

# Developments of Thermochromic VO<sub>2</sub>-Based Thin Films For Architectural Glazing

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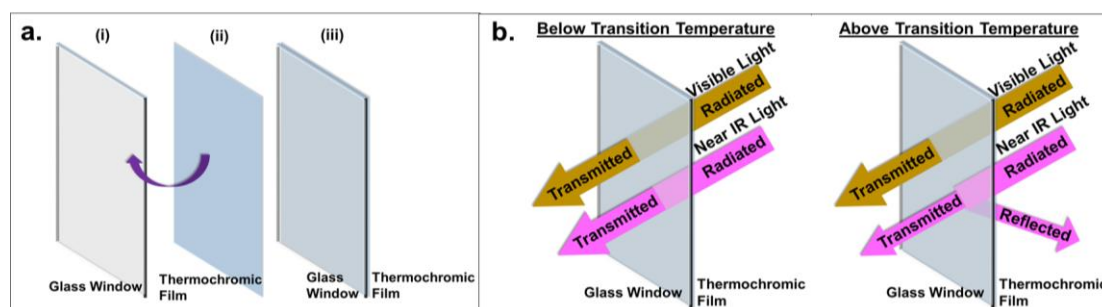
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**Abstract.** Investigation on properties of vanadium dioxide (VO<sub>2</sub>) thin films has received significant attention as it is a thermochromic material potentially for applications on architectural glazing in order to reduce energy consumption from usage of air-conditioning system. Most studies have focused on the hysteresis behavior of thermochromic VO<sub>2</sub> thin films that occurs at a certain phase transition temperature. Although large area coating techniques have recently been developed, there are still many obstacles in trying to deploy energy-efficient windows. Hence, this work concisely reviews on VO<sub>2</sub> thin films as thermochromic materials, and developments on preparation methodologies in order to enhance the thermochromic characteristics of VO<sub>2</sub> thin films.

## 1. Introduction

VO<sub>2</sub> thin films as thermochromic materials are widely known for its well-defined critical or transition temperature ( $T_t$ ) whereby no electrical power supply is needed. A simple illustration for thermochromic VO<sub>2</sub> thin films in architectural glazing is shown in Fig.1 (a). Thermochromic VO<sub>2</sub> thin films have been studied on glass substrates by several deposition techniques, for instances chemical vapor deposition [1], reactive pulsed laser deposition [2], sputtering [3], and solution-based methods [4].



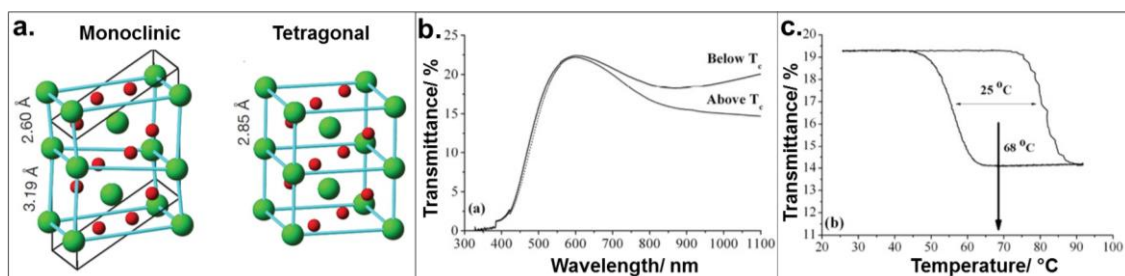
**Figure 1.** Schematic diagrams of (a) an example of glass window coating where (i) a glass window (ii) a thermochromic VO<sub>2</sub> film and (iii) thermochromic VO<sub>2</sub> thin film deposited on glass window, and (b) thermochromic VO<sub>2</sub> film deposited on glass window with temperature below and above  $T_t$ .

Fig.1 (b) shows schematic diagrams of thermochromic VO<sub>2</sub> films operating as intelligent window coatings. The illustration was suggested by Kiri et al. [5] in their study on thermochromic materials.

Theoretically, at first, the thermochromic VO<sub>2</sub> film transmits incident solar radiation quite well while acting as a semiconductor in its monoclinic state at low temperature (which preferably at room temperature) i.e. below the T<sub>t</sub>. Then, as the VO<sub>2</sub> film heats up which means its temperature increases and becomes higher than the T<sub>t</sub> due to high solar radiation and/or high outdoor temperatures, the thin film switches to a metal in its tetragonal state (or metallic state/ rutile state) and reflects infrared (IR) solar radiation. Therefore, this phenomenon is called semiconductor to metal transition (SMT) of thermochromic films and has been illustrated in Fig.2 (a) by Budai J.D. et al. [6]. This structural transformation can be first- or second-order in nature and may be reversible or irreversible, depending on the thermodynamics of the system [7].

Eventually, VO<sub>2</sub> is the only metal oxide that exhibits T<sub>t</sub> close to room temperature i.e. 68 °C [7,8]. The thermochromic properties can be seen in Fig.2 (b-c) which show the transmittance spectra of VO<sub>2</sub> films with heating effect. Fig.2 (b) represents a change in solar transmittance that can be influenced by increasing the temperature from 25 °C (below T<sub>t</sub> (which was also denoted as T<sub>c</sub>)) to 90 °C (above T<sub>t</sub>/T<sub>c</sub>). Fig.2 (c) shows a hysteresis loop representing the presence of phase transition of VO<sub>2</sub> films at 68 °C. However, it is difficult to deposit pure, stoichiometric single crystal of VO<sub>2</sub> films that has a distinct thermochromic effect due to the existence of many other vanadium oxides [7,9,10]. VO<sub>2</sub>(M) and VO<sub>2</sub>(B) are two different VO<sub>2</sub> structures i.e. monoclinic and metastable respectively, whereby high vanadium contents are required to get VO<sub>2</sub>(M) which has thermochromic property [11,12]. Besides that, VO<sub>2</sub>(M) films have to be crystallized to exhibit thermochromism, thus, substrate heating is needed. The substrate temperature was 300–500 °C during depositions without further annealing. On the other hand, some studies have annealed VO<sub>2</sub> films at 400–550 °C with or without argon (Ar) gas. Rapid thermal annealing in air has also been used as a possible alternative method to crystallize VO<sub>2</sub> films [13].

Four major obstacles for practical uses of thermochromic VO<sub>2</sub> thin films in architectural glazing are (i) T<sub>t</sub> is still high, (ii) visible light transmittance is too low at high temperature (i.e. above the T<sub>t</sub>), (iii) wide hysteresis width, and (iv) VO<sub>2</sub> is not a thermodynamically stable oxide which means its properties may alter with time. Hence, the following sections would concisely review several literatures on the developments of thermochromic VO<sub>2</sub>-based thin films with dopants and structured film systems.



**Figure 2.** (a) Illustrations on atomic structures of VO<sub>2</sub> in the monoclinic (semiconductor) and tetragonal (metallic) phases, with V and O atoms in green and red colours, respectively [6]. (b) Transmittance spectra of VO<sub>2</sub> thin films at 25 °C (below T<sub>t</sub> (or T<sub>c</sub>); semiconductor state) and 90 °C (above T<sub>t</sub> (or T<sub>c</sub>); metallic state), and (c) Transmittance at 1100 nm against heating temperature of the VO<sub>2</sub> thin films [1].

## 2. Elemental Dopants

Doped-VO<sub>2</sub> thin films can be prepared by embarking dopants during depositions of VO<sub>2</sub> thin films. Dopants were found to incorporate with VO<sub>2</sub> and have a significant potential in changing phase T<sub>t</sub> of VO<sub>2</sub> films. Hence, as a result, this makes doped-VO<sub>2</sub> thin films commercially viable. Atomic radius of dopants plays an important role i.e. when it is larger than V<sup>4+</sup> ion (of VO<sub>2</sub>), it results in a reduction in T<sub>t</sub> because of a charge-transfer mechanism taking place by extra electrons from the dopant into the vanadium d-bands [14,15]. Several dopants that have been applied in synthetizations of doped-VO<sub>2</sub>

thin films are aluminium ( $\text{Al}^{3+}$ ), cerium ( $\text{Ce}^{4+}$ ,  $\text{Ce}^{3+}$ ), fluorine (F), molybdenum ( $\text{Mo}^{5+}$ ,  $\text{Mo}^{6+}$ ), silicon ( $\text{Si}^{4+}$ ), titanium ( $\text{Ti}^{4+}$ ), and tungsten ( $\text{W}^{4+}$ ,  $\text{W}^{6+}$ ). Some of these dopants were reviewed particularly in the following sub-sections.

### 2.1. Aluminium Dopant

Al-doped  $\text{VO}_2$  thin films have been deposited on silicon (100) wafers by means of RF magnetron co-sputtering with V and Al targets at 490 °C [16]. Then, the Al-doped  $\text{VO}_2$  films were in-situ annealed. The prepared thin films exhibited almost the same Tt as undoped thermochromic  $\text{VO}_2$  thin films i.e. 67.9 °C as the films lost its special discontinuous change in electrical resistance as the Al doping increased.

### 2.2. Cerium Dopant

Ce-doped  $\text{VO}_2$  thin films have been prepared on muscovite substrates by spin coating method with a precursor i.e. a mixture powder of cerium (III) nitrate hexahydrate and  $\text{V}_2\text{O}_5$  heated at 850 °C for 30 mins and then stirred in 150 ml deionized water at room temperature for 2 h, forming a brown sol [17]. The films showed a single orientated (011) plane of monoclinic ( $\text{VO}_2$ ) at  $2\theta = 27.87^\circ$  and  $27.85^\circ$  for 0.84 % and 1.68 % of Ce doping, respectively, whereby the diffraction peaks were actually shifted from  $2\theta = 27.88^\circ$  diffraction peak for undoped  $\text{VO}_2$  films. In addition, phase Tt of the films decreased as Ce doping concentration increased i.e. the Tt was 64 °C and 60 °C for 0.84 % and 1.68 % of Ce doping, respectively.

### 2.3. Fluorine Dopant

Depositions of F-doped  $\text{VO}_2$  films on  $\text{SiO}_2$  coated float glass have been performed by aerosol assisted chemical vapour deposition with different vanadyl acetylacetonate, ethanol and F doping concentrations [18]. Phase Tt of the films was ~60 °C. RF-sputtered F-doped  $\text{VO}_2$  films on quartz glass have also been prepared at 327 °C [19]. As the F doping concentration increased from 0 % to 2.1 %, the Tt of the films decreased from 58 °C to 20 °C.

### 2.4. Molybdenum Dopant

Mo-doped  $\text{VO}_2$  films have been prepared on soda lime glass slides by dip coating method with a precursor i.e. a mixture powder of ammonium molybdate tetrahydrate and  $\text{V}_2\text{O}_5$  stirred in 500 ml deionized water at room temperature, and heated at 500 °C [20]. The Tt of the films decreased as Mo doping concentration increased i.e. the Tt was 62.5 °C, 47.5 °C, 34.0 °C and 24.0 °C for 0 %, 1 %, 4 % and 7 % of Mo doping concentrations, respectively. Optical reflectance of the films was higher than the undoped  $\text{VO}_2$  films in its metallic state, and increased with doping concentration in its semiconductor state.

### 2.5. Silicon Dopant

Si-doped  $\text{VO}_2$  thin films have been synthesized by DC magnetron sputtering on ITO-coated glass at 100 °C and in-situ annealing at 255 °C [21]. Optical transmittance and phase Tt of the films have been investigated to increase and decrease respectively with increasing Si doping concentration. When the Si/V ratio was 0.17, the Tt of the films was 46.1 °C.

### 2.6. Titanium Dopant

Ti-doped  $\text{VO}_2$  thin films have been RF magnetron sputtered on a  $\text{TiO}_2$  buffer layer that was deposited on silicon or fused quartz ( $\text{SiO}_2$ ) substrates [22]. The prepared films showed a decrease in Tt and a transmittance change with increasing doping concentration due to the thermochromism effect.

### 2.7. Tungsten Dopant

W-doped  $\text{VO}_2$  thin films have been deposited on silicon (100) wafers by means of RF magnetron co-sputtering with V and W targets at 490 °C [23]. Tt of the deposited films was 68.2 °C, 61.4 °C,

54.0 °C and 49.5 °C for sputtering power of 25 W, 75 W, 88 W and 100 W, correspondingly. By means of DC magnetron sputtering, W-doped VO<sub>2</sub> thin films have been prepared on Corning 7059 glass, standard glass and beryllium foil substrates at substrate temperature of 400 °C [24]. The deposited films showed lower T<sub>t</sub> than the undoped films of 65 °C. The T<sub>t</sub> was 32 °C with 0.0032 W/V ratio.

### 3. Structured Films

Another way to alter thermochromic characteristics of VO<sub>2</sub> films is by adding another layer(s) of anti-reflection and/or anti-oxidation and/or photocatalytic self-cleaning coatings into VO<sub>2</sub> film(s), hence making bilayer or multilayer structured films. Deposition techniques employed could be the same or different for all films in one structured film system. Several examples of the depositions were reviewed in the following sub-sections for bilayer and multilayer structured-based VO<sub>2</sub> thin films.

#### 3.1. Bilayer structured films

Al oxide films with 30 nm thickness have been deposited on 80 nm thickness thermochromic VO<sub>2</sub> films by DC magnetron sputtering with V and Al targets at 380 °C and annealed at 300 °C [25]. The prepared films exhibited a slight increase in visible transmittance with same IR transmittance in metallic state of VO<sub>2</sub>. The Al oxide also showed good protection and delayed oxidation for more than one day. Furthermore, 85 nm thickness VO<sub>2</sub> films have been prepared by RF magnetron sputtering on different substrates i.e. glass coated with ZnON (as a buffer layer), glass coated with SnO<sub>2</sub> (as a buffer layer), silica float glass and silicon [26]. The deposited VO<sub>2</sub> films at 300 °C and 400 °C showed thermochromic characteristics with highest visible transmittance of ~40 % and lowest T<sub>t</sub> of 43 °C obtained for glass/ZnON/VO<sub>2</sub> films deposited at 400 °C. Depositions of VO<sub>2</sub> films by DC magnetron sputtering at 300 °C on RF sputtered buffer layers i.e. TiO<sub>2</sub>, SnO<sub>2</sub> and SiO<sub>2</sub> have also been carried out [27]. All deposited films exhibited thermochromism except for glass/TiO<sub>2</sub>/VO<sub>2</sub> films because no change in optical transmittance was observed in both semiconductor and metallic states. The highest visible transmittance of ~40 % with lowest IR transmittance of ~8 % in metallic state and lowest T<sub>t</sub> of 55 °C were obtained for glass/SnO<sub>2</sub>/VO<sub>2</sub> films. This was due to the deposited VO<sub>2</sub> film on glass/SnO<sub>2</sub> being looser and more porous causing high visible transmittance. Moreover, SiO<sub>2</sub> can be used as an anti-reflection coating when deposited on VO<sub>2</sub> film by RF magnetron sputtering [28,29]. With 100 nm thickness of SiO<sub>2</sub> coating on the VO<sub>2</sub> film, an increase in luminous transmittance from 42 % to 55 % at semiconductor state and from 40 % to 50 % at metallic state was observed. The study also reported that thermochromism of the films was enhanced due to an improvement in film crystallinity during deposition of the anti-reflection coating, however the T<sub>t</sub> was constant at 70 °C. Vanadium oxide films have also been prepared on V, W, Fe, Ni, Ti and Pt metal buffer layers by RF magnetron sputtering at substrate temperature of 400 °C with a V target [30]. Nevertheless, thermochromic VO<sub>2</sub> films were obtained on V and W metal buffer layers of 10 nm thickness. Both bilayer structured films exhibited T<sub>t</sub> of 68 °C and 53 °C for silica glass/V/VO<sub>2</sub> and silica glass/W/VO<sub>2</sub> films, respectively. Thermochromic VO<sub>2</sub> film with 120 nm thickness have been overlaid with nanostructured CeO<sub>2</sub> film deposited by RF magnetron sputtering at room temperature [31]. Optical transmittance of the deposited films decreased from its semiconductor to metallic state with T<sub>t</sub> of 68 °C. 56 nm thick zirconium oxide (ZrO<sub>2</sub>) have been deposited on 50 nm thick VO<sub>2</sub> film by RF magnetron sputtering at 500 °C and room temperature for VO<sub>2</sub> and ZrO<sub>2</sub> thin films, respectively [32]. The structured films showed T<sub>t</sub> at 52 °C. Thermochromic VO<sub>2</sub> films have been layered with ZnO films that deposited by RF magnetron sputtering at room temperature [33]. The films exhibited visible transmittance of more than 40 % in semiconductor and metallic states, and IR transmittance of less than 20 % in its metallic state.

#### 3.2. Multilayer Structured Films

Multilayer structured glass/TiO<sub>2</sub>/VO<sub>2</sub>/TiO<sub>2</sub> and glass/TiO<sub>2</sub>/VO<sub>2</sub>/TiO<sub>2</sub>/VO<sub>2</sub>/TiO<sub>2</sub> thin films have been prepared by DC magnetron sputtering at substrate temperature of 450 °C [34]. For

glass/TiO<sub>2</sub>/VO<sub>2</sub>/TiO<sub>2</sub> films, the VO<sub>2</sub> and TiO<sub>2</sub> films had 50 nm and 75 nm film thickness, respectively, with refractive index of 2.2, whereas for glass/TiO<sub>2</sub>/VO<sub>2</sub>/TiO<sub>2</sub>/VO<sub>2</sub>/TiO<sub>2</sub> films, the VO<sub>2</sub> and TiO<sub>2</sub> films had 50 nm and 130 nm film thickness, respectively. Luminous transmittance of the films was 62.8 % and 58 % for three-layer films, and 45 % and 42.3% for five-layer films, in its semiconductor and metallic states, respectively. In addition, Tt of the films was 60 °C. A thermochromic VO<sub>2</sub> thin film deposited between two F-doped SnO<sub>2</sub> (FTO) films by DC magnetron sputtering whereby the FTO films were fabricated using photolithography and a chemical etching process, hence, this resulted in a multilayer structured films of conductive glass/FTO/VO<sub>2</sub>/FTO [35]. The maximum optical transmittance for the structured films was 50 % and 35 % for its semiconductor and metallic states, respectively. A multilayer structured silicon substrate/Ag/HfO<sub>2</sub>/VO<sub>2</sub> thin films where HfO<sub>2</sub> is hafnium oxide, has been prepared by DC magnetron sputtering, electron beam evaporation and RF magnetron sputtering for Ag, HfO<sub>2</sub> and VO<sub>2</sub> films, respectively [36]. The films exhibited a decrease in optical reflectance in its metallic state with Tt of ~58 °C. The films were further studied by using W-doped VO<sub>2</sub> film. The films showed decreasing Tt as the W doping concentration increased. Moreover, depositions of float glass/TiO<sub>2</sub>(1)/VO<sub>2</sub>:W/TiO<sub>2</sub>(2)/Si<sub>x</sub>N<sub>y</sub> structured films have been conducted with substrate temperature of 270 °C, 210 °C and 230 °C for W-doped VO<sub>2</sub>, TiO<sub>2</sub> and Si<sub>x</sub>N<sub>y</sub> films, respectively [37]. The Tt of the films were reduced to 33 °C with an increase in visible transmittance of ~58 % in both states. Furthermore, a thermochromic VO<sub>2</sub> film has also been stacked between two silicon suboxide (*a*-SiO<sub>x</sub>) films by RF magnetron sputtering with substrate temperature of 600 °C [38]. The fused quartz/*a*-SiO<sub>x</sub>/VO<sub>2</sub>/*a*-SiO<sub>x</sub> films with film thickness of 100 nm and 25 nm for VO<sub>2</sub> and *a*-SiO<sub>x</sub>, respectively, showed same visible transmittance of ~48 % in both states with lower IR transmittance of ~20 % in its metallic state while the thermochromism preserved. Multi-functions window coatings of glass/TiO<sub>2</sub>(R)/VO<sub>2</sub>(M)/TiO<sub>2</sub>(A) consisting of energy-saving, anti-fogging and self-cleaning effects have been obtained by medium frequency reactive magnetron sputtering [39]. The films exhibited Tt of 61.5 °C with visible transmittance of ~40 % in both states.

#### 4. Conclusion

Depositions of VO<sub>2</sub>-based thin films were developed accordingly with dopants and structured film systems to improve the thermochromic properties of VO<sub>2</sub> films. Dopants corporate with VO<sub>2</sub> very well i.e. as atomic radii of the dopants are larger than V<sup>4+</sup> ions (of VO<sub>2</sub>), Tt of VO<sub>2</sub> reduced, and vice versa. Meanwhile, structured films were also intensively studied by stacking films of different properties such as anti-reflection, anti-oxidation, photocatalytic self-cleaning, and anti-fogging, with thermochromic VO<sub>2</sub> films. Nevertheless, major challenges with preparing thermochromic VO<sub>2</sub>-based thin films for architectural glazing applications still remain. For instance, when Tt of the VO<sub>2</sub> films was lower than 68 °C, only slight changes were detected in the visible transmittance, and broad hysteresis width was obtained. Despite that, this research area is still of interest to many researchers which progresses at a healthy pace to achieve commercial application of intelligent window coatings.

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