films using AACVD gave the films a lighter color but still the unpleasant yellow/brown color of un-doped film didn't change (Kiri et al.). The changes in transmission (15%) and reflectance (5%) are less than those of tungsten-doped films. The key effect of fluorine is the better transmission in the visible range. In contrast to previous studies (Burkhardt et al., 1999a), it is reported that the transition temperature (~ 60 ^{o}C) didn't change noticeably from the un-doped case (Kiri et al.).

Performed titanium dioxide (TiO_2) and cerium dioxide (CeO_2) nanoparticles have been also used in producing VO_2 films. By utilizing these photocatalytic nanoparticles, films with both photocatalytic and TC characteristics can be afforded. Through the transition the transmission changes insignificantly (5-10%) at 2500 nm; whereas the reflectance changes about 30%. The nanoparticles used do not change the color of the film (Warwick et al., 2011). Moreover, CeO_2 can be used as a protective coating over VO_2 films to plunge the chemical deteriorations (Saitzek et al., 2007).

TiO_2 is used to fabricate double- (or multi-) layered VO_2 thin films. The anti-reflection feature of TiO_2 can enhance the visible transmittance up to 84 % (CHEN et al., 2011).

Deposition of platinum (Pt) on VO_2 films can improve the IR reflection while maintaining the TC characteristic. T_t has been also lowered by 9.3 ^{o}C to around 58 ^{o}C.Pt has depressed the visible transmittance which can be fortified by adding SiO_2 antireflection coating (Kang et al., 2010). Earlier, SiO_2 was used to improve the luminous transmittance to 75 % (in 700 nm) compared with 33 % of plain VO_2 case. SiO_2 has also lowered T_t to 61 ^{o}C (Chen et al., 2004).

Table 2-1: Effect of some materials on the thermochromic coatings

Material	**Effect on MST**	**T_t**	**Film Color**
Pure VO_2 crystals	-	68 ^oC(Leroux et al., 1998)	Brown/Yellow(Manning et al., 2004)
Un-doped VO_2 films	-	50-66 ^oC(Binions, Hyett, et al., 2007)	Brown/Yellow
Tungsten doping	23 % ΔT at 2500nm(Shi et al., 2007)	20 ^oC(Blackman et al., 2009) 1.56 at% 25 ^oC(Cho et al.) 2.7 mol %	Blue(Blackman et al., 2009)
Gold nanoparticle	35-40 % ΔT and 10 % ΔR at 2500 nm (Saeli et al., 2009)	15-20 ^oC (Saeli et al., 2009)	Green/Blue(Binions et al., 2008; Saeli et al., 2010) Varies in different temperatures
Fluorine doping	15 % ΔT and 5 % ΔR (Kiri et al.)	60 ^oC(Kiri et al.) 25 ^oC(Burkhardt et al., 1999a)	Brown/Yellow(Kiri et al.)
TiO_2	21.2 % IR-ΔT and 84% Vis-ΔT(CHEN et al., 2011) 5-10 % ΔT at 2500nm(Warwick et al., 2011)	50-60 ^oC(Warwick et al., 2011)	Brown(Evans et al., 2007; Warwick et al., 2011)
CeO_2	5-10 % ΔT at 2500nm(Warwick et al., 2011)	50-60 ^oC(Warwick et al., 2011)	Brown/Yellow(Warwick et al., 2011)

There are some materials which can be used as deposition precursor. The most common precursors are vanadium alkoxides(Binions, Hyett, et al., 2007; Livage, 1999; Maruyama and Ikuta, 1993; Parkin et al., 2008) and oxovanadium reagents (Barreca et al., 1999). Vanadium chloride should react with a source of oxygen (such as methanol or ethanol) the product of which is V_2O_5; heating the product in a reducing atmosphere results in deposition of VO_2 (Bramwell et al., 2000). Addition of tetraoctyl ammonium boromide (TOAB) as surfactant to the vanadium dioxide matrix can control the distribution, shape and size of gold nanoparticles. It is reported that surfactant TOAB can reduce T_t from 50-54 ^oC to 42-45 ^oC(Saeli et al., 2009) and from 52 ^oC to 34^oC (Saeli et al., 2009).

Surfactants are molecules, which can alter the structure of films due to their ability to affect the surface tension of liquids and deposition mechanism in hybrid CVD processes. Using surfactants can decrease T_t of VO_2 films (Saeli et al., 2009; Saeli et al., 2010).

2.3 Coating technologies

Deposition of TC thin films on glass substrates by physical vapor deposition (PVD) (Lee et al., 1996) and sol-gel and sputtering (Burkhardt et al., 2002; Burkhardt et al., 1999a; Greenberg, 1983; Jin and Tanemura, 1995; Nygren and Israelsson, 1969; Takahashi et al., 1996, 2001) techniques was executed by the early 2000's. In particular, VO_2 as the most appropriate TC material had been deposited using sol-gel (Beteille and Livage, 1998; Livage, 1999; Livage et al., 1998; Livage et al., 1997), sputtering (Cui et al., 2008; Granqvist et al., 2009; Guinneton et al., 2004) and pulsed laser techniques. These methods have been widely reviewed elsewhere in previous studies (Kiri et al., 2010; Nag and Haglund, 2008).

Low visible light transmission, high transition temperatures, low durability, poor transition performance and unpleasant visible colors didn't let these techniques be marketable. For instance, in an attempt to decrease T_t by doping Sn on VO_2 films using PVD, it was reported that the un-doped films showed much lower T_t(Lee et al., 1996). Even the very recent production of W-doped VO_2 and V_2O_5 films prepared by sputtering has not shown good switching performance (Luo et al., 2011). There have been some efforts to optimize the TC switching of films by controlling the deposition conditions. The best results are 76% for ΔT and 75 % for ΔR; though, T_t was still high (Guinneton et al., 2004).

On the other hand, chemical vapor deposition (CVD) shows potential in manufacturing glasses in commercial scale. Specifically, atmospheric pressure chemical vapor deposition (APCVD) is well matched with float-glass mass production lines. The deposition rates of VO_2 films are noticeably fast in this method (Blackman et al., 2009).

By the same token, the resulting physical properties such as durability and adhesion make this method more suitable (Saeli et al., 2010). There have been many researches investigating various CVD techniques and doping effects (Blackman et al., 2009; Manning and Parkin, 2004; Manning et al., 2004; Vernardou et al., 2007).

In a study conducted by Binions et al. (Binions, Hyett, et al., 2007) APCVD method was used to produce tungsten-doped VO_2 films by reaction of vanadylacetylacetonate and tungsten hexachloride with oxygen. It is reported that tungsten causes a considerable drop in T_t as well as a great change in near infra-red optical properties. The film thickness was found to influence the transmission (Binions, Hyett, et al., 2007) and extent of TC switching (Binions, Hyett, et al., 2007; Maruyama and Ikuta, 1993). The film thickness can be adjusted by changing the deposition time (Saeli et al., 2009).

Using APCVD, TiO_2 on VO_2 on SiO_2-coated glass and VO_2 on TiO_2 on SiO_2-coated glass have been grown and compared. In both cases, the T_t didn’t change significantly. The ΔT in the first multilayer film was 92 % noticeably more than that of the case of VO_2 over TiO_2 (71%). The two films showed ΔR of 55 % and -55 % respectively (Evans et al., 2007). In another study, two deposition methods were used: low pressure metal-organic CVD (MOCVD), and argon annealing of VO_2 (B) films by MOCVD. It was found that the film microstructure regulates the MST markedly (Sahana et al., 2002).

Manning et al. (Manning and Parkin, 2004; Manning et al., 2004) used water, vanadium and tungsten sources to prepare VO_2 thin films. The resulting films had the disappointing transmission of 11% to 40%. As previously suggested, the acceptable visible transmission level should be above 60% so that the window’s optical properties can live up to the building’s aesthetical and lighting standards (Sobhan et al., 1996).

Vernardou et al. (Vernardou et al., 2007) have studied the aftereffect of doping monoclinic VO_2 by atmospheric-pressure direct liquid injection metal-organic CVD (DLI-MOCVD). It was shown that T_t of tungsten-doped VO_2 drops from 60 ^oC to 35 ^oC. Aerosol assisted CVD (AACVD) is also another deposition process reducing V_2O_3 to V_2O_5 (Piccirillo et al., 2007). However, the AACVD techniques don't feature good mechanical properties and can be easily removed from the surfaces (Binions et al., 2004).

Hybrid atmospheric pressure and aerosol assisted (AA/APCVD) method can be used to prepare VO_2 thin films with reduced transition temperatures (Binions et al., 2008; Saeli et al., 2009). In this technique, the multifunctional feature of AACVD is mixed with the mechanical sturdiness of APCVD (Binions et al., 2008). This method has been also used to prepare gold doped VO_2 films. Due to the surface plasmon resonance (SPR) bands, the gold nanoparticles change the color of films from unpleasant yellow/brown color to more appealing green/blue colors. In addition, it reduces the T_t and causes a surge in reflectance. The hybrid method results in more adherent films compared with AACVD films. As MST takes place, a 10% change in reflectance and 30-40% change in transmittance is observed at 2500nm. The reason for this change may be the metallic nature of gold nanoparticles (Saeli et al., 2009). Hybrid AA/APCVD is also used to prepare VO_2 films by using a suspension of TiO_2 and CeO_2 (Warwick et al., 2011).

Blackman et al. (Blackman et al., 2009) used Water, vanadium chloride, and tungsten chloride in their experiments. Among the different afforded un-doped films, the optical properties of which having been measured between 300 nm to 2500 nm wavelengths, the 80 nm-thick films showed the best performance with 60 % transmission at 570 nm (visible range) and 35% change in transmission at 2500 nm (far infra-red range) through transition. Testing the tungsten doped films, the effect of different tungsten atomic percentages on reducing T_t has been evaluated. As it was previously reported (Jorgenson and Lee, 1986), by increasing the tungsten content $T_t$changes (linearly (Shi et al., 2007)) approximately by -20 ^{o}C/at% until 3 at% after which the reduction will be pseudo linearly. In addition, the powdery yellow/brown color of films can change to more adhering, more transparent and bluer/greener films by adjusting the vanadium precursor to water ratio and increasing the tungsten content of films to more than 2.5 at%.

As it is mentioned before, doping VO_2 films with tungsten can enhance their TC property. The doping and production methods include sputtering (Burkhardt et al., 1999a) sol-gel (Beteille and Livage, 1998; Greenberg, 1983; Livage, 1999; Livage et al., 1998; Livage et al., 1997; Takahashi et al., 2001), PVD (Lee et al., 1996; Sobhan et al., 1996), APCVD (Binions, Hyett, et al., 2007; Binions, Piccirillo, et al., 2007; Blackman et al., 2009; Manning and Parkin, 2004; Manning et al., 2004; Qureshi et al., 2004) and AACVD (Piccirillo et al., 2007, 2008).

2.4 Sputtering

Comparing the methods, it is concluded that PVD methods require expensive equipments and high vacuum pressure. In addition, they are time consuming and suffer from low film growth rates. On the contrary, in comparison to CVD, PVD methods are more suitable for synthesizing ultra thin films, require lower temperatures, are more environmentally-friendly, compatible to a wider range of substrates and more convenient for developing multi-layer thin films (Kiri et al., 2010; Livage, 1991).

Reactive sputtering is the most widely PVD method used to produce thermochromic thin films by means of ion beam sputtering(Jorgenson and Lee, 1986),DC magnetron sputtering (Krishna et al., 1998; Sobhan et al., 1996; Talledo and

Granqvist, 1994) and RF magnetron sputtering (Jin and Tanemura, 1994; Kana et al., 2008; Xue-Jin et al., 2008).

The relative merits of the sputtering technique include more efficient deposition, film uniformity and scalability to larger substrates (Kakiuchida et al., 2010). Comparing the sputtering techniques, RF sputtering equipments work at lower voltage and lower sputtering gas pressure and are capable of sputtering electrically insulating targets and additionally higher deposition rates are produced (Nag and Haglund Jr, 2008).

In RF magnetron sputtering of vanadium oxide, a vanadium target of high purity is placed at a fixed distance over the substrates; the chamber is vacuumed to a certain pressure and the substrates are kept at a fixed temperature on the substrate holder; RF power is applied and then argon (Ar) and oxygen (O_2) gasses are directed into the chamber with adjusted flow rates as the working gas and reactive gas respectively. The RF magnetron sputtering parameters and the details of the previous vanadium RF sputtering works are summarized in Table 2-2.

2.5 Summary

Although, there have been many works on VO_2 thin films, there has been merely a little number of reports in which clear glass is coated by means of RF magnetron sputtering to investigate the thermochromic transition of the films. The themrchromic thin films suffer from low visibility and low sight in transparent mode. The various methods to examine the thermochromic coatings performance are continually being investigated. Doping the lattice of material to increase the transmittance in visible range is widely reported. An alternative method is to investigate the effect of film thickness on transmittance which is focused on in this study.

Table 2-2: Summary of coating parameters in the previous vanadium oxide RF sputtering

Substrate	**Vacuum pressure (10^{-6}KPa)**	**Working pressure (Pa)**	**Substrate temp. (^{o}C)**	**Sputtering duration/ deposition rate/ film thickness**	**RF power (W)**	**O_2/Ar flow rate (sccm) or Ratio**	**Ref.**
Si (100) single crystal	-	1.5	250-500	4 – 19 nm/min	200	Ar+O_2: 100 O_2 : 0-8 %	**(Jin et al., 1998; Jin and Tanemura, 1994, 1996)**
(110) Si discs and quartz glasses	0.1	-	220 - 530	2-6nm/min 100 nm	200-400	0.16	**(Christmann et al., 1996)**
(110) Si discs and quartz glasses	0.1	0.1	120 - 530	80-120 nm	300	0.16	**(Burkhardt et al., 1999b)**
Normal glass	0.2	0.6	400	-	-	Varying flow rates	**(Kivaisi and Samiji, 1999)**
aSi(100)/SiO_2 /Pt substrate	-	1.3	Ambient temp.	200 nm	100	Ar:70 O_2: 0.7-7	**(Park et al., 2001)**
100-nm Pt / 40-nm Ti on SiO_2/Si wafer	-	-	-	1 to 10 h ; 175, 350, 800 nm	200	1 : 4	**(Park et al., 2002)**
amorphous silica (a-Si)	-	0.6-3.6	380-470	2.1 nm/min	-	0.5% - 2 %	**(Guinneton et al., 2004)**
(100) Si wafers with Pt current Collectors	0.79	0.66	Room temp.	0.833 nm/min	250	30 % and 50%	**(Yoon et al., 2004)**
corning glass	0.1	0.8	400	-	100	10%O_2/ 90% Ar	**(Kana et al., 2008)**
soda-lime glasses and fused silica	1	1	580	-	120	0.8% - 1.2%	**(Xue-Jin et al., 2008)**
-	2	0.6	600	-	100	Ar:32/O_2: 1.8	**(Kakiuchida et al., 2010)**
quartz/ TiO_2-Coated quartz glass	-	0.6	600	50 nm	160 & 180	Ar:30/O_2: 2.1	**(Ma et al., 2012)**

3 Materials and Methods

Heat travels through fenestration and windows based on three mechanisms: conduction, convection and radiation. Conduction is the heat flowing within a medium which can be solid, or fluid. Convection is the movement of heat by the movement of fluids (gases and liquids). Radiation is defined as the transfer of energy through space without requiring the existence of any medium. Radiation does not rely on conduction between the molecules of the medium or movement of them.

3.1 Ideal glazing

There are two different modes of radiation heat transfer:

- **Long-wave radiation heat transfer** which occurs between objects at different temperatures of indoor and outdoor environments. The objects at this range of temperatures emit radiations with 3 to 50 micrometers wavelength.
- **Short-wave radiation heat transfer** which is the radiation from the sun (with surface temperature of 6000K) at 0.3 to 2.5 micrometers wavelength. This wavelength range covers the ultraviolet, visible and infra-red radiation.

The radiation passing through windows includes both of the radiation modes; Long-wave radiation from the indoor objects and outdoor’s short-wave radiation from the sun. Figure 3.1

demonstrates the ideal spectral transmittance of windows in cold and hot states corresponding to heating demanding and cooling demanding conditions respectively.

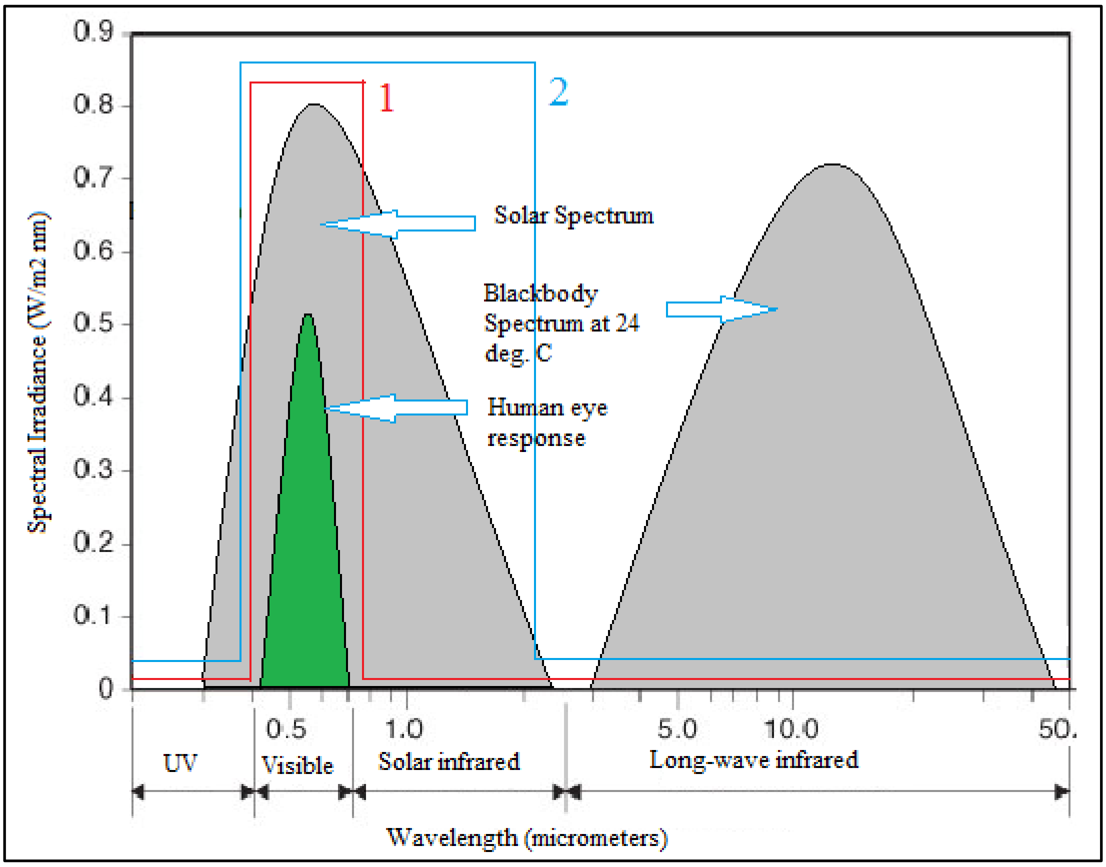

Figure 3.1: The ideal pattern of spectral transmittance of glazing in cold and hot weather conditions (adopted from (McCluney and Center, 1996))

The red line (line 1) indicates the ideal transmittance of a window with smart coating in cold state. Visible light should be transmitted and near infrared radiation should be reflected. Long-wave radiation is also reflected back to indoor. This transmittance approach leads to reduction of solar heat gain and is apt in nearly all climates. The blue line (line 2) indicates the ideal transmittance of a window with smart coating in hot state. Visible and near infrared radiation are transmitted while long-wave infrared is reflected to inside. This transmittance mode is suitable in low temperature climates where solar heat gain is desired.

Since these two spectrums have no interface, coatings can keep the transmission and reflection of near and far infrared radiation in line which can result in significant energy savings.

Different glazing types have different transparency to different sections of the visible and outside visible spectrum. Almost all glasses are partially transparent to UV radiation, nearly non-transparent to long-wave infrared radiation and transparent to near infrared radiation; while plastics are mostly opaque to UV. The comparisons and evaluation of different glazing types in this study will be based on the ideal glazing specifications discussed in this section. The benchmark of comparison is the amount of energy the glazing system consumes for maintinang heating and cooling demands in buildings as well as the energy consumed for electric lighting.

3.2 Basic glazing properties

There are four basic glazing properties that are critical in radiant energy transfer: *Reflectance, Transmittance,absorptance* and *emittance*.

Reflectance

Reflectance refers to the percentage of solar radiation which reflects off the surface of glass. Glass reflectivity is dependent on the glazing material, the surface quality, the coating, and the incident angle of the light.

Transmittance

When light reaches a surface or medium some part of it will pass through the glazing. There are different types of transmittance for different types of light and energy; for instance visible transmittance, UV transmittance and total solar energy transmittance. Visible transmittance indicates the efficiency of glass in providing clear views and daylight. Total solar energy transmittance corresponds to a wider range of spectrum including UV and near infrared radiation.

Absorptance

The percentage of energy which is not reflected off the surface or transmitted through glazing is absorbed by glass. The absorbed energy mainly transforms into heat, elevating the glass temperature. Since they absorb some heat from incident light, glasses can reduce cooling loads. However, the amount of energy saving due to glazing absorption is insignificant.

Emittance

The absorbed energy of glass is removed in two ways: convection to the surroundings and radiation from glass surface. Glass just like any other material emits long-wave far infrared energy at different surface temperatures. Therefore, one can improve energy efficiency of glass by reducing the window's emission.

There are also four main properties which affect the energy performance: *U-factor, Solar Heat Gain Coefficient (SHGC) or shading coefficient (SC)*, *Visible Transmittance* and *Air Leakage*. U-factor is the combined effects of conduction, convection and far infrared radiation due to temperature difference between interior and outdoor. Visible transmittance is an optical property of glass which indicates the fraction of visible radiation passing through glazing. SHGC or SC indicates the capability of glazing in controlling the amount of heat which is gained by direct or indirect solar radiation; not considering the environmental outdoor temperature. The cracks in the frame of window can also cause air leakage which leads to heat loss and heat gain.

The main focus of this study is to investigate the effect of thermochromic coatings on the reflectance and transmittance of light hitting the windows at UV, visible and near infra red spectrum. The other factors are introduced here but have not been considered in the present work. The ideal spectral behavior of TCWs is presented in Table 3-1. The visible transmission and reflectance should be equal in both sides of transition while the infra-red variations are from 0% to 65 %. It is advised that the change in transmission and reflectance should be able to cover near-IR (800-1200 nm) as this portion of the spectrum creates the highest amounts of heat (Saeli et al., 2010). In order to evaluate the thermochromic performance of coatings and to find the most appropriate thickness of the films the reflectance and transmittance measurements will be utilized. The major focus of the evaluation is placed on the measurements in visible and near infrared wavlengthes which are critical for electric lighting and cooling loads respectively.

The transition efficiency in terms of transmittance (ΔT%) and reflectance (ΔR%) can be calculated by using the following equations (Evans et al., 2007):

$$\Delta T\ \% = \frac{T_{T_R} - T_{T_t}}{T_{T_R}} \times 100 \tag{3.1}$$

$$\Delta R\ \% = \frac{R_{T_R} - R_{T_t}}{R_{T_R}} \times 100 \tag{3.2}$$

Where T is transmission, R is reflectance, $T_R$is the room temperature and T_t is the critical temperature or transition temperature.

Table 3-1: The Ideal optical performance of thermochromic windows (adapted from (Saeli et al., 2010))

state	**Monoclinic /Cold ($T<T_t$)**		**Rutile/Hot($T>T_t$)**	
wavelength	Visible (300-700 nm)	Infra-red (800-2500 nm)	Visible (300-700 nm)	Infra-red (800-2500 nm)
Transmission (T)	65 %	80 %	65 %	15%
Reflectance (R)	17 %	12 %	17 %	77%

The difference in transmittance and reflectance of the coated glass before (cold state) and after (hot state) thermochromic transition can be calculated by subtracting the corresponding values at a certain wavelengths.

$$\Delta T = (T_h - T_c) \tag{3.3}$$

And

$$\Delta R = (R_h - R_c) \tag{3.4}$$

Where $T_h$is the transmittance at hot state, $T_c$is the transmittance at cold state, R_h is the reflectance at hot state, and $R_c$is the reflectance at cold state.

3.3 Sputtering

Vanadium dioxide (VO_2) films were deposited on glass substrates using a water-cooled SG Control Engineering Pte Ltd series magnetron sputtering system using RF magnetron sputtering technique (see Figure 3.2). Since the study aims to investigate the application of thermochromic smart coatings for energy saving in architectural fenestration, clear glass is considered as thesubstrates. Various coating parameters and sputtering conditions presented in literature (see Table 2-2), were examined in the experiments. The samples were characterized for their structural and surface quality with XRD and FESEM tests. Ultimately, the most appropriate preparation condition was chosen. For cleaning purposes, the substrates were washed with liquid cleaner and then rinsed by flowing water. The cleaning process was followed by two consecutive ultra sonic baths in acetone and ethanol, 10 min each. Finally the substrates were rinsed with distilled water and dried by flow of purified nitrogen (99.999 %). The vanadium target (99.99% purity,10.16 cm diameter and 0.31 cm thickness) was placed in a target holder 15 cm above the substrates. The sputtering chamber was evacuated to 2.5×10^{-6}kPa before deposition by means of a turbo molecular pump and a rotary backing pump, charged with Foreline Trap and Oil Mist filters.

Figure 3.2: The SG Control Engineering Pte Ltd series magnetron sputtering system

In order to remove the contaminants and oxide layers from the target, it was pre-sputtered in an argon gas flow for 10 minutes.97.3sccm of Ar (99.999%) was introduced to the chamber as the working gas while getting mixed with 2.7 sccm of O_2 (99.999%) as the reactive gas. The working pressure was maintained at 1.3 Pa during the deposition. The substrates were heated up to350^{o}C before sputteringand remained at this temperature during deposition. The deposition time varied between 10 min and 60 min with 200 W of RF power in order to acquire different film thicknesses.The thickness was measured by a spectroscopic reflectometer (Filmetrics F20). By increasing the deposition time, film thickness was increased and samples of 20 nm, 50 nm, 80 nm and 120 nm were prepared.

3.4 Surface characterization

The structure and crystallinity of the films were characterized by means of X-Ray Diffractometer (Siemens Model-D 5000) between 5° and 80° using CuK$_{\alpha}$ radiation. The surface morphology of the films and their cross sectional structure were determined by a Field Emission Scanning Emission Microscope (Zeiss Auriga). The optical properties of the films were measured by means of a double beam UV-Vis-NIR spectrophotometer (JascoV-570) within 220-2200 nm wavelength range. Typically, there are two cutoff wavelengths beyond which glasses' overall transmittance drops drastically to near zero and they become highly absorbing. These cutoff lines are in far ultraviolet region at 170 nm and in the near infrared region at 2500 nm (Howell et al., 2011). The spectrophotometer was equipped with a self-designed heating unit. The film surface temperature was monitored with a temperature sensor while measuring the optical properties in the spectrophotometer. The reflectance and transmittance of the films were recorded in 20^{o}C as the cold state temperature and 90^{o}C as the hot state temperature.

4 Results and Discussions

4.1 Smart glazing comparison

The ideal windows are those, which let the light pass through in the visible range and block the unwanted radiation which cause heat loss or heat gain regarding the climate. The smart coatings such as electrochromic and thermochromic thin films feature spectrally selective behavior in the different wavelengths. Accordingly, in the visible range (400 nm – 700 nm) they are highly transmissive and in the near infrared (NIR) range (700 nm- 2500 nm) the reflectivity and transmissivity change in response to external triggers such as electricity, light and temperature. The infrared radiation due to its energy and wave nature is the greatest contributor to building heat among the different sections of spectrum (Saeli et al., 2010).

In order to compare different glazing technologies one should first define which goals take priority over the others. Is it wanted to block the IR radiation in the price of losing view or the view is more important? Is lighting energy is of more importance than cooling energy? Is the resulted color of the window important? How desirable is privacy?

Obviously, each coating has different effects on different parts of spectrum and results in diverse colors. Table 4-1 compares TC glazing, EC windows, LC technology and SPD in terms of their thermal effect, optical effect, visual performance, the activating factor and the challenges of these technologies. TC and EC windows show better upshot in reducing transmission and providing outside view.

Table 4-1: A comparison between Thermochromic, electrochromic, Liquid crystal and suspended particle devices (Addington and Schodek, 2005)

Glazing Type	**Thermal performance**	**Optical performance**	**View**	**Actuator**	**Challenge**
TC	Reducing transmitted radiation; UV transmissive in colored mode; operates best in the near IR	Low transmission in visible range	Transparent at high IR ; reduction in light intensity but still transparent	Heat (surface temperature)	Low visibility (can be solved by choosing the suitable dopant)
EC	reducing transmitted radiation	transparent in the short wavelength region coupled with opacity in the long wavelength region	Reduction in light intensity	Voltage or current	Electric field dependent; Wiring required
LC	Low reduction in transmitted radiation	Opaque in colored mode	Reduction in visibility; opaque	Voltage	High electricity consumption
SPD	Low reduction in transmitted radiation	Opaque in colored mode	Reduction in visibility; opaque	Current	High electricity consumption

As it is demonstrated in Figure 4.1: , electrochromic and thermochromic windows are the best glazing types in terms of reducing the required cooling load (Huovila, 2007). As it is mentioned earlier in the introduction, one of the most crucial parameters in evaluating the performance of smart windows is transmission modulation and their ability to pass through the visible light. Thermochromic and electrochromic windows fulfill this purpose. The overall energy consumption will also plunge considerably by using these two chromogenic smart windows. However, the necessity of wiring in electrochromic glazing and the better ability of thermochromic windows to maintain the visible transmission when it is properly doped (Kanu and Binions, 2010) besides their simple structure (Granqvist et al., 2009) have given thermochromic windows a cutting edge compared to the other counterparts.

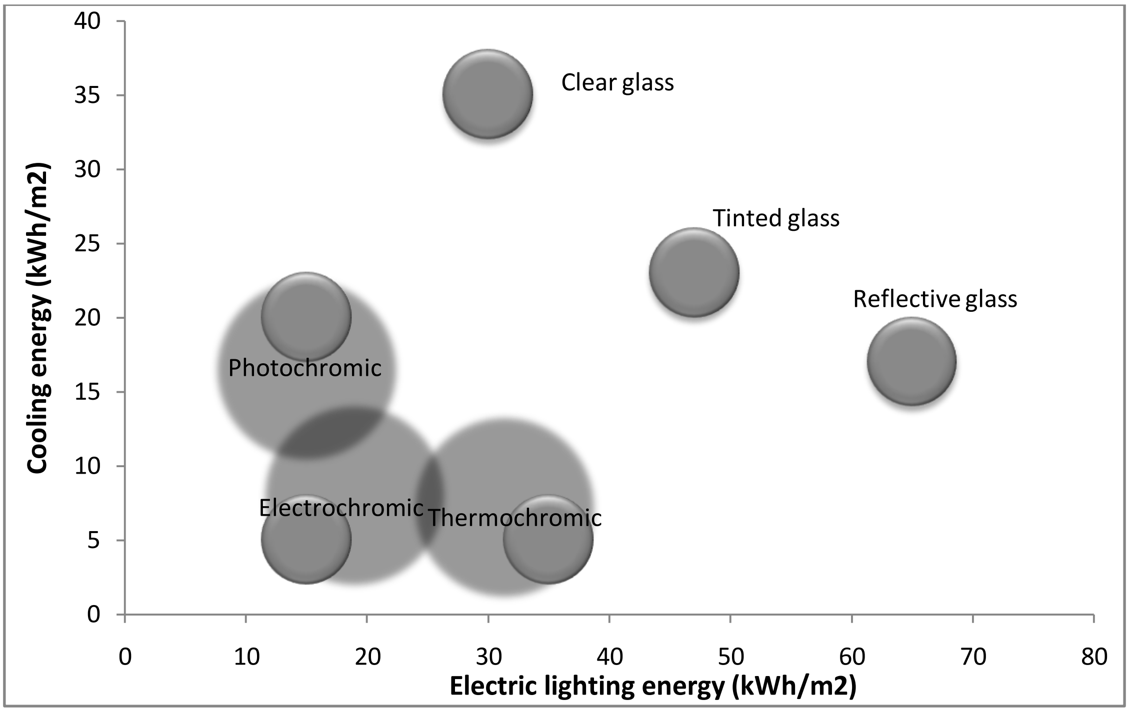

Figure 4.1: Comparison of electric lighting energy and cooling energy between different glazing types

As it is seen in the figure electrochromic and thermochromic windows consume less than around 40 kWh/m^2 for electric lighting energy and around 10 kWh/m^2 for cooling energy. Therefore, these two types feature better performance compared to other smart windows. It is clear that in order to acquire lower reflectivity, the refractive index of film should be lower. Hence, according to the application one should select the type of thin film and the value of refractive index. For fenestration in hot climates the desired window should be highly reflective in infrared while being transmissive enough to the visible light (Durrani et al., 2002). In this case, films should have higher refractive index in near infrared and should show lower refractive index in visible range. For instance, thermochromic thin films should have this characteristic in order to be effective in saving energy. According to experiments, at temperatures below the transition temperature, thermochromic films show higher reflectivity in visible range and lower reflectivity in NIR range. Whereas, at temperatures higher than transition point the optical properties are just reverse (Blackman et al., 2009).

4.2 Characterization results

The XRD result in Figure 4.2: demonstrates that the deposited VO_2 films on glass surface show a monoclinic structure. The dominant peak occurred at $2\theta = 29$ ° and it corresponds to a monoclinic vanadium dioxide with length of cell edges a= 12.09, b= 3.70, c= 6.43 and angle between them $\alpha = 90$ as the lattice parameters of the crystal.

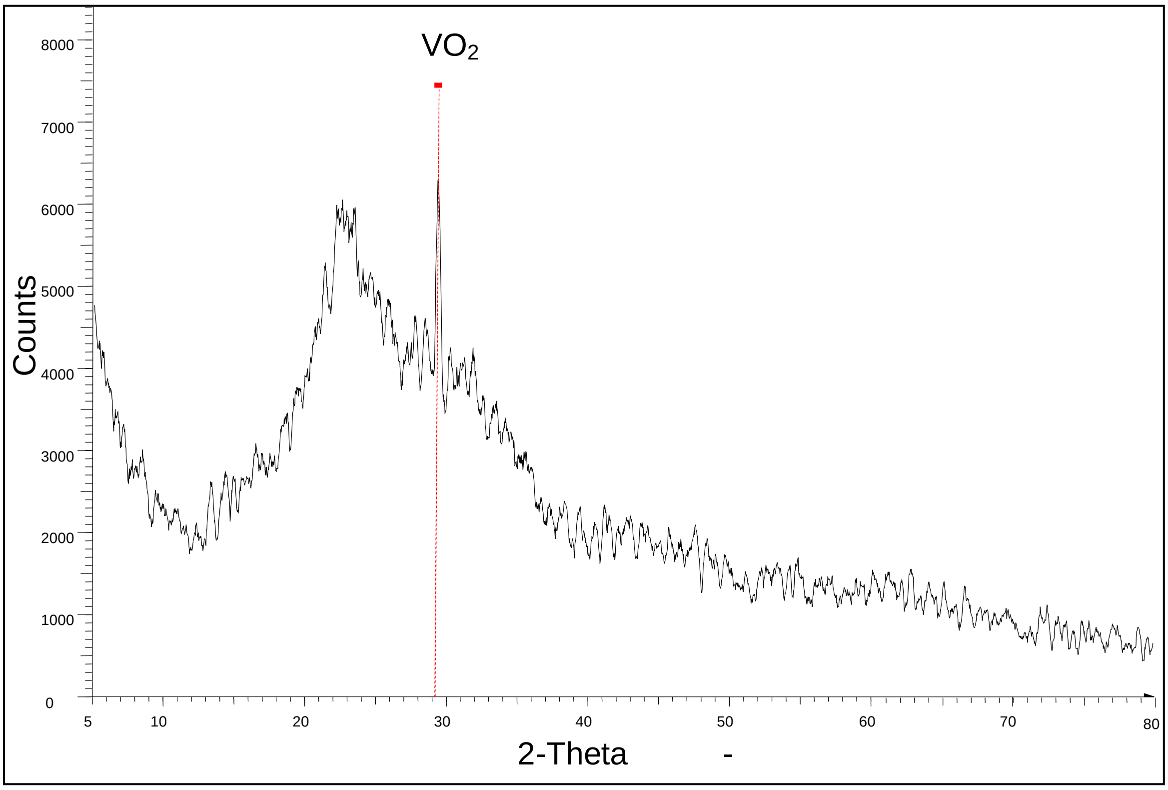

Figure 4.2: X-Ray diffraction pattern of VO_2/glass sample

Figure 4.3: (A) shows the uniform 80 nm thick deposited VO_2 film on the surface of glass. In the cross section image shown in Figure 4.3: (B), the sample is tilted 40° and as a result the film thickness should be measured considering the tilted angle.

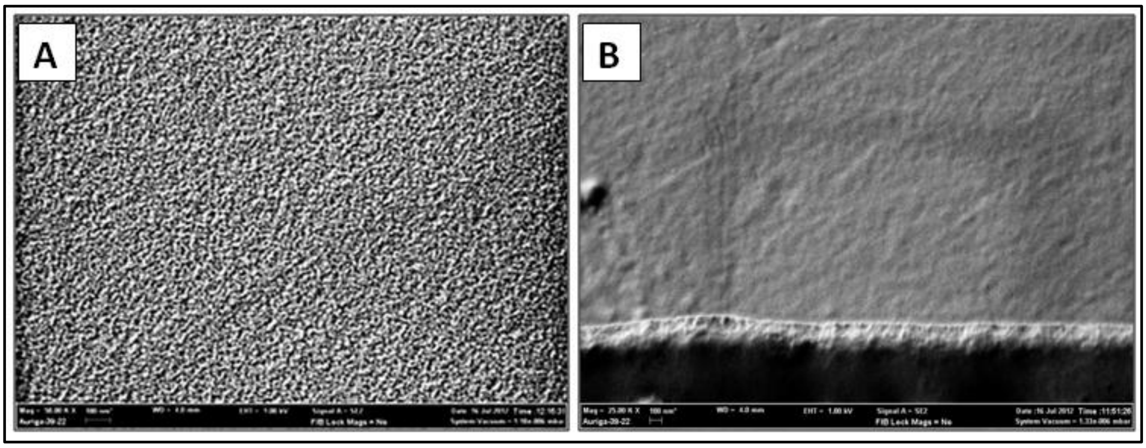

Figure 4.3: FESEM image of 80 nm thick VO_2 film deposited by RF magnetron sputtering on the surface of glass (A) surface top view ; (B) cross section (sample was tilted at 40°)

4.3 UV-Vis-NIR spectroscopy results

The samples with thickness more than 120 nm featured an undesirably low visible transmittance; and very thin films (lower than 20 nm) showed no obvious thermochromic transition. Consequently, the films with thickness between these two limits are the promising samples for glazing applications.Figure 4.4: illustrates the transmittance of VO_2/glass measured at 20 °C as the cold state and 90 °C as the hot state corresponding to monoclinic and rutile modes of VO_2crystals respectively. The transmittance decreased with the thickness of films and the samples with smaller thicknesses exhibited higher visible and infra red transmittance.

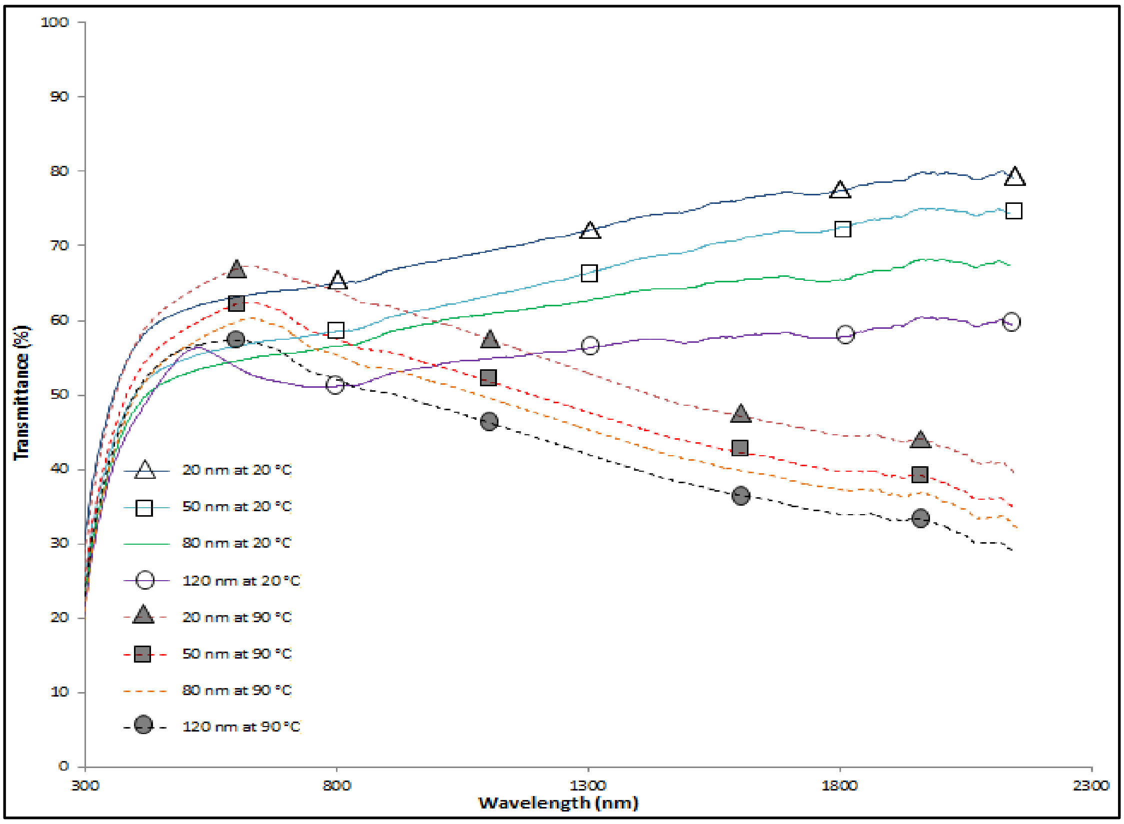

Figure 4.4: Transmittance measured from 300 nm to 2200 nm at 20 °C (solid line) and at 90 °C (dashed line)

As it can be observed in the transmittance results, in the near-IR range (780-1400 nm) the average transmittance decreased up to 22 % for 20 nm samples through transition while in the visible range (390-780 nm), the biggest increase in transmittance between hot and cold states was 6 % for the 50 nm sample. In average, the largest transmittance difference through the transition was 3.7 % and 10.5 % for 50 nm in visible range and for 20 nm in near-IR respectively. At 2200 nm, the transmittance increases by 40% for 20 nm samples. The summary of results showing the transmittance difference (ΔT) through thermochromic transition is calculated by using Eq. (3.3) and can be seen in Table 4-2.

Table 4-2: The effect of thermochromic transition on the samples transmittance: maximum transmittance difference (Max. ΔT), minimum transmittance difference (Min. ΔT) and average transmittance difference (Av. ΔT)

Sample	**20 nm**	**50 nm**	**80 nm**	**120 nm**
Wave Length	**Far-IR (1400-2200 nm)**			
Max. ΔT	40.1	39.7	35.2	30.6
Min. ΔT	22.3	21.6	19.9	16.6
Av. ΔT	32	31.7	28.1	23.8
Wave Length	**Near-IR (780-1400 nm)**			
Max. ΔT	22.2	21.5	19.9	16.6
Min. ΔT	-0.4	-0.4	-0.1	-2
Av. ΔT	10.5	10.1	9.9	7.2
Wave Length	**Visible (380-780 nm)**			
Max. ΔT	0.5	-0.5	-0.2	0.5
Min. ΔT	-4.2	-6	-5.7	-4.7
Av. ΔT	2	3.7	3.5	2.7

Thermochromic transition efficiency $\Delta T\% = \eta(\lambda)$ is calculated based on Eq. (3.1). This value can be used to evaluate the thermochromic switching performance of films. This efficiency is a function of wavelength and T_{20} and T_{90} are the transmittance of samples at 20 °C and 90 °C respectively. The performance of the films are estimated at 2200 nm and the η (2200 nm) of the 20 nm, 50 nm, 80 nm and 120 nm films are 51.3%, 54.3%, 53.2% and 52.6% respectively. The results show a similar thermochromic performance among all the samples with 50 nm film performing slightly better than others. In a previous research, thin films of 50 nm VO_2 on quartz glass exhibited 33% and 68% thermochromic efficiency depending on the quality of coating (Ma et al., 2012). Another reported thermochromic efficiency for 50 nm films was around 50% for VO_2 films prepared by a solution-based technique (Zhang et al., 2010).

Figure 4.5: shows the reflectance measurements of the samples of different thicknesses in their monoclinic (at 20 °C) and rutile (at 90 °C) states. At room temperature the samples with bigger thicknesses exhibited higher reflective behavior in infra red range. However, the 80 nm sample showed lower reflectance compared to the 50 nm sample.

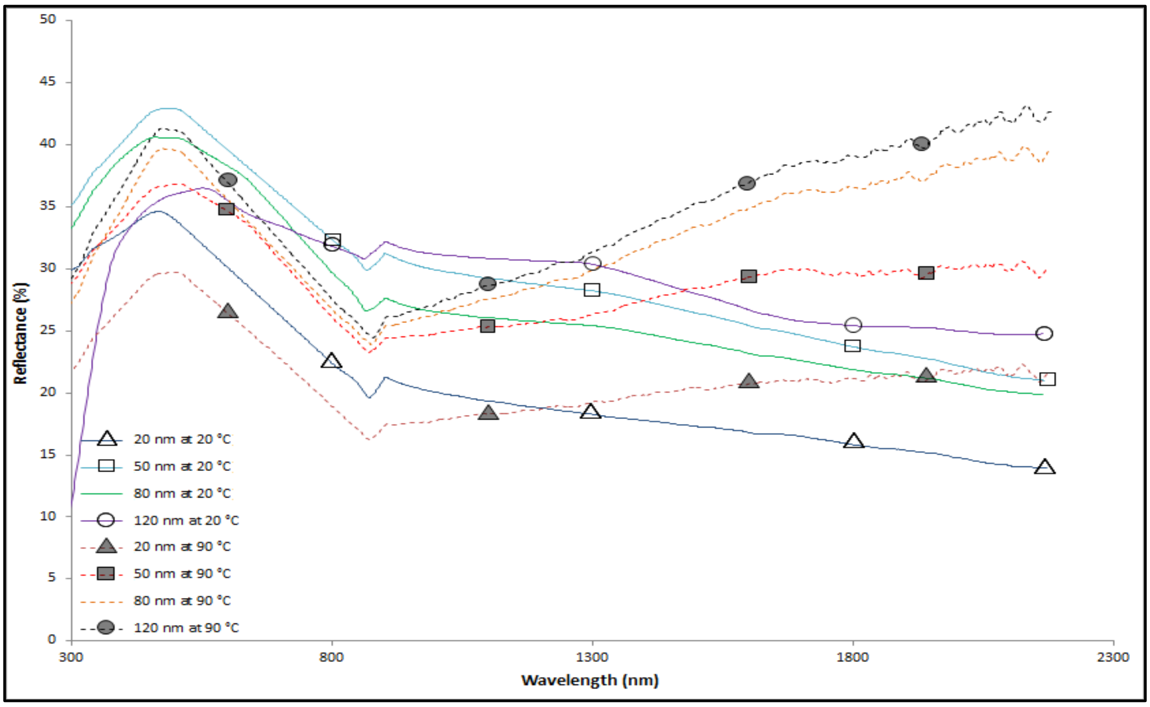

Figure 4.5: Reflectance measured from 300 nm to 2200 nm at 20 °C (solid line) and at 90 °C (dashed line)

The reflectance difference through thermochromic transition (ΔR) between 20 °C and 90 °C is also calculatedusing Eq. (4) and demonstrated in Figure 4.5: ; and the summary of the results are presented in Table 4-3.

Table 4-3: The effect of thermochromic transition on the samples reflectance: maximum reflectance difference (Max. ΔR), minimum reflectance difference (Min. ΔR) and average reflectance difference (Av. ΔR)

Sample	**20 nm**	**50 nm**	**80 nm**	**120 nm**
Wave Length		**Far-IR (1400-2200 nm)**		
Max. ΔR	9.4	10.6	21	19.4
Min. ΔR	1.9	-0.2	6.6	3.8
Av. ΔR	5.1	5.4	14.1	12.7
Wave Length		**Near-IR (780-1400 nm)**		
Max. ΔR	2.1	-0.1	6.7	3.8
Min. ΔR	-4.7	-7.8	-3.5	-7.3
Av. ΔR	-1.3	-4.2	1	-2.3
Wave Length		**Visible (380-780 nm)**		
Max. ΔR	-3.4	-4.6	-0.8	6.6
Min. ΔR	-6.7	-6.2	-4.5	-3.5
Av. ΔR	-4.2	-5.6	-2.7	2.1

The 80 nm sample exhibited the most desirable reflective behavior in near-IR range in terms of reflectance. Its reflectance experienced the maximum increase of 21 % in far-IR range, while in the near-IR wavelengths the reflectance increased up to 6.7 %. In the visible range the 120 nm sample showed more reflective behavior in average which is not preferable for building fenestration and large areas of glazing. On the other hand, 50 nm sample demonstrated the most suitable performance in passing the visible lightthrough.

5 Conclusions

The most common and modern technologies in smart windows have been reviewed through this study. It is seen that among the new smart windows, electrochromic and thermochromic windows by consuming less than around 40 kWh/m^{2}for electric lighting energy and around 10 kWh/m^2 for cooling energy feature better performance and the greatest efficacy in energy saving compared to other smart windows. Liquid crystal and suspended particle devices require excessive electricity to maintain the transparent mode while the electrochromic windows need electricity only for transition and colored mode. The only technology that doesn't need an electric field is the thermochromic windows which operate based on temperature variations. For thermochromic windows, there are two main challenges to overcome: lowering transition temperature and increasing the visible transmission which both can be solved by doping the coating by proper materials as well as finding the suitable thickness of films.

Vanadium dioxide thermochromic coatings on glass have shown the optimum thermochromic performance among the whole range of thermochromic materials. The coatings can be doped with different nano particles. Each dopant induces a special effect on the coating. Tungsten lowers the transition temperature, gold nanoparticles bring more pleasant film colors, fluorine increases the visible transmittance and titanium dioxide adds self-cleaning and mechanical strength to the films. Among the different deposition methods reactive sputtering PVD is the most widely method used to produce thermochromic thin films; and they benefit from more efficient deposition, film uniformity and scalability to larger substrates. Comparing the sputtering techniques, RF sputtering equipments work at lower voltage and lower sputtering gas pressure and are capable of sputtering electrically insulating targets and additionally higher deposition rates are produced.

All in all, the major aims that must be reckoned with thermochromic glazing are to maximize the change in infra-red (predominantly 800-1200 nm) Reflectivity and transmission, tapering the transition temperature to near room temperature and maintaining the proper visible transmission to conserve the lighting energy. By the same token, the emissivity of the films should be modulated. Since the emissivity of the coatings are high in both monoclinic and rutile states, this technology doesn't work well in cooler climates currently.

Regarding the third objective in this study, vanadium dioxide thin films have been deposited by RF magnetron sputtering. Different film thicknesses (20 nm, 50 nm, 80 nm and 120 nm) were deposited by altering the sputtering duration. The film characterization showed well developed and fine VO_2 coatings on the surface of clear glass substrates with monoclinic crystal structure. Based on the UV-Vis-NIR spectroscopy the desirable range of VO_2 film thickness is within 20-120 nm thickness range.

The measurements for reflectance and transmittance at 20 °C and 90 °C as the cold state and hot state respectively revealed that the smaller thicknesses will result in higher visible and infra red transmittance. Samples of 20 nm and 50 nm thickness exhibited better performance since they had thelargest transmittance decrease (-22 %) in near-IR and transmittance increase (6 %) in the visible range respectively. The 50 nm sample exhibited better reflective behavior at room temperature, greater reflectance difference (-5.6 %) in the visible range and highest thermochromic efficiency (η (2200 nm) = 54.3%). By the same token, the 80 nm sample performed the best in increasing the reflectance (6.7 %) in near-IR range.

To summarize concisely, 50 nm, 80 nm and 20 nm samples featured more preferable performance in increasing the visible light transmittance and increasing the near infra red reflectance. Nevertheless, the importance of reflectance and transmittance in each wavelength range and the purpose of glazing should be taken into account when the most suitable film thickness is to be selected.

6 Future Recommendations

It should be mentioned that there are a few works contributed to the energy modeling and heat transfer analysis of thermochromic thin films. This can be emphasized in the future attempts. Correlations should be adopted to relate the optical properties such as reflectance, transmittance and refractive index to radiation heat transfer in order to calculate the energy saving effect of smart coatings quantitavely. Comprehensive modeling and heat transfer study of the spectrally selective films are suggested for future studies.

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