

Infrared optical properties of doped and pure thermochromic coatings for solar thermal absorbers

Anna Krammer¹, Fabrice T. Demière¹ and Andreas Schüler¹

¹ Solar Energy and Building Physics Laboratory, École Polytechnique Fédérale de Lausanne (EPFL), Lausanne (Switzerland)

Abstract

A new generation of solar collectors is based on thermochromic thin film technology, where the remarkable optical changes of vanadium dioxide, through its reversible semiconductor-to-metal phase transition, are exploited. This study reports on the infrared optical properties of VO₂ based coatings deposited on Al substrates by reactive magnetron sputtering. Fourier transform infrared (FTIR) spectroscopy is used to determine the emittance of a VO₂ coated sample before ($\epsilon = \sim 6\%$) and after ($\epsilon = \sim 33\%$) the phase transition. The angular dependence of the thermal emittance for such coating is investigated. It is found that the emittance increases with increasing the angle from normal incidence. In literature it is widely reported that the transition temperature of vanadium dioxide can be tuned by doping with different elements. An increase in the transition temperature is desired for solar thermal applications and it is reached with the addition of Ge into the VO₂ matrix. Here we show that through Ge doping, the emittance switch, especially the emittance in the high temperature state, can be optimized as well. An increase of $\sim 10\%$ in emittance is recorded.

Keywords: Solar thermal, thermochromic absorber coating, doped vanadium dioxide, overheating protection

1. Introduction

Due to their simple design and operation, solar thermal collectors for domestic hot water generation and space heating are one of the most common solar energy harvesting systems in use today. Such collectors are typically designed to cover between 50-80% of the annual domestic hot water demand. During cold periods all the absorbed energy is useful. During hot periods, however, when solar radiation is abundant and demand is low, stagnation occurs. Storage is limited and excess heat cannot be diverted. The heat transfer fluid evaporates and temperature of the solar absorber can exceed 200°C. A self-draining system and special valves are then necessary. At such temperatures, glycol degradation and further damage of the collector occurs. Frame, thermal insulation, selective absorber coating deteriorate and become less efficient.

A novel type of thermochromic solar collector has been proposed [1, 2, 3]. Recently, industry has demonstrated functional collectors on the real scale [4]. These new collectors are based on switchable selective absorber coatings that can change their optical properties in the infrared spectral region so that they can absorb and repel heat in a controlled manner. Thus, the stagnation temperature is limited and overheating of the system is avoided. Until recently, this was one of the main drawbacks of thermal collectors.

The “smart” thermochromic absorber coating exhibits good selectivity (high absorptance, low emittance) up to a given temperature and bad selectivity (high absorptance, high emittance) above that temperature in order to prevent overheating. Here the material of choice is vanadium dioxide.

It undergoes a reversible thermochromic transition, during which its switch in thermal emittance and subsequent heat dissipation to the surroundings at high temperatures is sufficient to limit the stagnation temperature. Evaporation of the transfer fluid is avoided and thermal charges on the system reduced.

1.1 Vanadium dioxide

Vanadium dioxide is an emblematic thermochromic material. It undergoes an ultrafast and fully reversible first order semiconductor-to-metal (SMT) transition at 67°C.[5] Through the transition the crystal structure changes from the low temperature monoclinic (P21/c) to tetragonal rutile (P42/mnm) at high temperature and is accompanied by abrupt changes in electrical and optical properties.[6] A resistivity change of several orders of magnitude and significant changes in the optical constants – especially in the infrared range – occur at the transition. Due to these remarkable changes occurring close to room-temperature, vanadium dioxide has been the object of overwhelming fundamental and applied research. Vanadium dioxide shows potential in a wide range of applications ranging from smart windows[7] and radiators for space applications[8] to microelectronic and device applications such as steep-slope switches[9], tunable capacitors[10] etc. Meanwhile, the underlying mechanism – structural or charge driven transition – is still open to debate with recent studies [11] suggesting a correlation-assisted Peierls transition, stressing the joint effect of lattice symmetry breaking and Coulomb interactions. Additionally, discoveries of exotic VO₂ behaviors, such as the very recently reported one order-of magnitude breakdown of the Wiedemann-Franz law in the vicinity of the semiconductor-to-metal transition[12], push the fundamental research of VO₂ even further.

Through doping with different elements, the optical and electrical properties of vanadium dioxide can be tuned and, most importantly, its transition temperature can be tailored to suit various applications. W⁶⁺, Mo⁶⁺, Ta⁵⁺ and Nb⁵⁺ have been widely reported as dopants decreasing the transition temperature[6]. Tungsten has been regarded as one of the most efficient in doing so, enabling a reduction of 49-55°C per at.% dopant[13]. Therefore, for room temperature applications such as smart windows, tungsten doping is well-established. On the other hand, increasing the transition temperature through doping has been less studied and the identified dopants proved less efficient. Aluminium doping has been reported as both increasing and decreasing the transition temperature. In [13], authors show that Al³⁺ induces gradual amorphization of the thin films without significant effect on the transition temperature. Cr³⁺ and Fe³⁺ were reported to increase the transition temperature with no more than 3°C [14]. Thermochromic VO₂ based solar absorber coatings, as discussed in the present work, or the recent developments at microelectronic device level (where the required switching temperatures are higher than the normal operating temperatures of the device), underline the importance of an efficient and reliable doping which allows for a range of elevated transition temperatures to be achieved.

Authors have recently showed that Ge doping is successful in increasing the transition temperature of vanadium dioxide sputtered thin films and a transition temperature of ~95°C has been reached [15]. In comparison, the currently available commercial products, based on Al doped (4 – 12 at.%) vanadium oxide films, transition at 70° - 75°C. Therefore, the above 20°C temperature rise constitutes a significant increase and an important step in establishing efficient vanadium dioxide based absorber coatings. In the present work, authors determine the effect of Ge addition to the vanadium dioxide lattice from the thermal emissivity point of view. First, the spectral reflectance and emissivity of a pure VO₂ film in the mid-infrared range (2-15µm) is measured. The sample is measured both below and above the switching temperature. Then, the angular dependence of the thermal emittance is discussed. Finally, the spectral emissivity in two differently doped samples is measured and compared with that of a pure VO₂ film. Thus, the influence of Ge doping on the IR optical properties of the coatings - specifically their thermal emissivity - is determined.

2. Experimental

Pure and doped vanadium dioxide thin films have been deposited by reactive magnetron co-sputtering in sputter-up configuration. A schema of the deposition chamber and the process is shown in Fig. 1.

The base pressure of the chamber was below $5 \cdot 10^{-8}$ mbar. The process gas is Ar (purity 99.999%) and O₂ (purity 99.995%) is the reactive gas for oxide formation. A mass flow controller regulates the Ar gas feed to the chamber and the Ar flow is set to 17.4 sccm. Inside the chamber, a lambda-probe (Zirom XS22) oxygen sensor is installed. Based on the pressure readings, a Proportional Integral Derivative (PID) feedback control regulates the oxygen flow such that a constant oxygen pressure is maintained. The oxygen partial pressure during depositions is $5.25 \pm 0.25 \cdot 10^{-4}$ mbar, while the working pressure is $\sim 7.1 \pm 0.1 \cdot 10^{-3}$ mbar.

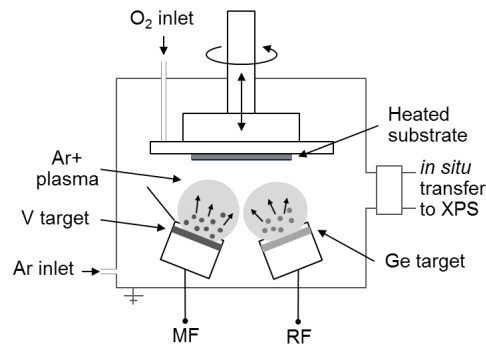


Fig. 1: Schematic representation of the sputtering chamber with targets, plasma glow and adjustable substrate holder

The magnetrons are run by DC power (MKS) for the vanadium target and radio frequency (RF) AC power (Advanced Energy) for the germanium target. The metallic target discs are provided by Testbourne Ltd. The purity of the 2" targets is guaranteed at 99.95% for the V and 99.999% for the Ge target. The power on the V target is set to 150 W, whereas for the Ge source, RF power (13.56 Mhz) of 8W and 12W are applied. To limit doping, magnets are removed from the magnetron, thus reducing the magnetic field and, subsequently, the plasma density.

The films are deposited on 0.5 mm thick, 50 mm x 50 mm sized Al foil (Goodfellow) for the Fourier transform infrared (FTIR) spectrometry, on stainless steel for the thermal imaging and on Si wafer for the angular dependence determination. The deposition takes place at high temperature – 600°C is measured by a stationary thermocouple above the rotating substrate holder. The thickness of the deposited films is estimated at ~320 – 340 nm.

A commercial thermographic camera (FLIR Systems, Inc.) is used to visualize the optical switch of VO₂ based coatings over the transition and to determine the angular dependence of the emissivity of these samples. The camera detects infrared radiation in the range of 7.5 - 13 μm.

The spectral reflectance is measured with a Bio-Rad FTS-175C Fourier transform infrared spectrometer equipped with a 3" golden integrating sphere and a high performance nitrogen-cooled MCT detector for the Mid-IR range (2-20 μm).

3. Results and discussion

3.1. Switching emittance

The optical switch of the thermochromic film in the infrared spectral region has been captured by thermal imaging (Fig.2). A VO₂ based coating has been deposited on reflecting stainless steel (SS) substrate. Below the transition temperature, the semiconducting VO₂ coating is transparent to the IR radiation and only the substrate is seen on the thermal image. However, above the transition temperature, the film - deposited in the middle of the SS sheet - appears on the thermal image as the VO₂ becomes opaque to the infrared radiation in its metallic state. Therefore, when deposited on a reflecting substrate such as stainless steel, copper or aluminium, the thermochromic coating has a low thermal emittance below and a high emittance above the transition temperature.

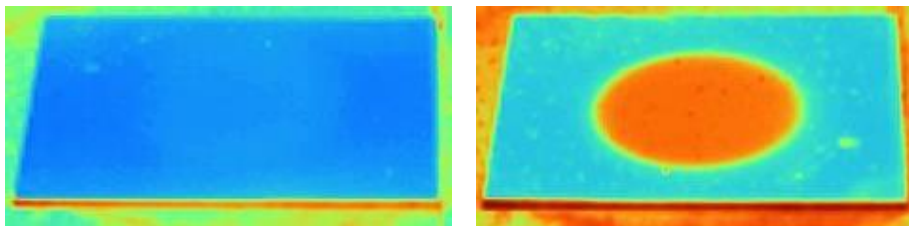


Fig. 2: Thermal image of the thermochromic absorber coating in the cold state with low emittance (left) and in the hot state with high emittance (right)

Then, with an FTIR spectrometer coupled with an integrating sphere and a Mid-IR MCT detector, the total reflectance spectra of a VO₂ coated aluminium sheet is determined. The measurement is done both below and above the transition temperature (T_C) of vanadium dioxide. Since the considered sample is opaque, from the measured reflectance spectra, the spectral emissivity can be determined and the results are displayed in Fig. 3. The thermal emittance of the thermochromic absorber in its two states considerably differs.

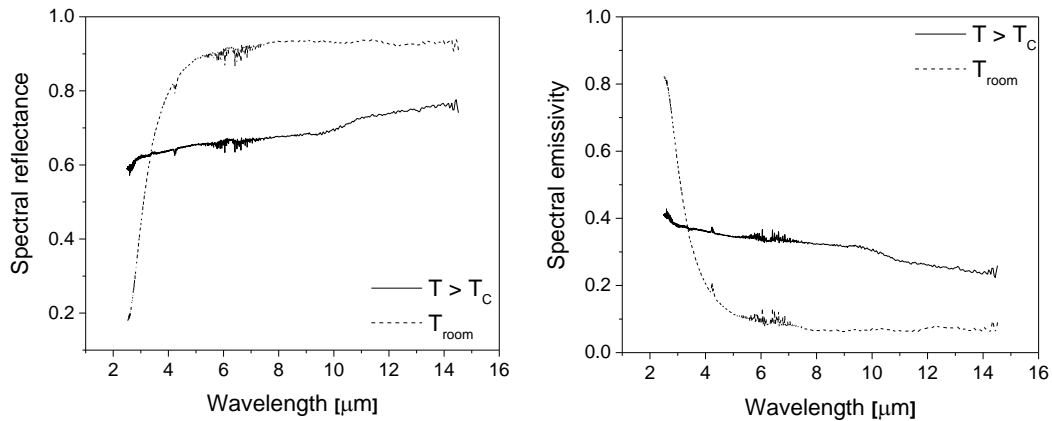


Fig. 3: Spectral reflectance and corresponding spectral emissivity of the thermochromic absorber both below and above the transition temperature of vanadium dioxide.

Above 100°C collector temperature, the operating temperature should be limited to avoid thermal stresses on the system. The spectral emittance of a blackbody at 100°C peaks at around 8 μm wavelength. Therefore, the emittance change in this spectral region is of special interest. In Fig. 3, at 8 μm, the emissivity changes markedly from ~6% below T_C to ~33% above T_C .

3.2. Angular dependence

The angular dependence of the emittance of a thermochromic VO₂ film deposited on Si wafer, above its critical transition temperature was determined. Since the coating is supposed to show metallic properties, the emittance versus angle for a rough oxidized aluminum plate was measured for comparison. The measurements were performed at 100°C for the VO₂ and aluminium samples. The results are shown in Fig. 4a. The curves are similar. The VO₂ coating in the metallic state follows the same trend of directional emissivity as the Al plate, whose values are similar to those given in tables. They are roughly constant from normal angles to about 60 degrees from the normal. At angles higher than 60 degrees the thermal emittance rises and reaches a maximum at grazing angles. The thermal emittance is expected to drop to 0 when parallel to the surface, but this measurement could not be made precisely with the experimental setup. This behavior is well described by the Fresnel's equation and typical results for metals are illustrated in Fig. 4b.

The emittance being higher at greater angles is beneficial as most thermal emittance measurements are done at normal angles. Therefore the thermochromic coating will be more efficient at dissipating heat via radiation than what normal measurements would predict.

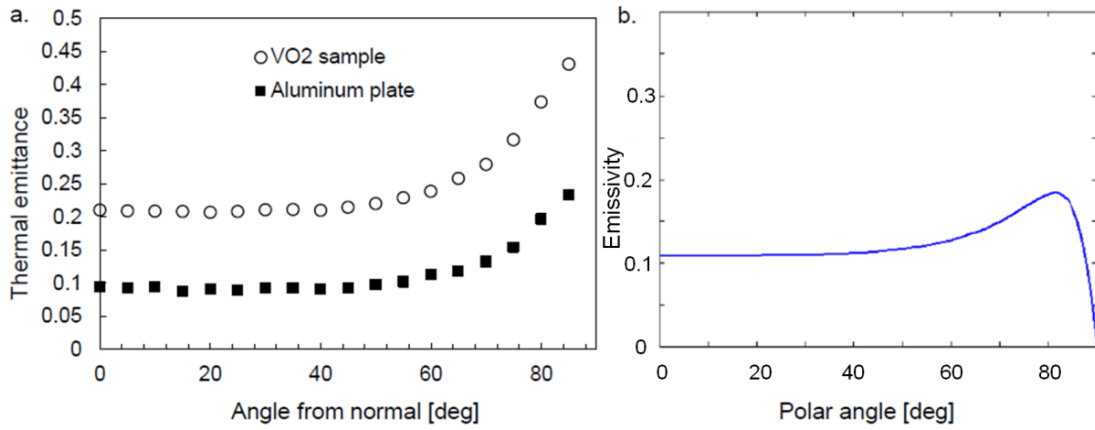


Fig. 4: a) Angular dependence of the thermal emittance of VO₂ and Al plate. b) Typical directional emissivity of a metal according to Fresnel's relation with $n=1.5$ and $k=7$ [16].

3.3. Thermal emittance of doped thermochromic samples

The transition from low to high emittance of the thermochromic absorber at a temperature of 67°C might be too low for solar thermal applications. Several elements have been reported to alter the phase transition temperature of vanadium dioxide. The authors have long studied dopants capable of increasing T_C to around 100°C. Recently [15], we have reported on the successful increase of the transition temperature to ~95°C. This has been reached with 5.9 at.% Ge doping. In the next step, our aim is to measure the effect of such doping on the thermal emittance of the samples. A pure and two Ge doped thermochromic coatings have been deposited on Al sheet. The Ge content in the doped samples has been varied by applying different power on the Ge target during deposition – 8W and 12W. This is calculated to correspond to 1.1 and 2.6 at.% Ge in the samples, leading to transition temperatures of ~75°C and ~77°C respectively. The three different samples have been compared and it is found that the emittance, notably in the hot state, is gradually increasing with doping. Roughly 10% increase in emittance between the pure and the strongly doped sample (with 12W applied on the Ge target) at 8 μm , is recorded. The results are shown in Fig. 5.

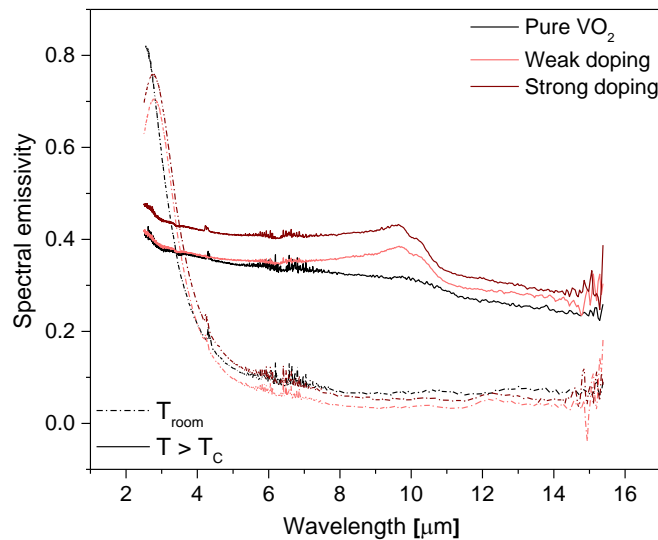


Fig. 5: Spectral emissivity change between the low (dashed line) and high temperature state (solid line) of three samples with different composition: pure VO₂, weakly doped and strongly doped coatings.

Using a simple model collector consisting of a glass cover, an air gap and a switchable absorber in thermal contact with the water pipes, *Baldi et al.*[17] calculated the stagnation temperature map plotted as a function of solar absorptance and thermal emittance. Based on this work and with the assumption that the switch only impacts the absorber emittance, while the solar absorptance remains relatively unchanged, the stagnation temperature is estimated to be lowered from $\sim 195^{\circ}\text{C}$ to $\sim 150^{\circ}\text{C}$ using pure VO_2 based absorbers and from $\sim 185^{\circ}\text{C}$ to $\sim 140^{\circ}\text{C}$ for Ge doped VO_2 based absorbers. At these reduced stagnation temperatures, the degradation of glycols is mostly prevented and, at the typical pressures present in the collector (3 bars), the evaporation of the heat transfer fluid is overcome.

4. Conclusions

Adding a thermochromic function to the currently available selective solar absorber coatings could bring forward a new generation of smart solar thermal collectors where the stagnation temperature is limited and overheating prevented. In this work, pure and Ge doped vanadium dioxide based thermochromic coatings have been deposited by reactive magnetron co-sputtering on highly reflective substrates. Their optical properties in the Mid-IR range have been determined. Pure VO_2 films show high potential as their emissivity changes significantly from 0.06 to 0.33 at the wavelength of interest of $8\ \mu\text{m}$. Moreover, the angular dependent emittance measurements show that the emittance of the coatings in the hot state (above the transition temperature of the thermochromic layer) is increasing with the angles from the normal. This suggests that normal emittance measurements underestimate the total emittance of the coatings. Finally, it is shown that, besides raising the phase transition temperature to 95°C , Ge doping has the additional advantage of increasing the emissivity of the thermochromic coating above T_C and, therefore, decreasing the stagnation temperature of the collector.

Acknowledgements

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5. References

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