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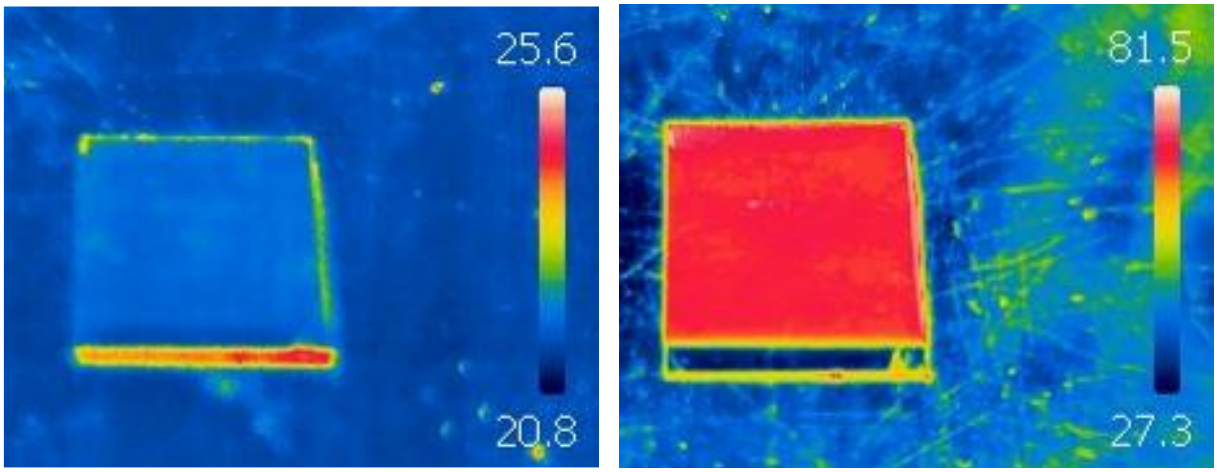
Thermochromic coatings for overheating protection of solar thermal collectors

Towards industrial implementation



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Summary

With the advent of a new generation of switchable absorber coatings, overheating and the resulting stagnation of solar thermal collectors – until recently a common problem even in central European latitudes – can be successfully overcome. Based on thermochromic thin films, these absorbers exhibit a change in thermal emittance at a critical temperature T_C. The collector temperature is passively regulated through this thermal emittance change from low thermal emittance below T_C to high thermal emittance above T_C. The transition temperature of the vanadium oxide-based films is usually around 68°C, but in the framework of previous research at EPFL/LESO-PB a novel type of doping has been determined which allowed for the successful increase of the transition temperature to above ~95°C. Besides the considerable increase in transition temperature, Ge doped thermochromic films have been shown to have the additional benefit of an increased thermal emittance above the critical temperature. This allows for a better heat dissipation and lower stagnation temperatures in the collector. The thermal emittance modulation of such absorbers of above 40% is substantial, allowing a considerable reduction of the stagnation temperatures below the evaporation temperature of the heat transfer fluid and the degradation of glycols is mostly prevented. Such “smart” solar collectors allow for a better dimensioning of solar thermal systems.

In this project, suitable designs of multi-layered coatings for maximized performance shall be developed, with an emphasis on industry-compatible deposition methods. The lifetime of the coatings shall be determined and optimized. In addition to this, new designs with a maximized emittance switch will be explored.

Zusammenfassung

Mit dem Aufkommen einer neuen Generation von schaltbaren Absorberbeschichtungen die Überhitzung und die daraus resultierende Stagnation von thermischen Sonnenkollektoren - bis vor kurzem ein selbst in mitteleuropäischen Breiten verbreitetes Problem - erfolgreich überwunden werden. Die thermochromen selektiven Absorberbeschichtungen weisen eine Änderung der thermischen Emissivität bei einer kritischen Temperatur T_C auf. Durch diese Änderung von niedriger thermischer Emissivität unterhalb von T_C zu hoher thermischer Emissivität oberhalb von T_C wird ein unerwünschtes zu starkes Ansteigen der Absorbertemperatur verhindert. Die Übergangstemperatur der vanadiumoxidhaltigen Filme beträgt normalerweise etwa 68°C. Im Rahmen der Forschung an der EPFL (Labor LESO-PB) wurde jedoch ein neuartiger Dotierungstyp gefunden, der es ermöglichte, eine Übergangstemperatur von über 95°C zu erreichen. Neben dem erheblichen Anstieg der Übergangstemperatur haben mit Germanium dotierte thermochrome Filme den zusätzlichen Vorteil einer erhöhten thermischen Emissivität oberhalb der kritischen Temperatur. Dies ermöglicht eine bessere Wärmeabstrahlung und niedrigere Stagnationstemperaturen im Kollektor. Die Modulation der thermische Emissivität solcher Absorber ist mit über 40% erheblich, was eine Verringerung der Stagnationstemperaturen unter die Verdampfungstemperatur des Wärmeträgerfluids ermöglicht, und auf diese Weise den Abbau von Glykolen größtenteils verhindert. Solche «intelligenten» Solarkollektoren ermöglichen eine bessere Dimensionierung von Solarthermieanlagen.

In diesem Projekt sollen geeignete Designs für mehrschichtige Beschichtungen mit besten Leistungseigenschaften entwickelt werden, wobei der Schwerpunkt auf industriell umsetzbaren Abscheideverfahren liegt. Die Lebensdauer der Beschichtungen soll bestimmt und optimiert werden. Darüber hinaus werden neue Designs mit besonders stark ausgeprägter Emissivitätsänderung untersucht.

Résumée

Avec l'avènement d'une nouvelle génération de revêtements d'absorbeurs intelligents, la surchauffe et la stagnation des capteurs solaires thermiques qui en résulte - un problème commun, même sous les latitudes d'Europe centrale - peuvent être surmontées. Grâce aux revêtements thermochromes, des nouveaux absorbeurs solaires présentent une modification de l'émissivité thermique à une température critique T_C. La température du collecteur est régulée passivement par ce changement d' émissivité thermique, qui passe d'une émissivité thermique faible inférieure à T_C à une émissivité thermique élevée supérieure à T_C. La température de transition des films à base d'oxyde de vanadium se situe généralement autour de 68°C. Dans le cadre de recherches antérieures à l'EPFL (au laboratoire LESO-PB), un nouveau type de dopage a été déterminé, qui permet d'obtenir une température de transition au-dessus de 95°C. Outre l'augmentation considérable de la température de transition, il a été démontré qu'au-dessus de la température critique les couches minces thermochromes dopées au Ge présentent l'avantage supplémentaire d'une émissivité thermique accrue. Cela permet une meilleure dissipation de la chaleur et des températures de stagnation inférieures à l'intérieur du capteur solaire. La modulation de l'émissivité thermique de ces absorbeurs monte à 40%, ce qui permet une réduction considérable des températures de stagnation en dessous de la température d'évaporation du fluide caloporteur et empêche en grande partie la dégradation des glycols. De tels capteurs solaires «intelligents» permettent un meilleur dimensionnement des systèmes thermiques solaires.

Dans le cadre de ce projet, des conceptions appropriées de revêtements multicouches offrant des performances maximales seront développées, en mettant l'accent sur les méthodes de dépôt compatibles avec l'industrie. La durée de vie des revêtements doit être déterminée et optimisée. De plus, de nouvelles conceptions pour un changement d'émissivité thermique maximal seront explorées.

Contents

List of abbreviations

SFOE	Swiss Federal Office of Energy
EPFL	École Polytechnique Fédérale de Lausanne
LESO-PB	Laboratoire d'Énergie Solaire et Physique du Bâtiment (Solar Energy and Building Physics Laboratory)
STM	Scanning Tunneling Microscopy
STS	Scanning Tunneling Spectroscopy
FTIR	Fourier Transform Infrared
SEM	Scanning Electron Microscopy
SMT	Semiconductor – to – Metal Transition
XRD	X-Ray Diffraction
UV	Ultraviolet
VIS	Visible
NIR	Near Infrared

1 Introduction

Due to their simple design and operation, solar thermal collectors for domestic hot water generation and space heating are 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 even in central European latitudes. 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 and selective absorber coating deteriorate and become less efficient.

An innovative solution to overheating lies in the successful integration of a thermochromic function into a multilayered selective solar absorber coating. A “smart” solar absorber should exhibit good selectivity (high absorptance, low emittance) at normal operating temperatures and bad selectivity (low absorptance, high emittance) at excessive operating temperatures. Thermochromic vanadium dioxide thin films undergo a semiconductor-to-metal phase transition at a critical temperature T_C = 68°C leading to drastic changes in its optical properties. Through the perfectly reversible transition, the thermal emittance of a thermochromic absorber changes markedly, from ~5% emissivity below T_C to ~35-40% above T_C. The switch in emissivity and subsequent heat dissipation to the surroundings at high temperatures is sufficient to limit the stagnation temperature so that the evaporation of the heat transfer fluid is avoided. Moreover, excessive thermal stress on the collector materials is also avoided, and stagnation times are considerably reduced.

2 Context

2.1 Background / State of the art

In the framework of previous Swiss Federal Office of Energy (SFOE) projects [Kra18, Pao15], a novel thermochromic material for a new generation of solar collectors has been developed by the Solar Energy and Building Physics Laboratory (LESO-PB) of EPFL. The proposed multilayered absorber consists of a highly reflective Al substrate on which a vanadium dioxide based thermochromic layer, a selective absorber and an antireflective top layer are deposited by magnetron sputtering. The smart coating can absorb and repel heat in a controlled manner by changing its optical properties in the infrared spectral region according to temperature. This prevents overheating of the system which, until recently, was one of the main drawbacks of thermal collectors.

Recently, upscaling of such switching absorber coatings was demonstrated and the thermochromic approach has been experimentally proven to successfully limit the stagnation temperature at the collector level. Viessmann, one of the leading European solar thermal collector manufacturers, is the first to commercially launch a thermochromic solar collector, the Vitosol ThermProtect [Vie16].

Viessmann has experimentally demonstrated that the emissivity switch of the thermochromic layer at 75°C is sufficient to decrease the stagnation temperature of the ThermProtect absorber by more than 35°C compared to a standard absorber. Limiting the temperature to below 150°C, at 3 bar overpressure present in the system, the evaporation of the heat transfer fluid is avoided. Moreover, stagnation time is reduced by more than 70%. [Mer16]

Reliability of the thermochromic absorber was also confirmed by accelerated and cyclic aging tests. Experimental measurements on the thermochromic collectors have proven the foreseen advantages

such as simpler construction, very low maintenance, no evaporation or degradation of heat transfer fluid and extended lifetime. Limitations on the installed collector area are lifted.

However, the reported 75°C transition temperature is relatively low. The coatings developed at LESO-PB have been engineered to increase the transition temperature of 67 – 68°C of pure vanadium dioxide to above 90°C. This increase in the phase transition temperature is achieved by germanium doping. With a ~6 at.% Ge concentration in the vanadium dioxide film a transition temperature of ~96°C has been reached [Kra17]. This is one of the highest transition temperatures reported in literature for doped vanadium dioxide thin films.

Furthermore, authors have shown that by Ge doping the thermal emissivity of the material – especially in the high temperature state – is also increased [Kra17-2]. Above the transition temperature, the thermal emittance of a Ge doped thermochromic absorber coating calculated over the 2.5 – 14 µm range was determined to be ~0.045 larger than that of the pure VO_2 based absorber (0.443 compared to 0.398).

Finally, the angular dependence of the emittance of a thermochromic VO_2 film was studied. It is shown that the emittance is 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 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 predict.

2.2 Motivation of the project

Co-sputtering at an industrial scale is challenging and sputtering from alloyed targets is proposed instead. High quality switching thermochromic thin films should be deposited from alloy targets of different compositions and the best target composition should be identified.

Furthermore, the thermochromic layer must be integrated into the multi-layered absorber coating of the industrial partner. Therefore, optical simulations should be performed based on the optical constants of the substrate and selective absorber employed in the industrial process and the LESO-PB developed thermochromic coating. The constituting layers should be tailored so that the resulting smart absorber coating has an optimized optical performance.

Lifetime analysis is also crucial for samples intended for large scale production. Hence evaluation and optimization of the lifetime of deposited multi-layered coatings is envisaged. For an enhanced emissivity modulation – theoretically predicted for Fabry-Pérot type of structures – deposited multilayers will be characterized.

2.3 Objectives of the project

1. Identify best target composition for sputtering from a mixed V-Ge target
2. Identify promising multilayer designs with suitable solar absorption and switching thermal emissivity
3. Deposit experimentally the selected multilayer designs
4. Evaluation of the lifetime of the deposited multilayered coatings
5. Optimization of the lifetime of the deposited multilayered coatings
6. Experimental assessment of the theoretically predicted giant emissivity switch
7. Dissemination of the obtained results in SFOE reports and peer-reviewed journal articles.

3 Approach and methodology

3.1 Approach

WP1: Sputtering from V-Ge alloy targets

In close collaboration with the industrial partner, Savosolar questions such as:

- What is the best composition for a mixed target in order to produce Ge doped VO_2 films with the correct transition temperature from one magnetron alone?
- Can the process be run in a stable mode, in spite of different sputter-yields for the elements?

are answered. The suitable Ge concentration and process parameters in the sputtering process shall be determined.

Milestone MS1: Choice of target composition and process parameters

WP2: Simulations of multilayered absorber designs

Computer simulations of thin film interference are performed. The theoretical predictions of the multilayered absorber performance are based on the optical constants n and k of the constituting layers. Thermochromic based multilayered absorber coatings, with optimized solar absorptance, α_{sol} and thermal emittance ε_{th} are selected. Methods: M4.

Milestone MS2: Choice of promising multilayer designs with suitable solar absorption and switching thermal emissivity

WP3: Deposition of the designed multilayered coatings

The selected multilayered designs are deposited by means of sputtering. The coating development is carried out in an iterative sequence, until sufficient optical performance is achieved:

deposition → characterization → correction of process parameters → deposition → characterization etc.

The thermo-optical properties of the deposited multilayers, such as solar absorptance, α_{sol} and thermal emittance, ε_{th} are measured as function of temperature. Methods M3, M5.

Milestone MS3: Samples of the selected multilayer designs with suitable solar absorption and switching thermal emissivity

WP4: Accelerated ageing tests

To determine the environmental stability and service lifetime of the thermochromic absorber coating, accelerated aging tests are carried out at high temperature in dry air and in 100% relative humidity as well. The thermo-optical properties, solar absorption and thermal emittance, are evaluated after each aging step. Methods M3, M6.

Milestone MS4: Evaluation of the lifetime of the produced multilayered coatings

WP5: Optimization of ageing properties

In order to optimize the maximum lifetime of the thermochromic absorber coating, eventual identified during the aging tests shall be addressed. If necessary, new, improved coatings shall be deposited and tested. The optimization process is based on the feedback cycle between WP4⇔WP5. Methods M3, M6.

Milestone MS5: Optimization of the lifetime of the produced multilayered coatings

WP6: Giant emissivity switch

Can the theoretical prediction of the giant emissivity switch be demonstrated experimentally?

Thin film multilayered stacks, exhibiting surprisingly large emissivity switch, will be deposited according to the theoretical designs. The switching performance is investigated by FTIR spectrophotometry coupled with an integrating sphere. Methods M3, M5.

Milestone MS6: Experimental assessment of the theoretically predicted giant emissivity switch

WP7: Reporting
Submission of annual and final SFOE reports summarizing the progress of the project.

3.2 Methodology

M1: Deposition of individual thermochromic layers for various analyses, studies of process parameters

Individual thermochromic layers will be deposited by reactive magnetron sputtering. A special focus will be on doped VO_2 films sputtered from mixed vanadium/germanium targets in argon/oxygen atmosphere. Monitoring the oxygen partial pressure by means of a lambda probe will allow a real time control of the process parameters. Plasma cleaning of substrate and chamber contributes to the purity of the deposited films. The likewise prepared samples will be used for a thorough characterization of the material properties (see method M2).

M2: Structural, electrical and optical characterization of the deposited films

The individual thermochromic layers deposited by method M1 will be analyzed by various techniques, such as:

M2A: Analysis of sample topography by Scanning Tunneling Microscopy

Thermochromic sample surfaces at the nanometer/atomic scale are observed with the newly installed SPECS STM 150 Aarhus system. Besides providing topographic information, the investigation of the local electronic properties and band gaps on the atomic scale, is possible through scanning tunneling spectroscopy (STS). For doped samples this could give an invaluable insight into the homogeneity of doping. Whether the individual grains have all similar bandgaps or there is segregation in the film could significantly help advance our understanding of the thermochromic behavior of such films. The new STM/STS is especially suited for thermochromic sample characterization as the temperature ranges

from 90 to 400K. The STM housing vacuum chamber is built directly on the deposition chamber, thus, permitting an in-line vacuum transfer between the two and preventing the sample surface from contamination.

M2B: Temperature dependent electrical resistivity measurements

Temperature dependent electrical resistivity measurements allow us to quickly identify thermochromic samples which exhibit the characteristic semiconductor-to-metal phase transition. The quality of the deposited films is assessed from their thermochromic properties such as the transition temperature, steepness of the transition or hysteresis width.

M2C: Temperature dependent FTIR spectrophotometry

The spectral reflectance/emittance of the thermochromic Ge doped VO_2 films is measured with a Fourier transform infrared spectrometer equipped with a 3" gold integrating sphere and a high-performance nitrogen-cooled MCT detector for the Mid-IR range (2.5-15 µm). To precisely control the sample temperature during the FTIR measurements and determine the thermal emittance of the layer in both the low and high temperature state, a customized portable heating stage has been designed.

M3: Optical Characterization

M3A: Multiangle UV-VIS-NIR and FTIR spectrophotometry

UV-VIS-NIR and FTIR spectrophotometry, with suitable integrating spheres, allow for the determination of the solar absorptance and thermal emittance of the deposited absorber coatings. To precisely control the sample temperature during the measurements and to determine the thermal emittance and solar absorptance of the coatings in both the low and high temperature state, a customized portable heating stage is designed.

M3B: IR emissiometry

Digital infrared imaging techniques will allow us to directly image and quantify the switch in the thermal emissivity of the coatings. Values obtained for the cold state are cross-checked with an IR-emissiometer (TIR100).

Figure 1: Bio-Rad FTS-175C FTIR spectrometer equipped with the golden integrating sphere, MCT detector for the Mid-IR range and the designed heating stage.

M4: Computer simulations of the properties of the multilayered thin films

Based on the knowledge of the optical constants previously derived from ellipsometry, the optical properties of the multilayered thermochromic coating are predicted. These simulations allow for the determination of the optimal composition and thickness of the conventional and thermochromic layers. The computer simulations are based on the method of characteristic matrices representing each individual layer in a stack. The dielectric function is determined not only in the UV-VIS-NIR spectral range, but also in the mid-infrared (MIR) range. Therefore, not only the solar absorptance, but also the MIR-reflectance and the thermal emissivity can be simulated.

M5: Deposition of multilayered stacks

Based on the individual thin film characterization results (method *M2*) and the multilayered stack simulations (method *M4*), selected multilayered thin film stacks are deposited by means of magnetron sputtering. To control the thickness of the individual layers the deposition rates must be calibrated for each constituting layer. Alternating magnetron sources with shutters are employed in building up the designed multilayered stack.

M6: Lifetime assessment

Absorber stacks deposited according to method *M5*, undergo accelerated aging tests at high temperature and in dry air in a laboratory oven with programmable heating cycles. The aging test is carried out according to the current ISO 22975-3:2014 standard on “Absorber surface durability”. For classification of solar absorber durability, a performance criteria, PC is defined:

$$PC = -\Delta\alpha_S + 0.5\Delta\varepsilon_T \leq 5\%,$$

where

$\Delta\alpha_S$ is the change in solar absorptance between the actual test time, $\alpha_{S,t}$ and the initial value of solar absorptance, $\alpha_{S,i}$;
$\Delta\varepsilon_T$ is the change in thermal emittance betw**e**en the value measured at the time of the test, $\varepsilon_{T,t}$ and the initial thermal emittance, $\varepsilon_{T,i}$.
The absorber coating is qualified for a service lifetime of at least 25 years if the performance criteria is fulfilled.

4 Results and discussion

4.1 WP1: Sputtering from V-Ge alloy targets

Sputtering from alloy V-Ge targets has been proven feasible and Ge-doped thermochromic thin films have been successfully sputtered from alloy targets after slight adjustments of the working parameters [Kra18-2]. V-Ge alloy target with 5 at.% Ge has been identified as suitable target composition. An alloy target with 7 at.% Ge has also been tested, but the resulting films displayed no switching behaviour as the Ge concentration is, likely, too high.

The sputtered Ge doped VO_2 thin films have been characterized in-depth by four-point probe electrical resistivity measurement, Scanning Tunneling Microscopy (STM) and Fourier transform infrared spectrometry.

Four-Point Probe Resistivity Measurement

Four-point probe resistivity measurement is the standard measurement for the determination of thermochromic behavior and phase transition temperature. The temperature dependent electrical resistivity has been recorded and plotted in Figure 2. The measurement was carried out from ~40°C to 100 – 110°C.

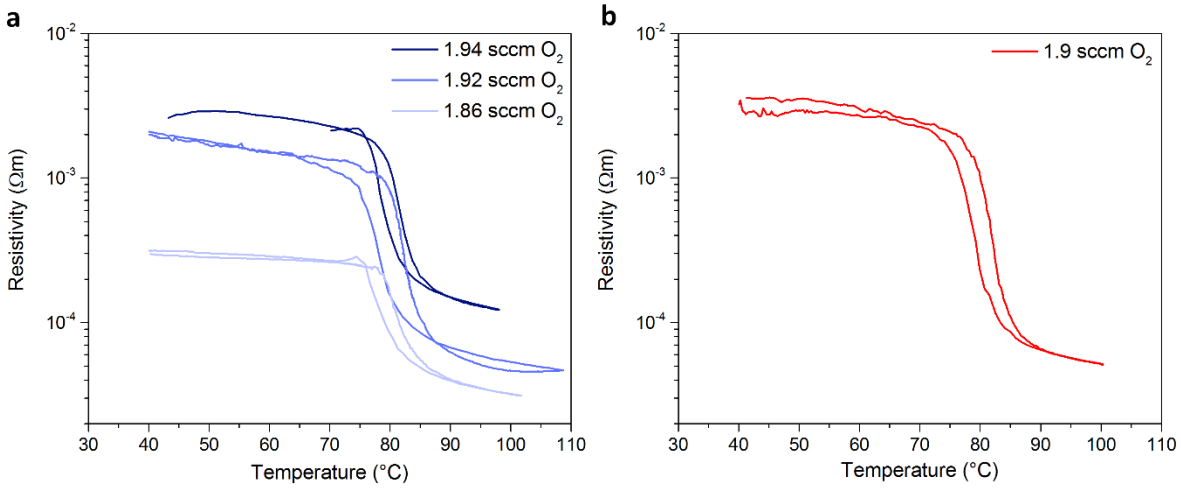

Figure 2: Temperature dependent electrical resistivity of VO_2:Ge films on Si (100) substrates deposited at different oxygen flows.

The oxygen partial pressure during deposition is important, affecting greatly the resistivity modulation and the absolute values of electrical resistivity. In general, samples deposited at higher oxygen flows exhibit higher resistivity values and lower oxygen flows lead to more conductive films. While the magnitude of the thermochromic transition and the absolute resistivity values are strongly dependent on the oxygen partial pressure/flow, the thermochromic transition temperature is rather constant for all films deposited from the alloy target with 5 at.% Ge, $T_t \approx 82$°C. This is ≈ 15°C higher than the transition temperature of pure VO_2 thin films with $T_t \approx 68$°C.

The films generally undergo a ~1 order of magnitude transition, with the highest resistivity modulation of 1.6 orders of magnitude measured for the film deposited with 1.9 sccm oxygen flow (O_2/Ar = 1/9.1). Pure VO_2 films generally exhibit three or more orders of magnitude increase in conductivity, but for doped samples smaller modulations are typical and a 1.6 order of magnitude transition in a sample switching at 82°C is remarkable.

Deposition from alloy targets instead of co-sputtering is the preferred process for industry and the relatively straightforward deposition of high-quality switching Ge doped films with elevated transition temperature from such alloy targets prove that the upscaling of Ge doped VO_2 based selective absorber coatings is feasible.

Scanning Tunneling Microscopy (STM)

The surface topography of the deposited Ge doped VO_2 films has been investigated by STM. The observed grains vary in shape and size, ranging from ~20 to 60 nm. Examples are shown in Figure 3. Spherical or rounded grains are typical for pure vanadium dioxide films. However, the acicular shape is particular and has been previously observed in Ge doped films obtained by co-sputtering (Figure 4).

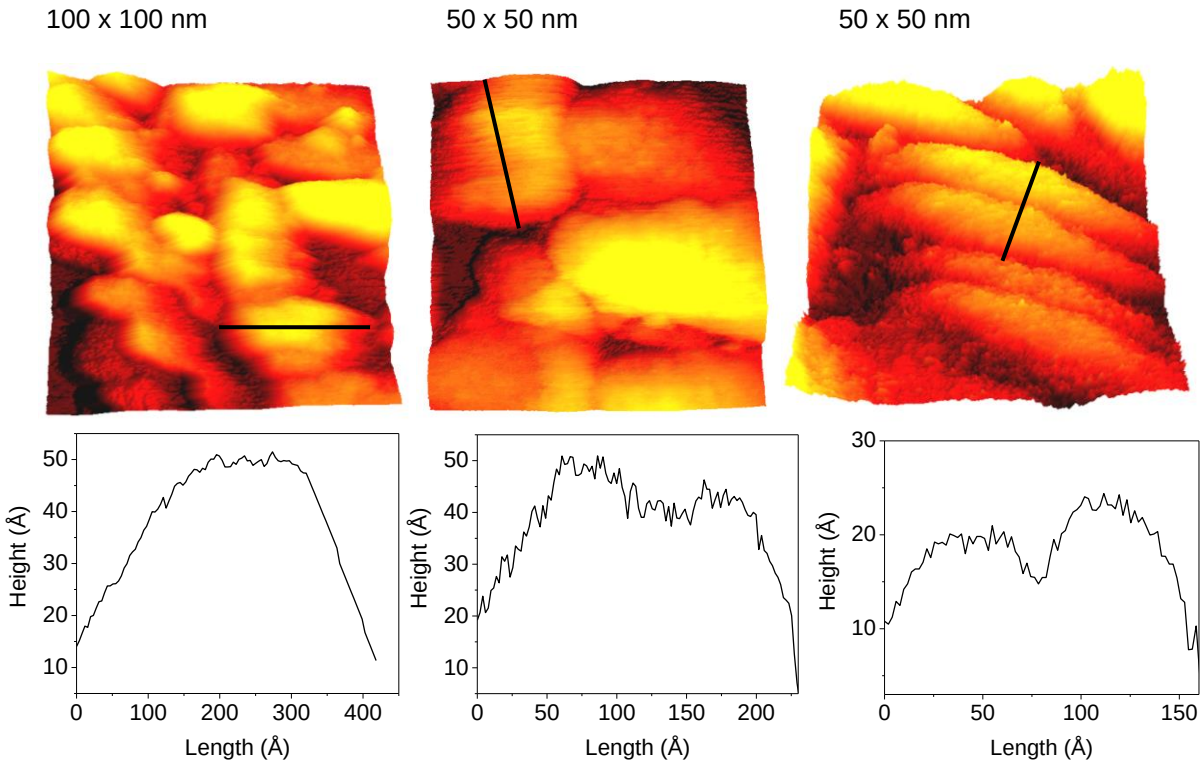

Figure 3: Different topographies and grain sizes of the Ge doped VO_2 thin films.

Hence, Ge segregation or phase separation (e.g. GeO formation) in such acicular grain regions might be suspected. With high-resolution scanning tunneling microscopy, sample surface inspection at the nanometric grain level is possible. Using the Scanning Tunneling Spectroscopy (STS) function, I-V curves are recorded locally on individual neighboring grains in a voltage interval from -1 to 1 V giving information on the surface density of states. From the flat section near the inflection point of the measured I-V curves, the band gap of the material can be determined.

Measured single-point STS spectra show similar characteristic I-V curves and t a band gap of ~0.5 eV has been calculated for both acicular and rounded or spherical grains. In [Yin11], authors claim that a VO_2 surface exhibiting a homogeneous insulating behaviour has a typical band gap of 0.5 eV at room temperature. This is in perfect agreement with our measurements of Ge doped VO_2. Theoretical calculations on Ge doping of VO_2 lattices predict a slight decrease of the band gap, but the expected change being rather small and the band gaps determined from the flat section of I-V curves being prone to measurement errors in noisy datasets, conclusions on the effect of Ge doping on the band gap – based solely on the measurement of characteristic I-V curves – should be cautious.

However, the identical band gap values determined for the different grain types suggest a rather homogeneous sample from the electronic point of view and contradicts the assumption of Ge segregation, phase separation or differential doping of the sample.

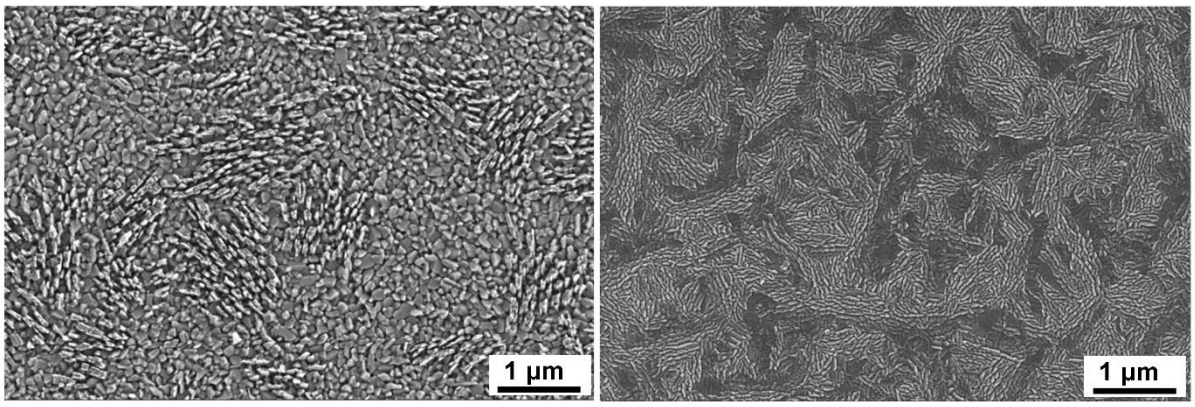

Figure 4: SEM images of two Ge doped VO_2 samples deposited by co-sputtering: one with relatively low Ge concentration (left) and another with a relatively high Ge content (right). The acicular grain formation is more pronounced in the sample with the higher Ge content.

Further details on local STS measurements available in the Confidential Appendix. The corresponding section of the Confidential Appendix contains unpublished figures based on which publications are envisaged.

Fourier Transform Infrared Spectrometry

The mid-infrared reflectance of a ≈ 250 nm VO_2, a ≈ 250 nm co-sputtered VO_2:Ge and a ≈150 nm VO_2:Ge film sputtered from alloy target are measured by FTIR spectrometry. All films are deposited onto Al substrates and the determined emissivity spectra are plotted in Figure 5.

In the cold state, the spectral reflectance of all three samples exhibits the same trend with only the absolute values varying as the emissivity is thickness dependent. However, in the high temperature state, the emissivity spectra differ. The emissivity of the co-sputtered sample is rather high and constant until around 10 µm after which it suddenly decreases. On the other hand, the VO_2:Ge film sputtered from alloy target and the pure VO_2 film exhibit gradually decreasing spectral emissivity over the measured range (2.5 – 14.5 µm). Comparing the different behaviour of the two VO_2:Ge films, it is likely that the film sputtered from the alloy target is more homogeneous and, thus it shows a similar behaviour to pure VO_2 films, whereas the VO_2:Ge deposited by co-sputtering exhibits some phase mixture leading to the more elevated emissivity (and feature between 8 – 11 µm). Indeed, in the XRD spectra of previously co-sputtered VO_2:Ge films, besides the usual peaks associated with the VO_2 monoclinic crystal structure, a peak corresponding to GeO has been identified.

The emissivity of the ≈150 nm VO_2:Ge film sputtered from the alloy target changes from ≈0.02 at room temperature to ≈0.31 at 100°C in the region of interest at 8 µm. This yields an important modulation of $\Delta\varepsilon$ (8 µm) = 0.29, that is comparable to that of the much thicker, ≈250 nm VO_2 film with $\Delta\varepsilon$ (8 µm) = 0.3 indicating the high-quality and superior optical modulation of VO_2:Ge films sputtered from V-Ge alloy target when similar thicknesses are considered.

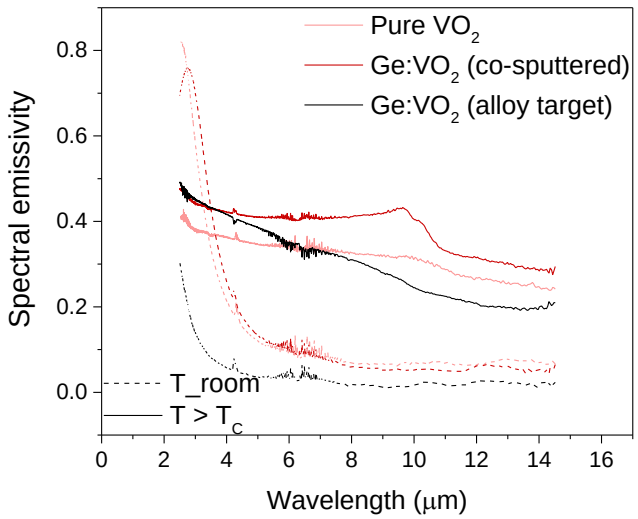

Figure 5: Spectral emissivity change between the low (dashed line) and high temperature state (solid line) of three thermochromic samples deposited on Al substrates: pure VO_2, VO_2:Ge deposited by co-sputtering and VO_2:Ge deposited from alloy target.

4.2 WP2: Simulations of multilayered absorber designs

Computer simulations of thin film interference, based on the transfer matrix method, allow to calculate the optical response of a multilayered thin film stack for given thicknesses and optical constants of the constituting layers.

Due to the changes induced by the thermochromic transition occurring mainly in the near- and mid-infrared spectral ranges, in a first approach, only the switch in thermal emittance has been considered, while the solar absorptance has been neglected. Hence, multilayered absorber coatings with optimized switch in the mid-infrared range (2.5 – 14 µm) are simulated. However, the deposited and measured samples proved that, while the thermal emittance is increasing significantly (~30% increase) with temperature, the solar absorptance is not constant over the thermochromic transition, switching to even higher values at higher temperatures and it is not suitable for the envisaged solar absorber application.

This increase in solar absorptance is mostly due to the presence of a reflectance peak around 1.8 µm wavelength in the room temperature spectra, that disappears in the high temperature state (Figure 6a).

Therefore, a second simulation campaign is carried out with the aim of minimizing the near-infrared reflectance peak below the thermochromic transition temperature. Moreover, a maximized near-infrared reflectance at high temperatures is targeted so that enhanced thermochromic absorber coatings with high thermal emittance and low solar absorptance at high temperatures could be envisaged.

Indeed, after complete readjustment of selective absorber material and layer order, the new simulations yield thermochromic absorber designs that exhibit a switch not only from low to high thermal emittance, but also from high to lower solar absorptance once the thermochromic transition temperature is reached.

At low temperatures, the NIR reflectance peak is still present, however, it has been shifted to above 2 µm wavelength, whereas at high temperatures a reflectance peak around 1.2 µm is now present that allows to reflect an important part of the incoming solar radiation (Figure 6b). The detailed design with the specific oxide types and thicknesses employed are available in the Confidential Appendix of this report.

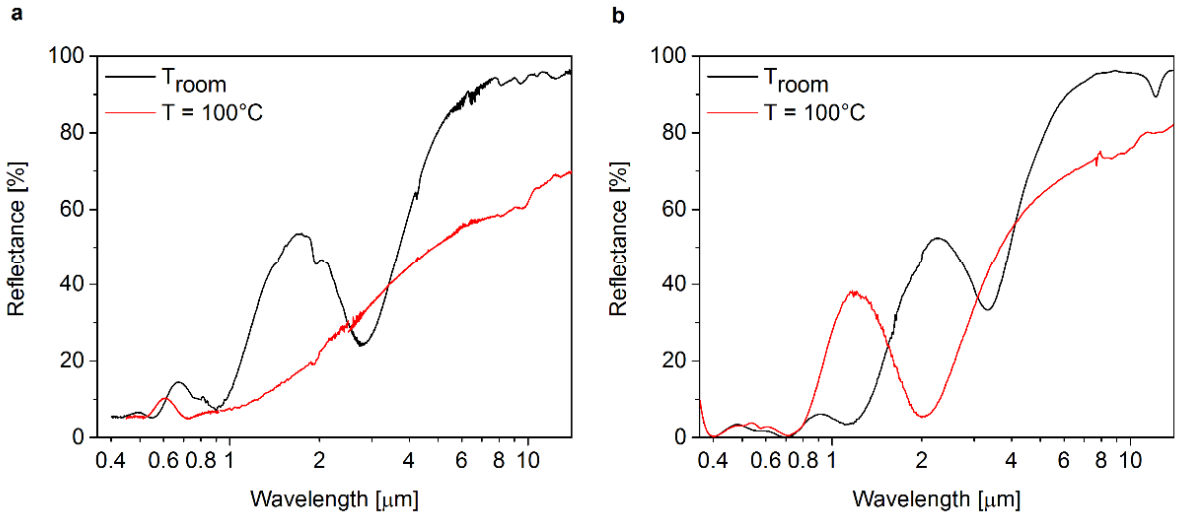

Figure 6: Spectral reflectance curve of a first and experimentally measured (a) and improved, simulated (b) thermochromic absorber coating design, below and above the thermochromic transition temperature.

Table 1: Simulated solar absorptance, α_{sol} and thermal emittance, ε_{th} values of the proposed novel multilayered coating designs with appropriate switching for both α_{sol} and ε_{th}.

Coating example	α_{cold} [%]	α_{hot} [%]	ε_{cold} [%]	ε_{hot} [%]	$\Delta\alpha$ [%]	$\Delta\varepsilon$ [%]	ΔTot [%]
	93.9	89.0	10.6	27.0	4.9	16.4	21.3

Lastly, using the new design approach for limiting the α_{sol} with temperature, a third simulation campaign is carried out based on the multilayered absorber design of the industrial partner. The aim is to integrate the thermochromic layer into the existing commercial multilayered absorber in the most efficient way.

We report, that absorber coating designs based entirely on the commercial absorber and an additional thermochromic layer, exhibiting both an increase in thermal emittance and decrease of solar absorptance at high temperatures, have been successfully simulated. The detailed design is disclosed in the Confidential Appendix of this report.

4.3 WP3: Deposition of the designed multilayered coatings

The selected multilayered designs are deposited in collaboration with the industrial partner. The thermochromic film is sputtered at LESO-PB laboratory, all other layers are deposited by the partner, on the large, industrial coater.

The experimentally deposited layers vary by a few nanometers from the thicknesses used in the simulation. Furthermore, while the simulations yield the best results for rather thin thermochromic layers, in practice, well-crystallized films exhibiting a large thermochromic modulation are challenging to obtain. Therefore, absorber coating containing thermochromic layers of several thicknesses are deposited.

Solar absorptance values of above 90% and thermal emittances as low as 8.5% have been determined. These values are reasonably close to the standard 95% absorptance and 5% emittance. For all samples, a significant modulation in thermal emittance have been measured. Furthermore, several coatings exhibit the previously only simulated decrease in α_{sol} with temperature.

4.4 WP4 + WP5: Accelerated aging tests and optimization of aging properties

Three samples, S1, S3 and S4 deposited according to the previously determined designs, are subjected to accelerated aging tests in order to evaluate their environmental stability. Samples S1 and S3 are tested in the original sample size, while S4 is cut in four identical, smaller pieces and, therefore, one smaller sample with two newly exposed cross-sections is selected for aging.

The aging procedures are the following:

- S1: aging for 600h at 300°C in dry air (measured before and after aging)
- S3: aging for 600h at 40°C and 100% relative humidity (measured before and after aging)
- S4: aging for 600h at 278°C in dry air (according to ISO 22975-3:2014 standard and measured at each aging step: 0 h, 18 h, 36 h, 75 h, 150 h, 300 h and 600 h)

The detailed results of the aging tests are summarized in the Confidential Appendix of this report.

All samples have successfully fulfilled the performance criteria according to the ISO 22975-3:2014 standard for a minimum of 25 years of life-time service (PC < 5%).

Table 1: Determined performance criteria, PC after 600 h of corresponding accelerated aging treatment.

Samples after aging	**PC**
S1	-1.9
S3	4.8
S4	-1.6

Full sized samples S1 and S3 have shown no degradation of the thermochromic switch with aging. On the contrary, the sample aged in humid conditions, while showed an increase of thermal emittance below 3% at room temperature, it did improve by a remarkable 10% in the high temperature state resulting in an even larger modulation of thermal emittance. The solar absorptance decreased by only ~3% during the accelerated aging.

Sample S3, aged in dry air, showed an improvement in solar absorptance at normal operating conditions by 2%, while maintaining the same thermal emittance.

Finally, the smaller sample cut from S4 and aged in dry air, exhibits a remarkable stability in the optical properties measured at room temperatures, with the beneficial, increase in solar absorptance also present.

However, in the case of S4, the thermochromic modulation shows a steady decrease at each aging step (Table 3). In the high temperature state, the solar absorptance increases, while the thermal emittance decreases gradually. Hence, the overall thermochromic modulation is significantly limited. Deterioration of vanadium dioxide based thermochromic films in air, due to exposed surfaces and interfaces has been already reported in literature [Cha19].

After sample cutting, sample S4 has two exposed cross-sections through which the VO_2 film is readily oxidized to the thermodynamically stable V_2O_5. However, samples S1 and S3 which are covered by an antireflective and oxidation barrier top coating, show no signs of degradation of the thermochromic properties. These findings confirm the importance of exposed VO_2 surfaces, but also prove that the current designs with undamaged AR top layer can adequately protect the thermochromic layer from oxidation.

Table 3: Evolution of the emittance during the accelerated aging test in dry air (600 h at 278°C).

Sample	ε_{cold} [%]	ε_{hot} [%]	$\Delta\varepsilon$ [%]
S4 at t = 0h	8.1	23.9	15.8
S4 at t = 18h	9.4	24.2	14.8
S4 at t = 36h	8.4	21.6	13.2
S4 at t = 75h	8.9	21.6	12.7
S4 at t = 150h	8.2	18.6	10.4
S4 at t = 300h	9.2	18.0	8.8
S4 at t = 600 h	9.2	16.9	7.7

4.5 WP6: Giant emissivity switch

Thermochromic technologies have already impacted the building sector with the advance of vanadium dioxide based smart windows. Much enhanced thermal switching could be promising for radiative cooling applications and heat island mitigation in future cities (e.g. for thermal regulation of roofs or building envelopes).

The concept of reflection interference filters, inspired from Fabry-Pérot interferometers (two metallic layers and a dielectric cavity), is adapted to thermochromic layers which behave as dielectrics below and become metallic above the critical transition temperature.

The wavelength of the radiation passing through the Fabry-Pérot filter depends on the refractive index and thickness of the spacer. Due to this wavelength selectivity, reflection interference filters can be designed to exhibit enhanced optical reflection or transmission over the desired wavelengths or spectral bands. In the context of this work, the aim is to maximize the thermal modulation of the thermochromic multilayered coatings, especially in the mid-infrared 7 – 10 µm spectral range.

In literature, a similar concept has been discussed with an emittance modulation of 0.49 obtained across the semiconductor-to-metal transition for a Au//SiO_2 (850 nm)//VO_2 (~30 nm) multilayer [Hen13]. Nonetheless, due to the thick SiO_2 layer, the stack shows a large absorption in the mid-infrared region around 8-9 µm, region of high importance in radiative applications.

In this work package, the experimental validation of Fabry-Pérot type thermochromic multilayers with enhanced thermal emissivity modulation was attempted. Pre-experiments have been performed and promising emittance modulation of ≈ 0.34 at the wavelength of interest of 8 µm (Figure 7). The total thermal emittance modulation calculated over the 2.5 – 10 µm spectral region is nearly 0.3 (from a thermal emittance of 0.44 below the thermochromic transition temperature to 0.73 above the thermochromic transition temperature) for a 30 nm thin thermochromic layer. This represents a 30-fold enhancement compared to the emittance modulation of a 30 nm thermochromic layer without dielectric spacer layers.

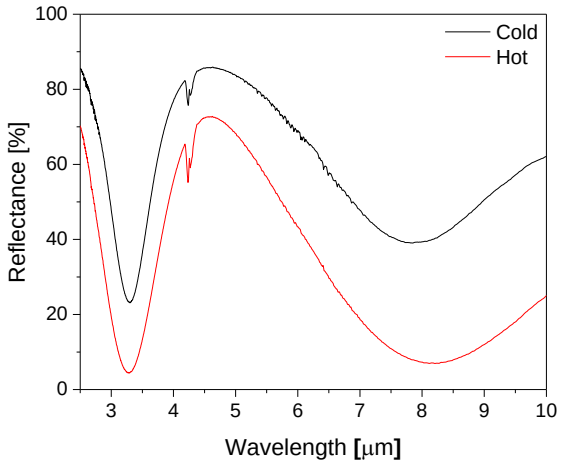

Figure 7: Measured reflectance spectra of an Al substrate//dielectric spacer//30 nm VO_2//dielectric spacer multilayer.

4.6 Complementary study

For practical applications and industrialization, reducing the deposition temperature is critical. In a 2020 meeting with the SFOE it has been decided to place a strong focus on the magnetron deposition of thermochromic VO_2 based thin films at deposition temperatures under 400°C in order to preserve the mechanical stability of the aluminum sheet substrates employed in the absorber manufacturing. Here we report on the successful deposition of switching, thermochromic films at substrate temperatures as low as ≈ 310°C (Figure 8). Although the magnitude of the electrical modulation decreases with the substrate temperature, a respectable, more than one order of magnitude transition is obtained at ≈ 310°C, thus indicating the industrial feasibility of Al absorbers with black selective thermochromic coatings.

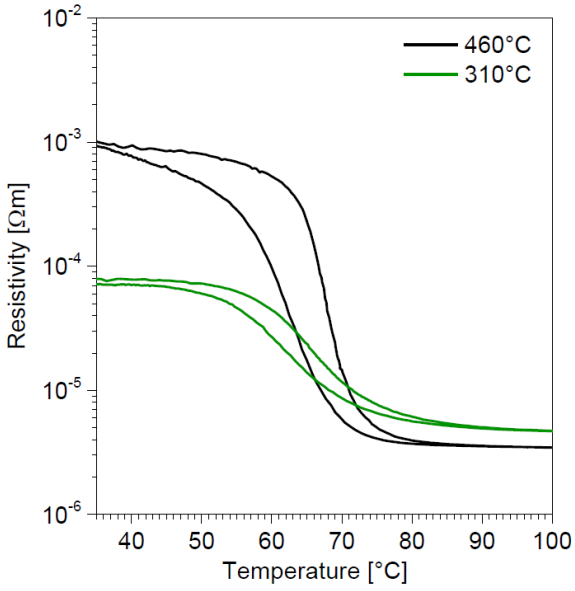

Figure 8: Temperature dependent electrical resistivity curves of two thermochromic films deposited at 460°C and 310°C.

5 Conclusions and outlook

All objectives of the project have been achieved:

- High-quality Ge doped VO_2 thermochromic films have been successfully deposited from V-Ge alloy targets, marking an important step toward the industrial upscaling of VO_2:Ge based absorber coatings. Films sputtered from alloy targets with 5 at.% Ge are homogeneously doped and exhibit a remarkable 1.6 order of magnitude transition at 82°C. The optical modulation in the mid-infrared is important, reaching up to 0.3 for a ≈150 nm thin film.

- Promising multilayered absorber designs with suitable solar absorptance (>90%) and thermal emittance have been identified. Moreover, for the first time, designs with decreasing solar absorptance accompanying the sudden increase in thermal emittance at the thermochromic transition temperature have been proposed. Simulations proved that the thermochromic layer could be integrated into a commercial multilayer absorber design, while maintaining the newly optimized solar absorptance switch, from high to low, with increasing temperature.

- Selected designs have been successfully deposited in collaboration with the industrial partner. Best performing sample reached α_{sol} > 92% and ε_{th} ~8% at normal operating temperatures. Importantly, at temperatures above the thermochromic transition, the α_{sol} decreases by 2% compared to the low temperature state, while a significant increase (~17%) in ε_{th} is maintained. This marks the first experimental proof of samples with both decreasing α_{sol} and increasing ε_{th} over the thermochromic transition.

- The lifetime of the deposited thermochromic absorbers has been evaluated and the requirements of a minimum service life of 25 years have been met according to the ISO 22975-3:2014 standard. Samples successfully passed both accelerated aging test in dry air at 300°C during 600 h and in 100% relative humidity at 40°C during 600 h. Remarkably, in samples measured as-deposited, the thermochromic modulation has not been affected during aging. Samples with newly exposed interfaces between thermochromic layer and air showed a steady degradation of the switching properties, underlining the importance of complete coverage of the thermochromic layers by the antireflective and oxidation barrier top layers.

- The theoretically predicted enhanced emissivity switch in Fabry-Pérot inspired thermochromic interference coatings is experimentally demonstrated. Due to the integration of dielectric spacer layers (Fabry-Pérot cavity), the thermal emittance modulation of a 30 nm thin VO_2 layer is enhanced 30-times compared to that of a 30 nm thermochromic coating on Al, increasing from 0.44 to 0.73 over the 2.5 – 10 µm spectral range.

- Switching thermochromic films have been deposited below 400°C substrate temperature.

6 Publications

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