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**Swiss Federal Office of Energy SFOE**  
Energy Research

Final report

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# **Thermochromic coatings for overheating protection of solar thermal collectors – novel type of doping**

## **TARGET95**

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Swiss Federal Office of Energy SFOE  
Research Programme Solar Heat and Heat Storage  
CH-3003 Bern  
[www.bfe.admin.ch](http://www.bfe.admin.ch)  
[energieforschung@bfe.admin.ch](mailto:energieforschung@bfe.admin.ch)

**Agent:**

École Polytechnique Fédérale de Lausanne EPFL  
Solar Energy and building Physics Laboratory LESO-PB  
CH-1015 Lausanne  
[www.leso.epfl.ch/nano\\_solar\\_energy](http://www.leso.epfl.ch/nano_solar_energy)

**Author:**

Anna Krammer, EPFL/LESO-PB, [anna.krammer@epfl.ch](mailto:anna.krammer@epfl.ch)  
Dr. Andreas Schüler, EPFL/LESO-PB, [andreas.schueler@epfl.ch](mailto:andreas.schueler@epfl.ch)

**SFOE head of domain:** Andreas Eckmanns, [andreas.eckmanns@bfe.admin.ch](mailto:andreas.eckmanns@bfe.admin.ch)  
**SFOE programme manager:** Dr. Elimar Frank, [elimar.frank@frank-energy.com](mailto:elimar.frank@frank-energy.com)  
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**The author of this report bears the entire responsibility for the content and for the conclusions drawn therefrom.**



## Highlights of this report

- The elevated thermochromic transition temperature in **Ge doped vanadium dioxide films is confirmed.**
- A transition temperature of **95°C** is reached with **~5.9 at.% Ge** doping.
- The elevated transition temperature is accompanied by **increased emissivity of Ge doped vanadium dioxide films** above the transition temperature.
- **The thermal emittance** of vanadium dioxide films in the high temperature state **is increasing with the angle from normal incidence.**
- **Full multilayered coating designs** are proposed for **novel switching smart absorber.** Based on simulations, first experiments have shown promising results.
- Important **contacts with industry and theoretical physicists** are **established.**



## Summary

Within this project, a novel absorber material has been developed for a new generation of “smart” solar collectors. A coating which can absorb and repel heat in a controlled manner – by changing its optical properties – according to temperature is envisaged. The innovation consists in the successful integration of a thermochromic thin film into a multilayered selective solar absorber coating. Inorganic vanadium dioxide films undergo a perfectly reversible thermochromic transition, at a critical temperature of  $T_C = 68^\circ\text{C}$ . Through the transition, the optical properties in the infrared spectral region change drastically implying a considerable change of the thermal emissivity (e.g. from ~5% below  $T_C$  to ~35-45% above  $T_C$  at ~8  $\mu\text{m}$  wavelength). This switch in emissivity and subsequent heat dissipation to the surroundings at high temperatures is sufficient to limit the stagnation temperature to values below the degradation temperature of glycol (160°C-170°C). Evaporation of the heat transfer fluid and excessive thermal stresses on the collector materials can be avoided, while the stagnation times are also reduced. Thus, thermochromic coatings provide an elegant solution to the overheating of solar thermal collector systems, without the use of any mechanical device (e.g. for shading or for pressure release) and allow for a better dimensioning of solar thermal systems.

Nonetheless, the transition temperature of 68°C of the pure  $\text{VO}_2$ , is relatively low and for solar thermal applications a higher switching temperature is required. Using a novel type of Ge doping, it is possible to significantly increase the transition temperature of pure vanadium dioxide films. A maximum transition temperature of ~95°C is reached with ~5.9 at.% Ge. Furthermore, Ge doping is also shown to have the added benefit of increasing the thermal emittance modulation of the switching films.

In the high temperature state, the thermal emittance of vanadium dioxide films is angle dependent and it increases with the angle from normal incidence. This indicates that the coating is more efficient at dissipating heat in the high temperature state than normal incidence measurements predict.

Thermochromic based full multi-layered absorber coatings are simulated based on  $n$  and  $k$  optical constants of the constituting individual layers. An absorber design, with a solar absorptance,  $\alpha \sim 97\%$  and thermal emittance,  $\epsilon \sim 6\%$  is selected and deposited. Designs of multi-layered coatings with maximized switching performance are developed. An alternative thermochromic oxide is investigated. Finally, a variety of applications are explored, and promising fields for market introduction are identified.



## Zusammenfassung

In diesem Projekt wurde ein neuartiges Absorbermaterial für eine neue Generation "intelligenter" Solarkollektoren entwickelt. Es wird eine Solarabsorber-Beschichtung angestrebt, die bei Überhitzung kontrolliert Wärme abstrahlt - durch Änderung ihrer optischen Eigenschaften entsprechend der Temperatur. Die Innovation besteht in der erfolgreichen Integration einer thermochromen Dünnschicht in eine mehrschichtige selektive Solarabsorberschicht. Anorganische Vanadiumdioxidfilme durchlaufen einen perfekt reversiblen thermochromen Übergang bei einer kritischen Temperatur von  $T_C = 68^\circ\text{C}$ . Durch den Übergang ändern sich die optischen Eigenschaften im infraroten Spektralbereich drastisch, was eine beträchtliche Änderung des thermischen Emissionsvermögens bewirkt (z.B. von  $\sim 5\%$  unter  $T_C$  zu  $\sim 35 - 45\%$  über  $T_C$  bei  $\sim 8 \mu\text{m}$  Wellenlänge). Dieser Emissionsgradwechsel und die dadurch bewirkte Wärmeabgabe an die Umgebung bei hohen Temperaturen reicht aus, um die Stagnationstemperatur auf Werte unterhalb der Zersetzungstemperatur von Glykol ( $160^\circ\text{C} - 170^\circ\text{C}$ ) zu begrenzen. Die Verdampfung der Wärmeträgerflüssigkeit und übermäßige thermische Belastungen der Kollektormaterialien können vermieden werden, während die Stagnationszeiten ebenfalls reduziert werden. Ohne die Verwendung irgendeiner mechanischen Vorrichtung (z. B. zum Abschatten oder zur Druckentlastung) stellen thermochrome Beschichtungen somit eine elegante Lösung für die Überhitzung von Solarkollektoren bereit und ermöglichen eine bessere Dimensionierung von Solarthermie-Systemen.

Allerdings ist die Übergangstemperatur von  $68^\circ\text{C}$  des reinen  $\text{VO}_2$  relativ gering. Daher wird für solarthermische Anwendungen eine höhere Schalttemperatur benötigt. Mit einer neuartigen Germanium-Dotierung ist es möglich, die Übergangstemperatur von reinen Vanadiumdioxidfilmen deutlich zu erhöhen. Eine maximale Übergangstemperatur von  $\sim 95^\circ\text{C}$  wird mit  $\sim 5,9 \text{ at.}\%$  Ge erreicht. Darüber hinaus weist die Germanium-Dotierung auch den zusätzlichen Vorteil auf, dass sie die Modulierung der thermischen Emission der schaltenden Filme erhöht.

Im Hochtemperaturzustand ist das thermische Emissionsvermögen von Vanadiumdioxidfilmen winkelabhängig und nimmt mit wachsendem Abstrahlungswinkel zu. Dies deutet darauf hin, dass die Beschichtung im Hochtemperaturzustand wirksamer die Wärme ableitet, als dies aufgrund Messungen bei normalem Einfall vorhergesagt wird.

Thermochrom basierte mehrschichtige Absorberschichten werden unter Verwendung der optischen Konstanten  $n$  und  $k$  der einzelnen Schichten simuliert. Ein Absorberdesign mit einem Solarabsorptionsgrad  $\alpha \sim 97\%$  und einem thermischen Emissionsvermögen  $\varepsilon \sim 6\%$  wird ausgewählt und entsprechende Beschichtung werden im Labor hergestellt. Designs von mehrschichtigen Beschichtungen mit maximaler Schaltleistung werden entwickelt. Ein alternatives thermochromes Oxid wird untersucht. Schließlich werden eine Vielzahl von Anwendungen untersucht und vielversprechende Felder für die Markteinführung identifiziert.



## Résumé

Dans le cadre de ce projet, un nouveau matériau absorbant a été développé pour une nouvelle génération de capteurs solaires «intelligents». Un revêtement pouvant absorber et repousser la chaleur de manière contrôlée - en modifiant ses propriétés optiques en fonction de la température - est envisagé. L'innovation consiste en l'intégration réussie d'un film mince thermochrome dans un revêtement multicouche d'absorbeur solaire sélectif. Les films inorganiques de dioxyde de vanadium subissent une transition thermochrome parfaitement réversible, à une température critique de  $T_C = 68^\circ\text{C}$ . Grâce à cette transition, les propriétés optiques dans la région spectrale de l'infrarouge changent radicalement, ce qui implique un changement considérable de l'émissivité thermique (par exemple de  $\sim 5\%$  en dessous de  $T_C$  à  $\sim 35 - 45\%$  au-dessus de  $T_C$  à une longueur d'onde d'environ  $8 \mu\text{m}$ ). Ce changement d'émissivité aux températures élevées et la dissipation thermique à l'environnement impliquée suffisent pour limiter la température de stagnation aux valeurs inférieures à la température de dégradation du glycol ( $160^\circ\text{C}$  à  $170^\circ\text{C}$ ). L'évaporation du fluide caloporteur et les contraintes thermiques excessives sur les matériaux collecteurs peuvent être évitées, tandis que les temps de stagnation sont également réduits. Ainsi, les revêtements thermochromiques apportent une solution élégante à la surchauffe des systèmes de capteurs solaires thermiques, sans utilisation de dispositif mécanique (par exemple pour l'ombrage ou la libération de pression) et permettent un meilleur dimensionnement des systèmes solaires thermiques.

Néanmoins, la température de transition de  $68^\circ\text{C}$  du  $\text{VO}_2$  pur est relativement faible et, pour les applications thermiques solaires, une température de transition plus élevée est requise. En utilisant un nouveau type de dopage au germanium, il est possible d'augmenter de manière significative la température de transition des films de dioxyde de vanadium purs. Une température de transition maximale de  $\sim 95^\circ\text{C}$  est atteinte avec  $\sim 5,9\%$  at. En outre, le dopage de germanium présente également l'avantage supplémentaire d'augmenter la modulation de l'émittance thermique de ces films dynamiques.

Dans l'état à haute température, l'émittance thermique des films de dioxyde de vanadium dépend de l'angle et augmente avec l'angle par rapport à l'incidence normale. Cela indique que, dans l'état au-dessus de la température de transition, le revêtement est plus efficace pour dissiper la chaleur que ne le prédisent les mesures d'incidence normale.

Les revêtements absorbants multicouches à base thermochromique sont simulés sur la base des constantes optiques  $n$  et  $k$  des couches individuelles. Une conception du revêtement absorbant, avec un coefficient d'absorption solaire,  $\alpha \sim 97\%$  et une émittance thermique,  $\varepsilon \sim 6\%$ , est sélectionnée et des revêtements correspondants sont déposés. Des conceptions de revêtements multicouches avec des performances optimisées sont développées. Un oxyde thermochrome alternatif est étudié. Enfin, diverses applications sont explorées et des domaines prometteurs pour l'introduction sur le marché sont identifiés.





# Contents

<b>Highlights of this report</b> .....	<b>3</b>
<b>Summary</b> .....	<b>4</b>
<b>Zusammenfassung</b> .....	<b>5</b>
<b>Résumé</b> .....	<b>6</b>
<b>Contents</b> .....	<b>8</b>
<b>List of abbreviations</b> .....	<b>10</b>
<b>1 Introduction</b> .....	<b>11</b>
<b>2 Context</b> .....	<b>11</b>
2.1 Background / State of the art.....	11
2.2 Motivation of the project .....	12
2.3 Goals .....	13
<b>3 Approach and methodology</b> .....	<b>14</b>
A. Novel type of doping for increasing the transition temperature of vanadium dioxide based films....	14
B. Maximizing switching contrast for multilayers.....	15
C. Alternative thermochromic materials .....	16
D. Application scouting.....	16
<b>4 Results</b> .....	<b>17</b>
A. Novel type of doping for increasing the transition temperature of vanadium dioxide based films....	17
A1. Confirmation and characterization of the effect of the novel Ge doping.....	17
A1.1. Electrical properties of Ge doped thermochromic films .....	17
A1.2. Structural and morphological investigation of pure and Ge doped thermochromic samples .....	18
X-ray Diffraction (XRD).....	18
Atomic Force Microscopy (AFM) .....	19
A1.3. Chemical investigation of pure and Ge doped thermochromic samples .....	22
Energy-dispersive X-ray Spectroscopy (EDX) .....	22
X-ray Photoelectron Spectroscopy (XPS) .....	26
Rutherford Backscattering Spectroscopy (RBS) .....	27
A1.4. Design of a customized heating stage for FTIR spectrometry measurements.....	28
A1.5. Thermal emissivity switch of pure and Ge doped thermochromic thin films.....	30
A1.6. Angle dependent IR optical investigation of VO <sub>2</sub> films.....	32
A1.7. Thermochromic switch in the visible spectral range .....	34
A2. Understand doping mechanism by means of detailed characterization of the films and theoretical considerations.....	34
A2.1. Study of the electronic properties of pure and Ge doped VO <sub>2</sub> by UPS and XPS.....	34
A2.2. Investigation of an alternative dopant element, Si with similar valence and electrical properties to Ge .....	35



Four-point resistivity measurement .....	35
UV Photoelectron Spectroscopy.....	37
X-ray Photoelectron Spectroscopy.....	38
A2.3. Optical bandgap determination of pure and Ge doped vanadium dioxide thin films and comparison with the results of recent theoretical predictions.....	39
A3. Doping optimization: How high can be doped? Which maximal transition temperature $T_c$ can be achieved? Which switching contrast can be achieved? .....	39
A3.1. Determination of optimum Ge doping levels for thermochromic vanadium dioxide based thin films with elevated $T_c$ . .....	39
A3.2. Optimization of parameters other than the doping level, for a better control of the thermochromic behaviour of Ge doped vanadium dioxide based thin films.....	40
B. Maximizing switching contrast for multilayers.....	41
B1. Develop concept for multilayered interference thin film stacks.....	41
B2. Determination of the minimum thickness for individual thermochromic coatings with good enough crystallization .....	41
B2.1. Minimum thickness for switching vanadium dioxide based thin films.....	42
B2.2. Investigation of the dependence of IR behavior of $VO_2$ thin films with film thickness .....	43
B3. Simulate and optimize multilayers based on the knowledge of the optical constants $n$ & $k$ of individual layers .....	44
B3.1. Multi-layered absorber design simulation based on optical constants, $n$ and $k$ .....	44
B3.2. Optimization of the deposition parameters for sputtered selective absorber coating.....	45
B3.3. Optical and structural characterization of the sputtered selective absorber coating. ....	45
B3.4. Optical characterization of the deposited multi-layered stacks.....	45
C. Alternative thermochromic materials .....	45
C1. Deposition of alternative thermochromic oxide films .....	45
C2. Characterization of the alternative thermochromic oxide films.....	45
D. Application scouting.....	45
D1. Applications in the field of solar thermal collectors.....	46
D2. Applications in the field of smart building envelopes .....	46
D3. Applications in the field of photovoltaics .....	46
D4. Applications in the field of automotive mobility .....	47
D5. Applications in the field of microelectronics.....	47
<b>5 Discussion of results .....</b>	<b>48</b>
<b>6 Conclusions and outlook.....</b>	<b>48</b>
6.1 Next steps after end of project.....	49
<b>7 Publications .....</b>	<b>50</b>
<b>8 References .....</b>	<b>53</b>



## 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
XRD	X-ray Diffraction
AFM	Atomic Force Microscopy
SEM	Scanning Electron Microscopy
XPS	X-ray Photoelectron Spectroscopy
UPS	UV Photoelectron Spectroscopy
EDX	Energy-dispersive X-ray Spectroscopy
RBS	Rutherford Backscattering Spectrometry
FTIR	Fourier Transform Infrared
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
VIS	Visible
NIR	Near-infrared
SMT	Semiconductor-to-Metal Transition
FWHM	Full Width at Half Maximum
SS	Stainless Steel



# 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, demand is low and storage is limited, the excess heat cannot be diverted and stagnation occurs.

Overheating of solar thermal collectors is a common problem even in central European latitudes. The temperature of the solar absorber can exceed 200°C. At such temperatures, the heat transfer fluid evaporates, the glycols degrade and stresses occur in the collector with increasing vapour pressure. Special precautions are necessary to release this pressure. Additionally, the occurring elevated temperatures lead to degradation of the materials that compose the collector, such as sealing, thermal insulation and the selective absorber coating. A protection of solar thermal systems without any mechanical device (e.g. for shading or for pressure release) might be provided by thermochromic coatings which exhibit a change in optical properties at a critical temperature  $T_c$ . Desired are a high solar absorptance and a low thermal emittance below the  $T_c$ , and a low solar absorptance and a high thermal emittance above  $T_c$ . Such “smart” solar collectors allow for a better dimensioning of solar thermal systems.

## 2 Context

### 2.1 Background / State of the art

Traditional strategies for stagnation handling and overheating protection of solar thermal collectors include the addition of expansion vessels to the closed loop circuit so that the volume change of the heat transfer fluid can be accommodated for. The use of safety valves able to release the built-up pressure during heat transfer fluid evaporation is another common solution. Mechanical shading devices constitute another approach to overheating prevention. However, all these options complicate the construction of solar thermal systems and, therefore, add to the system costs.

There are also approaches where the overheating protection is part of the collector concept. Such an example is the solar thermal collector commercialized by the company TIGI. The particularity of the TIGI honeycomb collector is its transparent insulation with an integrated overheating protection device at the collector level, which releases heat to the environment above a pre-set temperature. The TIGI solution is based on dual fluid composition with a secondary fluid loop independent of the primary heat transfer loop. An internal evaporator is coupled to the absorber plate and connected in a close loop to a condenser situated outside the collector case in order to dissipate heat to the surroundings. When the absorber temperature reaches the boiling temperature in the evaporator the heat dissipation starts without any dependence on the transfer fluid in the primary loop. [Fra15]

Another straight-forward, embedded solution to collector overheating is found in thin film technology. The integration of a very thin thermochromic oxide layer into the solar absorber coating results in a smart switching absorber capable of regulating the collector temperature by changing its own thermal emittance with temperature. In 2016, Viessmann – a leading European solar collector manufacturer, launched the first thermochromic flat plate collectors based on vanadium oxide thin films and show that with this technology the stagnation temperature is limited to temperatures below 150°C.



Since 2008, thermochromic films for absorber coatings for solar thermal applications have been developed at EPFL/LESO-PB. First it has been shown that the durability of organic thermochromic paints is not high enough for the considered application [Huo08]. The focus then shifted toward inorganic, thermochromic transition metal oxides, particularly vanadium dioxide thin films. The transition temperature of pure vanadium dioxide based films is usually around 68°C, temperature typically considered too low for solar thermal applications. In former projects, different dopant elements such as Al and Cr, have been investigated, but, until now, sufficiently increasing the transition temperature of vanadium dioxide films proved elusive. Preliminary experiments have shown that by a novel Ge type of doping, the thermochromic transition temperature can be raised considerably (e.g. to ~95°C). Therefore, in the present project, the optimization of Ge doping is in focus.

## 2.2 Motivation of the project

The motivation of this project is to investigate Ge doped VO<sub>2</sub> films which should be further developed to limit the stagnation temperature of solar collectors to a value below the boiling point of the heat transfer fluid without degrading the optical performance of the selective coating during normal operation.

Advantages:

- Evaporation of the heat transfer fluid due to overheating is avoided and the hydraulic system is simplified.
- The lifetime of the collector materials used for thermal insulation, the joints and the selective coating itself is increased.
- Glycol degradation is avoided.
- Low/no maintenance.
- Better dimensioning of solar thermal systems.
- Stagnation temperature and stagnation time are reduced.



## 2.3 Goals

We target an optical switching behaviour for selective coatings. This change in the optical properties will occur at a critical temperature  $T_c$ . For solar thermal collectors a suitable transition temperature would be approximately 95°C. The temperature range under the critical temperature defines the standard working condition for the collector. In this range, the solar absorptance  $\alpha$  should correspond to 95% and the thermal emittance  $\epsilon$  to maximum 5%. The solar collector suffers overheating connected problems and resulting stagnation above the transition temperature. In this temperature range, the thermal emittance  $\epsilon$  should be increased considerably to above 40%.

Within this project we focus on the following goals:

- A. Novel type of doping for increasing the transition temperature of vanadium dioxide based films
  - A1. Confirmation and characterization of the effect of the novel Ge doping
  - A2. Understand the doping mechanism by means of detailed characterization of the films and theoretical considerations
  - A3. Doping optimization: How high can be doped? Which maximal transition temperature  $T_c$  can be achieved? Which switching contrast can be achieved?
  
- B. Maximizing switching contrast for multilayers
  - B1. Develop concept for multilayered interference thin film stacks
  - B2. Determination of the minimum thickness for individual thermochromic coatings with good enough crystallization
  - B3. Simulate and optimize multilayers based on the knowledge of the optical constants  $n$  &  $k$  of individual layers
  
- C. Alternative thermochromic materials
  - C1. Deposition of alternative thermochromic oxide films
  - C2. Characterization of the alternative thermochromic oxide films
  
- D. Application scouting



## 3 Approach and methodology

### A. Novel type of doping for increasing the transition temperature of vanadium dioxide based films

#### A1. Confirmation and characterization of the effect of the novel Ge doping

At a critical temperature  $T_c$ , thermochromic metal oxide films undergo a reversible phase transition from a metallic to a semiconducting state, resulting in a sudden change in thermal emissivity and in a resistance change of typically three orders of magnitude. Pure VO<sub>2</sub> coatings switch from semiconducting to metallic state at critical temperatures around 68°C. [Per13]

The transition temperature of these doped films can be altered by suitable doping [Goo71]. Doped thermochromic metal oxide films are deposited by reactive magnetron co-sputtering of metallic targets in argon/oxygen atmosphere.

Experiments have shown that a novel Ge doping can significantly increase the transition temperature (up to ~ 95°C) of VO<sub>2</sub> based thin films.

The crystalline phase is investigated by X-ray diffraction (XRD). Thin film morphology is determined by means of atomic force microscopy (AFM) and scanning electron microscopy (SEM).

Chemical analyses of the deposited films are performed by X-ray photoelectron spectroscopy (XPS). This allows for the precise determination of the atomic concentration of dopant elements present at the film surface. A chemical analysis is also carried out by Energy-dispersive X-ray Spectroscopy (EDX). The EDX technique allows us to qualitatively estimate the respective atom concentrations of the elements present in the film. For a high accuracy determination of the dopant concentration in the films, Rutherford Backscattering Spectrometry (RBS) is performed. This method also gives the precise film thicknesses.

The optical properties of the thermochromic films are investigated with a special interest on their behavior in the thermal infrared range. The angular dependence of the thermal emissivity of VO<sub>2</sub> films is done by thermal imaging. Good quality samples of pure and Ge doped thermochromic films deposited on commercially available Al sheets are characterized by means of FTIR spectrometry in the mid-infrared range. By measuring the samples both in the low and high temperature phase, the emissivity switch between the two states is determined. For carrying out these measurements with better control of temperature a portable heating stage is developed and adapted to the integrating sphere coupled to the FTIR spectrometer. Thus, besides increasing the transition temperature, the influence of doping on the thermal emittance switch is investigated.

#### A2. Understand the doping mechanism by means of detailed characterization of the films and theoretical considerations

Pure and Ge doped thermochromic samples are investigated by X-ray and UV photoelectron spectroscopy. Our experimental setup consists of a high-vacuum deposition chamber connected to an UHV ultraviolet and X-ray photoelectron spectrometer. Therefore, the samples can be transferred from one system to the other without breaking the vacuum.



From the shifts in core level peak positions, valuable information on the chemical states and local chemical environments can be extracted. Additionally, UPS He I and He II valence band spectra offer an insight on the electronic structure of the deposited films and the effect of Ge doping on these properties is discussed.

Moreover, the in-situ thermochromic transition and the change of the valence band spectra with temperature for both pure and Ge doped samples are depicted by means of UPS.

It is not yet clear whether the increase in transition temperature is driven by structural or electronic factors. Another dopant element Si, from the same group, therefore similar properties, is investigated to help understand the probable determining factor in the transition.

The optical band gap of pure and Ge doped thermochromic samples are determined from reflectance and transmittance measurements in the near-infrared range. The absorption coefficient is then found and from the Tauc plot the optical bandgap of the material is determined.

Contact with theoretical physics group involved in density functional calculations of semiconductors and hybrid density functional calculations for correct band gap determination is established. Preliminary calculations on Ge and Si doped vanadium dioxide films are carried out. As both dopants are from the same group, similar properties are expected. Experimentally, both have been shown to increase the transition temperature of vanadium dioxide.

**A3. Doping optimization: How high can be doped? Which maximal transition temperature  $T_c$  can be achieved? Which switching contrast can be achieved?**

Based on the results of sample characterization, a range of optimum doping levels is determined. The effect of process parameters other than the doping level, e.g. oxygen partial pressure, on the thermochromic switching is discussed.

## **B. Maximizing switching contrast for multilayers**

### **B1. Develop concept for multilayered interference thin film stacks**

Structures of thermochromic thin layers with dielectric spacers between are proposed and tested for their expected enhanced optical behaviour.

### **B2. Determination of the minimum thickness for individual thermochromic coatings with good enough crystallization**

For multilayer designs, rather thin thermochromic films with thicknesses in the range from 20 nm to 100 nm might be of special importance. There are vague indications in the literature that vanadium oxide based thin films become thermochromic only above a certain minimum thickness, but there is no obvious fundamental physical reason for this limitation. The minimum thickness for thermochromic behavior of vanadium dioxide based thin films is determined by experiment (variation of deposition time, substrate temperature and oxygen flow).

The dependence of IR behavior of VO<sub>2</sub> thin films deposited on a highly reflective substrate with film thickness is determined by Fourier Transform Infrared Spectroscopy (FTIR) measurements.



### B3. Simulate and optimize multilayers based on the knowledge of the optical constants $n$ & $k$ of individual layers

A multilayered absorber design consisting of an Al substrate, thermochromic vanadium dioxide based layer, selective absorber layer and an antireflecting top layer has been proposed. Starting from the  $n$  and  $k$  optical indexes of each individual layer, the samples' reflectance curves between 0.36 – 10  $\mu\text{m}$  wavelength could be simulated. From these, the solar absorptance,  $\alpha$  and thermal emittance,  $\epsilon$  of successful designs has been calculated. For a good multilayered design, the deposition of high quality absorber coating by means of magnetron sputtering is required. The appropriate applied power, oxygen flux and deposition temperature were determined. The films were then characterized by Fourier Transform Infrared Spectrometry (mid-infrared range), VIS-NIR photospectrometry, scanning electron microscopy (SEM), profilometry and X-ray diffraction (XRD).

## C. Alternative thermochromic materials

### C1. Deposition of alternative thermochromic oxide films

Alternative thermochromic oxides are considered and a careful literature study and preparation of the experiment is carried out. The purity and chemical composition of the selected sputter target is determined. Thermochromic thin films are sputter deposited and working parameters are selected.

### C2. Characterization of the alternative thermochromic oxide films

Films deposited at ambient temperature are subjected to annealing in air and its effects are investigated. The structural analysis of the obtained thermochromic films is done by X-Ray Diffraction (XRD). Finally, temperature dependent reflectance measurements are carried out.

## D. Application scouting

Extensive literature research has led to novel ideas and new concepts have been proposed.



## 4 Results

### A. Novel type of doping for increasing the transition temperature of vanadium dioxide based films

#### A1. Confirmation and characterization of the effect of the novel Ge doping

Literature on doping elements that can increase the transition temperature of thermochromic VO<sub>2</sub> films is often contradictory and many elements were shown to induce different behavior in thin films than in single crystals. We have previously identified Ge as a very effective dopant element in raising the transition temperature. The effect has been confirmed and the results are discussed in the following. Furthermore, we investigate the influence of Ge doping on the optical properties of the thermochromic samples (e.g. evolution of the thermal emittance with temperature).

#### A1.1. Electrical properties of Ge doped thermochromic films

Five VO<sub>2</sub> based thin films, with different Ge content, are deposited by changing the applied power on the Ge target. All the other deposition parameters are kept constant (process pressure, oxygen partial pressure, deposition time, deposition temperature).

The temperature dependent resistivity curves of the pure and Ge doped samples are plotted in Figure 1. The curves reveal a strong correlation between the SMT characteristics, most notably the transition temperature and doping concentration. In order to quantitatively investigate these properties and precisely determine the phase transition temperature and hysteresis parameters, the derivatives of the resistivity variation curves,  $\log_{10}\rho(T)$  vs.  $T$  are plotted for both heating and cooling cycles. The resulting curves are fitted with Gaussian functions whose well-defined minima are taken as the phase transition temperature during heating,  $T_h$  and cooling,  $T_c$ . Thus, the SMT is characterized by (i) the phase transition temperature,  $T_{SMT}$  defined as  $T_{SMT} = \frac{1}{2} \cdot (T_h + T_c)$ ; (ii) the hysteresis width  $\Delta T_t$ , taken as the difference between  $T_h$  and  $T_c$ , and (iii) the full width at half maximum (FWHM) of the derivative curve describing the sharpness of the transition. Smaller value means sharper change of the slope. Detailed parameters are summarized in Table I. The doped samples show a clear increase in the transition temperature as compared to the reference sample. Furthermore, the transition temperature is steadily increasing with the level of doping up to a critical dopant concentration above which the transition is lost (sample Ge<sub>0.086</sub>V<sub>0.914</sub>O<sub>2</sub> did not exhibit a semiconductor-to-metal transition). Film resistivities increase as well, mainly in the high temperature phase. This in turn leads to lowered amplitude modulation of the SMT. The transition magnitude is gradually lowered from ~3 orders, for the pure VO<sub>2</sub> sample, to just slightly more than 1 order for the sample with 5.9 at.% Ge. Finally, the FWHM is steadily increasing with Ge addition. Hence, the transition becomes less abrupt, extending over a wide range of temperatures. The hysteresis width is generally narrowed with doping and vanishes completely at high Ge concentrations.

Sample	Applied power [W]	Ge content [at.%]	$T_h$ [°C]	$T_c$ [°C]	$T_{SMT}$ [°C]	$\Delta T_t$ [°C]	FWHM [°C]
1	0	0.09	70.0	62.5	66.3	7.5	5.7
2	5	0.48	73.6	65.6	69.6	8	7.8
3	15	4.28	78.1	73.5	75.8	4.6	14.0
4	17	5.93	96.6	90.6	93.6	6	30.1
5	20	8.65	-	-	-	-	-

Table 1: Detailed switching parameters as function of the Ge at.% (adapted from [Kra17]).

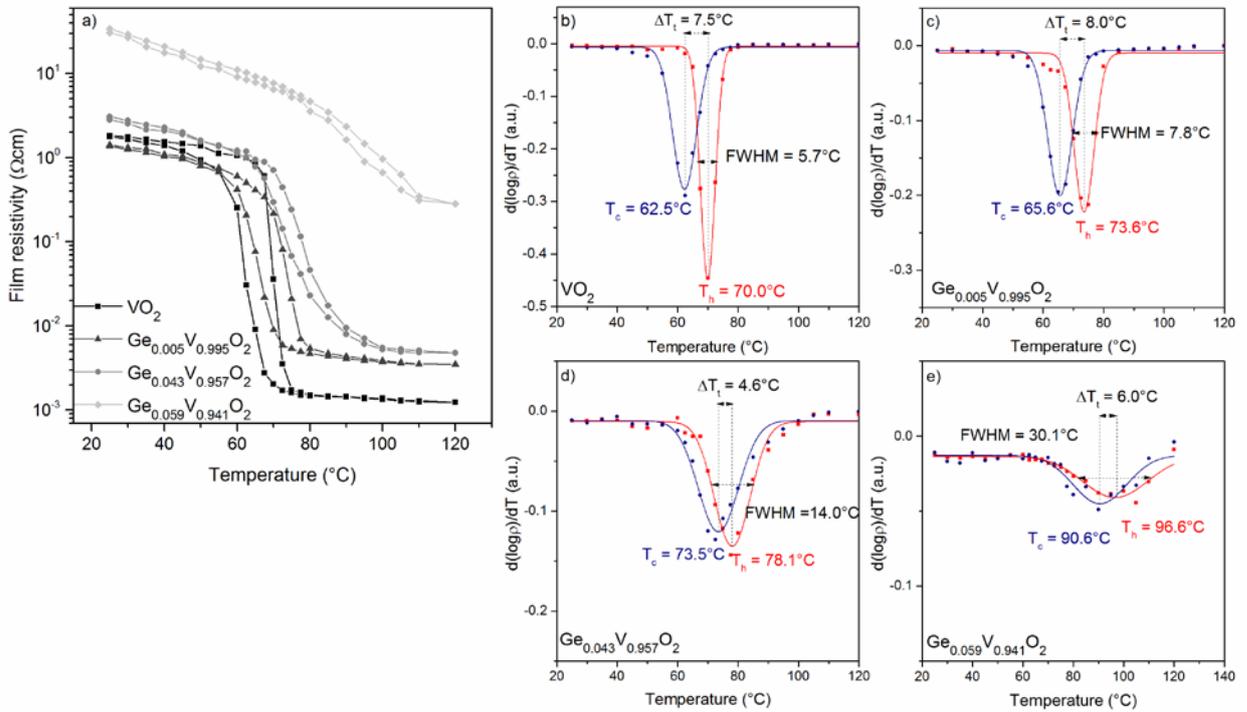


Figure 1: a) Temperature dependent electrical resistivity of VO<sub>2</sub> and Ge<sub>x</sub>V<sub>(1-x)</sub>O<sub>2</sub> films on Si (100) substrate. The transition temperature is progressively increasing with the Ge content. b-e) The d(log<sub>10</sub>ρ)/dT vs T curves are plotted for all samples. Measured data points (symbols) are fitted with Gaussian functions (lines) whose minima denote the transition temperatures upon heating, T<sub>h</sub> and cooling, T<sub>c</sub>. The difference between T<sub>h</sub> - T<sub>c</sub> gives the hysteresis width ΔT<sub>i</sub>, while the FWHM determines the sharpness of the SMT [Kra17].

A T<sub>SMT</sub> of ~96°C has been reached, which to our knowledge is the highest transition temperature ever reported for doped VO<sub>2</sub> based thin films. The effect of doping is reproducible and confirmed. Further optimization is necessary in order to reach a reasonable trade-off between high transition temperature and loss in switching contrast.

## A1.2. Structural and morphological investigation of pure and Ge doped thermochromic samples

### X-ray Diffraction (XRD)

Structural information was gathered with XRD. All samples exhibited polycrystalline structure and typical diffraction peaks of the M1 VO<sub>2</sub> phase (space group P121/c1, a = 0.5742(4), b=0.4521(3), c=0.5373(4) nm, α = 90, β = 122.60(5), γ= 90°). Furthermore, no characteristic peaks of other vanadium oxide phases have been observed, indicating phase pure VO<sub>2</sub> films. Exception from the above was the film with 8.65 at.% Ge which appears to have suffered an amorphization as diffraction peaks vanished. For clarity, only the XRD patterns of the least and most doped samples are displayed, that of pure VO<sub>2</sub> and of the Ge<sub>x</sub>V<sub>(1-x)</sub>O<sub>2</sub> samples with ~5.9 at.% and 8.6 at.% Ge (Figure 2). The absence of certain peaks in the pure sample ([002], [012]) suggests a textured film with preferential orientation of the crystallites. In the Ge<sub>0.059</sub>V<sub>0.941</sub>O<sub>2</sub> film, the [002], [012] peaks are present as well.



However, the intensity of the [1 1 -1] peak is much larger than that of the others peaks, indicating preferential orientation in the (1 1 -1) direction. The polycrystalline films are single phase  $\text{VO}_2$  nonetheless.

With doping, a shift of the diffraction peaks toward higher angles is observed. This indicates smaller distances between the crystal planes which can be explained by the smaller ionic radius of Ge atoms compared to that of V. Interestingly, the  $\text{Ge}_{0.086}\text{V}_{0.914}\text{O}_2$  sample, with the highest Ge content appears to have suffered an amorphization of the film as diffraction peaks vanished. This is consistent with the absence of the SMT during the electrical resistivity measurements.

The broadening of the peaks in the Ge containing sample is attributed to the decrease of average grain size in the polycrystalline film with doping. This is an expected effect as Ge doped into  $\text{VO}_2$  introduces disorder in the lattice, which results in smaller grain sizes. Grain refinement leads to less intense and less abrupt transitions. This trend has also been observed from the electrical resistivity plots of our samples.

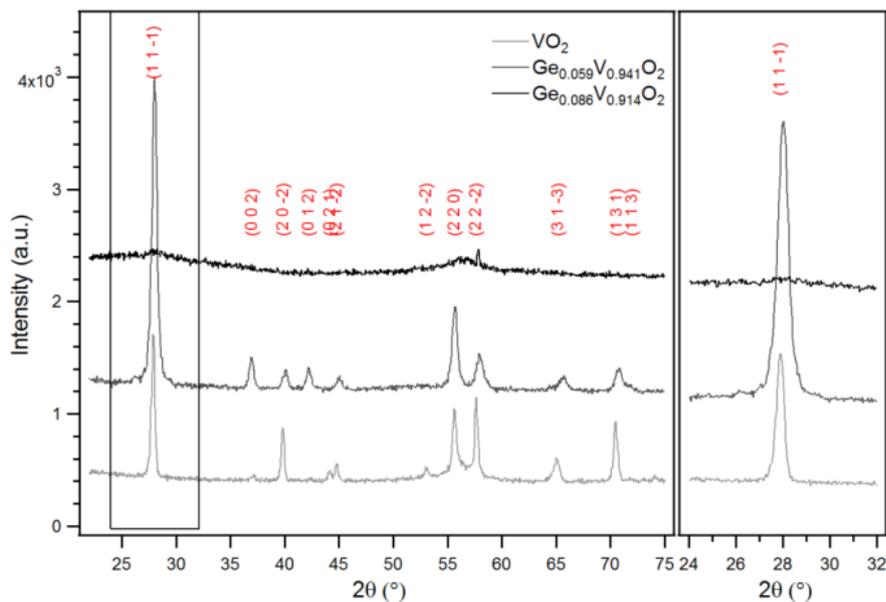


Figure 2: XRD spectra of  $\text{VO}_2$ ,  $\text{Ge}_{0.059}\text{V}_{0.941}\text{O}_2$  and  $\text{Ge}_{0.086}\text{V}_{0.914}\text{O}_2$  films on Si (100) substrate. All diffraction lines were assigned to the stoichiometric  $\text{VO}_2$  monoclinic phase. Peak broadening and peak shifting is shown on the zoomed in (1 1 -1) peak. [Kra17]

### Atomic Force Microscopy (AFM)

The pure  $\text{VO}_2$  film, the doped film with highest transition temperature and over-doped film with no diffraction peaks distinguishable were also characterized by means of AFM in order to correlate the results of XRD measurement with the film morphology.

The pure  $\text{VO}_2$  film (Figure 3.a) is well crystallized and exhibits a granular structure with grain sizes in the range of 100-200 nm. The doped sample with elevated transition temperature (3.b) also shows a crystalline structure with well-defined grains, but the grain sizes are significantly lowered as it was



expected and predicted from the XRD peak broadening. Grains are now in the range of 50-60 nm. The sample with a too high concentration of dopant, loses its crystalline character as determined from the vanishing diffraction peaks in the XRD spectra. In the AFM image this amorphization manifests through the disappearance of the well-defined grains and the roughness of the film is considerably decreased (3.c).

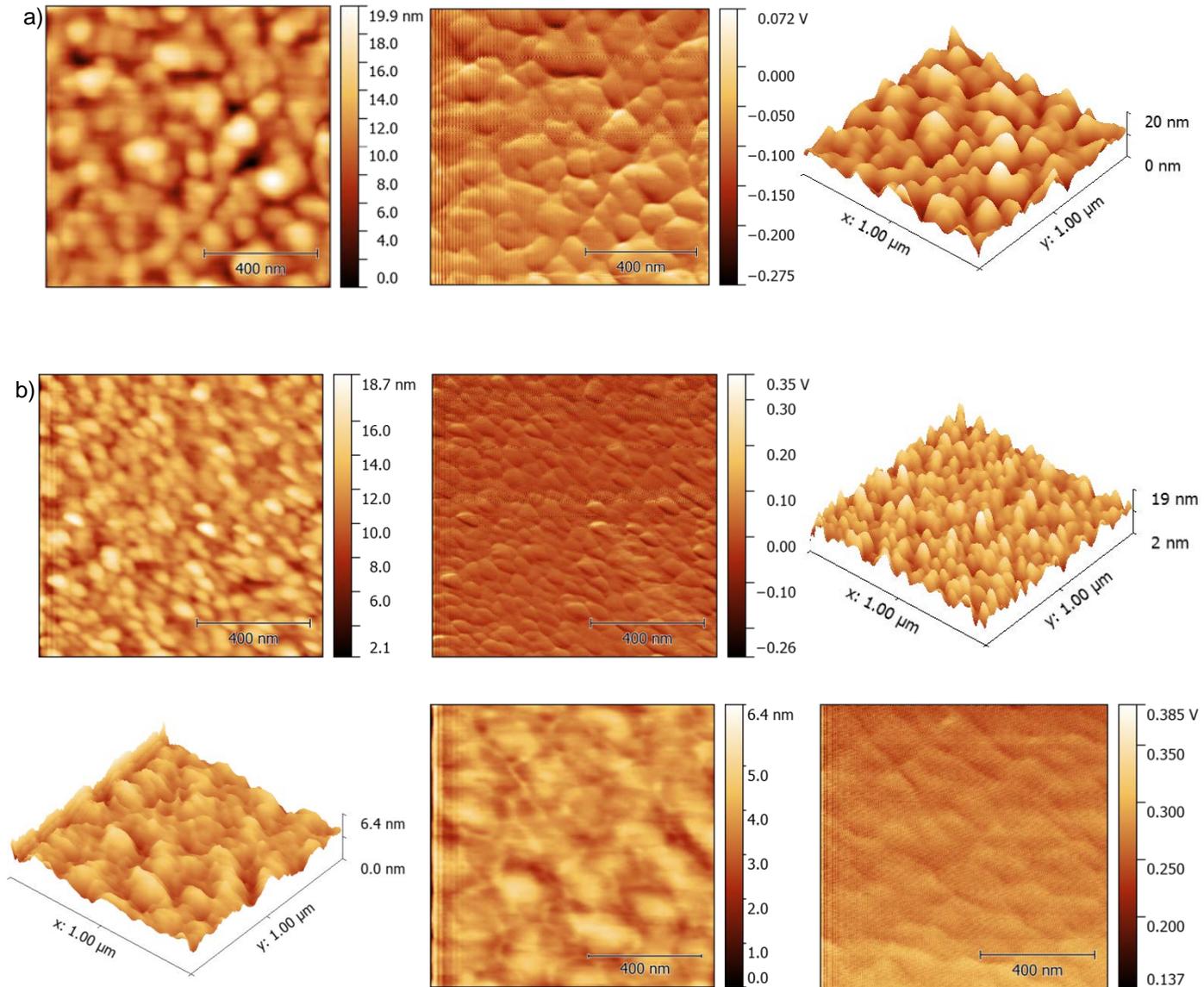


Figure 3: Topographic (left) , lateral (center) and 3D (left) AFM images of pure (a), highly doped with high transition temperature (b) and over-doped amorphous VO<sub>2</sub> based thin films. [Kra17]



## Scanning Electron Microscopy (SEM)

Two differently doped films, one with 10W and another with 20W applied power on the Ge target, are also investigated by SEM.

The plan and cross sectional view SEM images for the lightly doped sample are shown in Figure 4. Some grains show advanced growth in the plane perpendicular to the substrate. Patterns made up from several parallel oriented grains can be distinguished. From the cross sectional view, the film thickness is determined to be ~200 nm.

For the more strongly doped sample, with 20W applied power on the Ge target, the SEM images at different magnifications are shown in Figure 5. The pattern formation appears to be enhanced and uniformly distributed over the film. These patterns are made up by small, parallel oriented crystallites. The film is homogeneous and well crystallized. Grain sizes are below 200 nm and are elongated in shape. Film thickness is around 200 nm and it is rather constant.

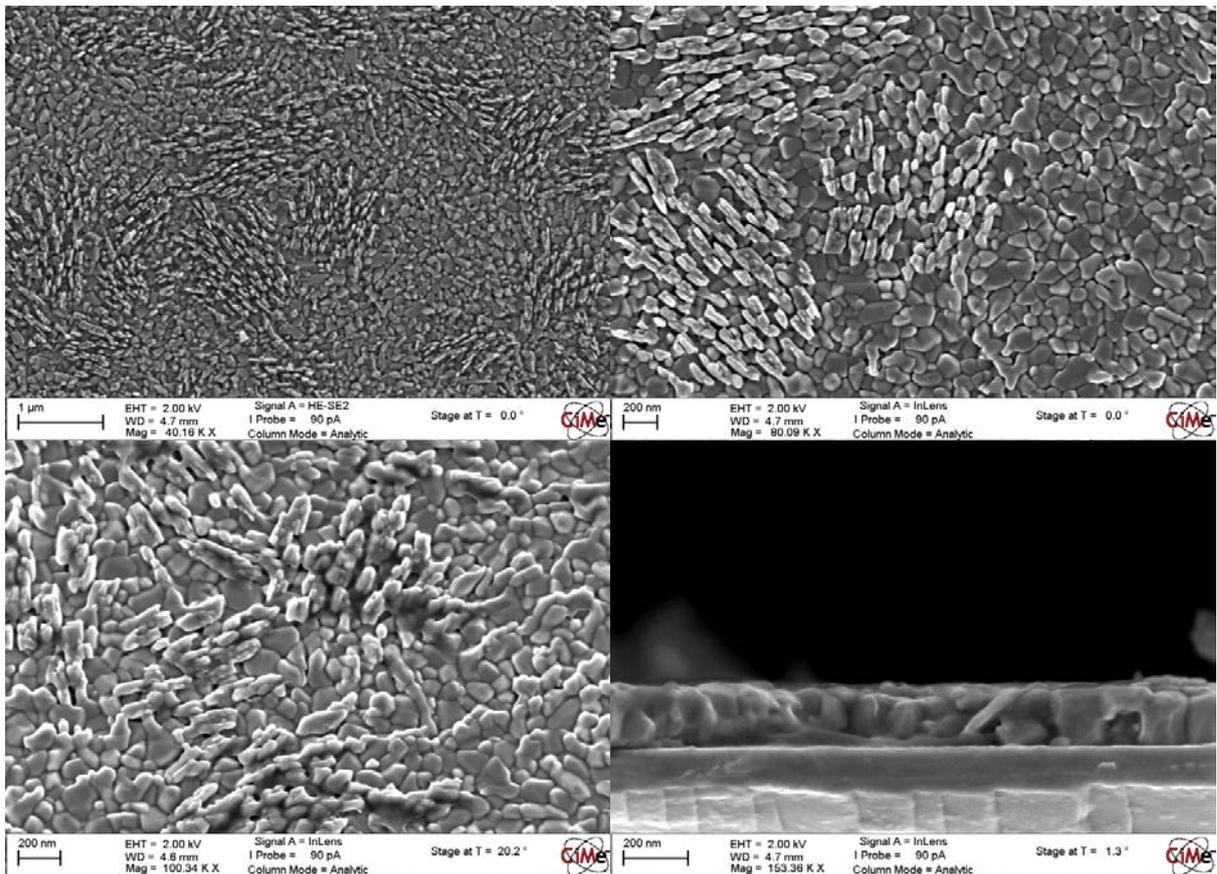


Figure 4: Cross sectional and plan view SEM images of 10W Ge doped VO<sub>2</sub> sample.

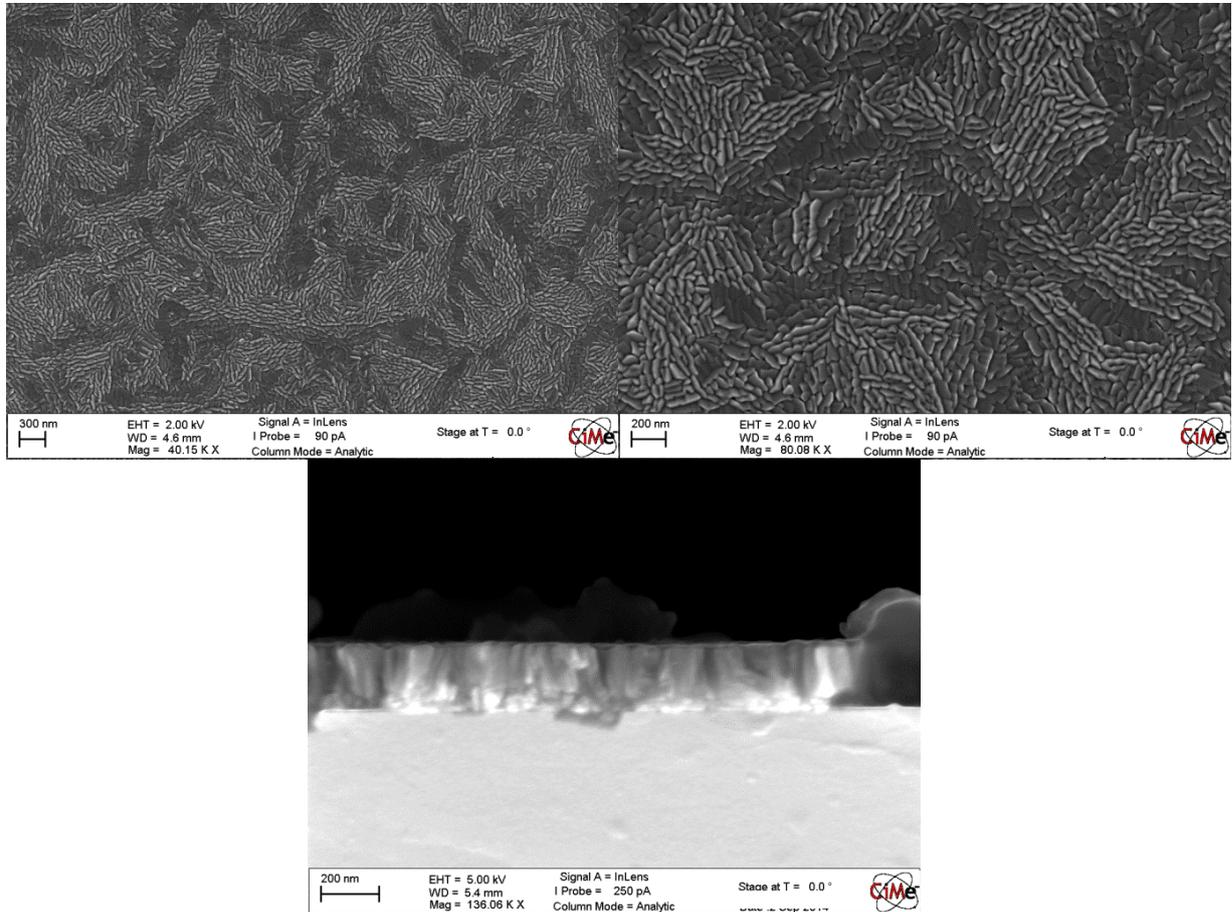


Figure 5: Cross sectional and plan view SEM images of 20W Ge doped VO<sub>2</sub> sample.

### A1.3. Chemical investigation of pure and Ge doped thermochromic samples

#### Energy-dispersive X-ray Spectroscopy (EDX)

EDX measures spectra of X-rays emitted by a sample which is irradiated by high energy electrons. Excited atoms lose energy by emitting characteristic X-rays. Each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum. EDX can then be used for qualitative analysis, to determine the composition of a sample and it can also provide semi-quantitative results on the atomic concentrations of elements present in the films. EDX systems are attachments to Scanning Electron Microscopes, therefore, the samples with 10W and 20W applied on the Ge target, measured by SEM and discussed in the previous section, are also investigated by EDX. Information on the chemical composition of films is obtained.



In the EDX spectra, strong Si peaks are evident. These peaks are coming from the substrate. In the measurement an electron beam of 10 kV is applied and this can be enough to penetrate through the 200 nm thick VO<sub>2</sub> film. Using a simple Monte Carlo simulation software, CASINO v2.48, the escape depth of scattered and backscattered electrons from a 200 nm thick VO<sub>2</sub> film deposited on a Si substrate is simulated for a 10kV electron beam (Figure 6). The electron beam is calculated to penetrate up to nearly 1µm depth into the sample and this can be correlated with the presence of strong Si peaks in the EDX spectrum.

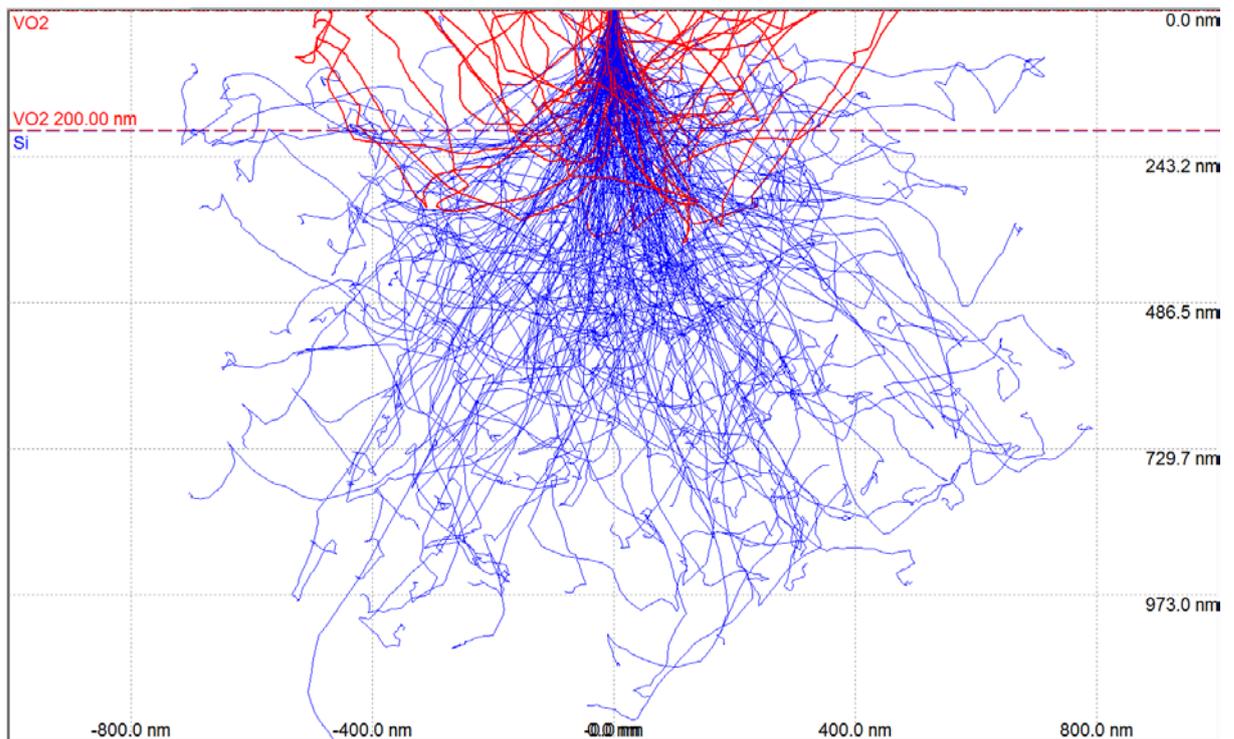
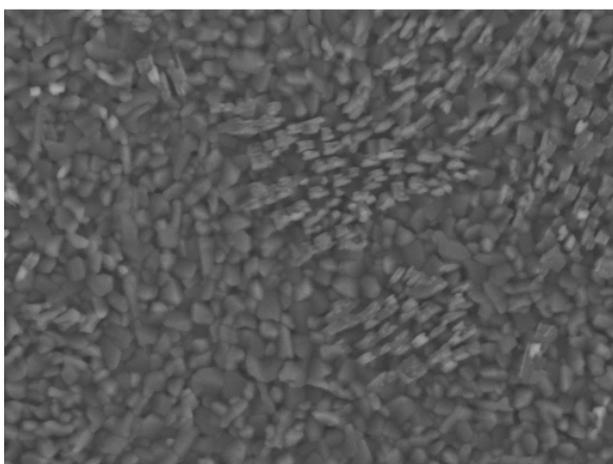


Figure 6: Monte Carlo simulation of the escape depth of scattered (blue) and backscattered (red) electrons from a 200 nm VO<sub>2</sub> film deposited on a Si substrate. Simulation using CASINO v2.48

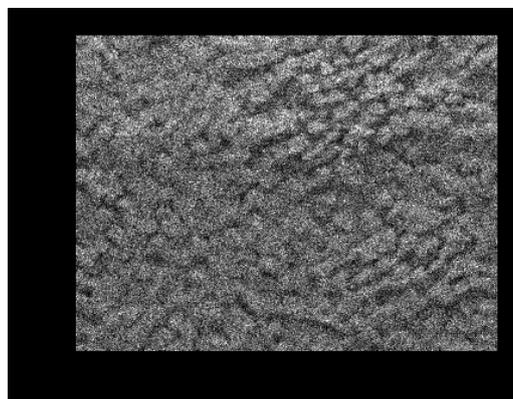
The Ge content of the film with 10W applied power on the dopant target was found to be 0.35 at.%. Moreover, Ge seemed to be homogeneously scattered across the film, suggesting that it could successfully accommodate in the VO<sub>2</sub> crystal lattice. For the more strongly doped sample, with 20W Ge, the EDX investigation yielded an atomic concentration of ~ 3 at.% Ge. Here too, the dopant appears to be evenly scattered across the sample and to enter the film's crystal structure.



EDX results of a VO<sub>2</sub>:Ge sample with 10W Ge



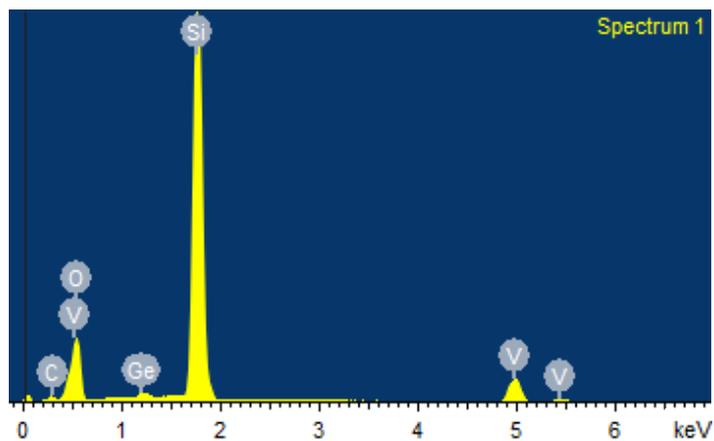
Electron Image 1



V La1\_2



Ge La1\_2

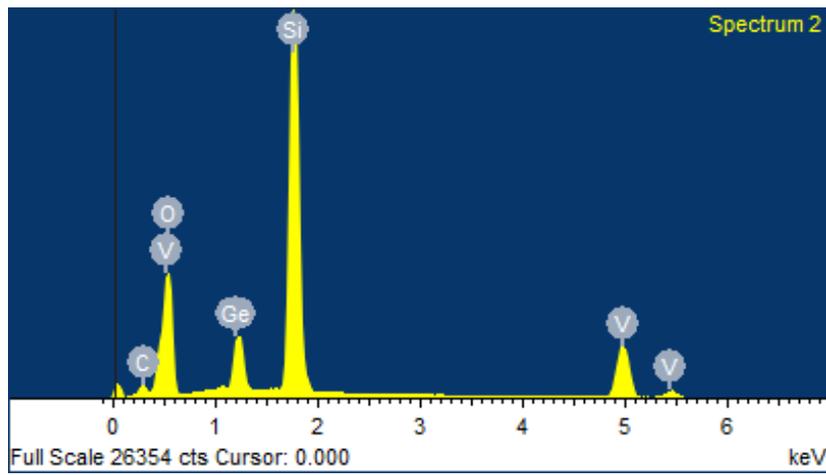
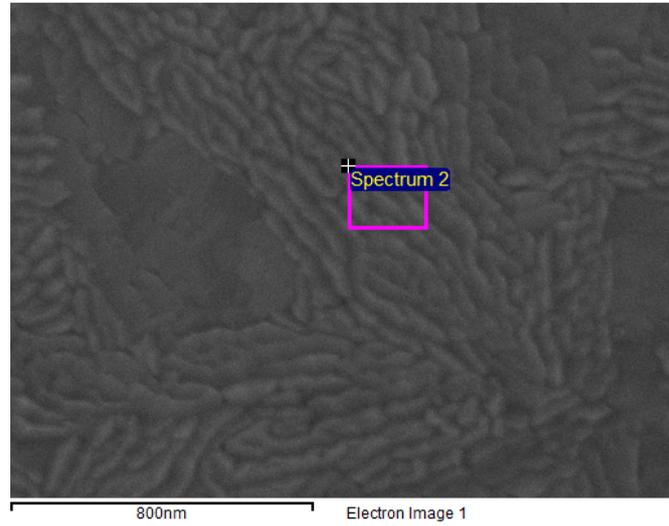


Element	Weight%	Atomic%
C K	2.78	6.38
O K	15.40	26.54
Si K	52.14	51.17
V K	28.77	15.57
Ge L	0.91	0.35
Totals	100.00	

Figure 7: Elemental EDX mapping of the V and Ge present in the region displayed in the electron image. The corresponding EDX spectrum and elemental composition table are shown.



EDX results of a VO<sub>2</sub>:Ge sample with 20W Ge



Element	Weight%	Atomic%
C K	2.95	7.16
O K	18.79	34.22
Si K	32.57	33.78
V K	38.20	21.84
Ge L	7.49	3.01
Totals	100.00	

Figure 8: The EDX spectrum and elemental composition table for the sample with higher Ge concentration are shown.



## X-ray Photoelectron Spectroscopy (XPS)

Pure and Ge doped samples are investigated by *in situ* XPS. As the films are transferred *in-situ* to the photoelectron spectrometer, carbon contamination is not detected. Peaks attributed to Ge become visible for the doped sample, while only peaks associated with V and O are present in the pure film.

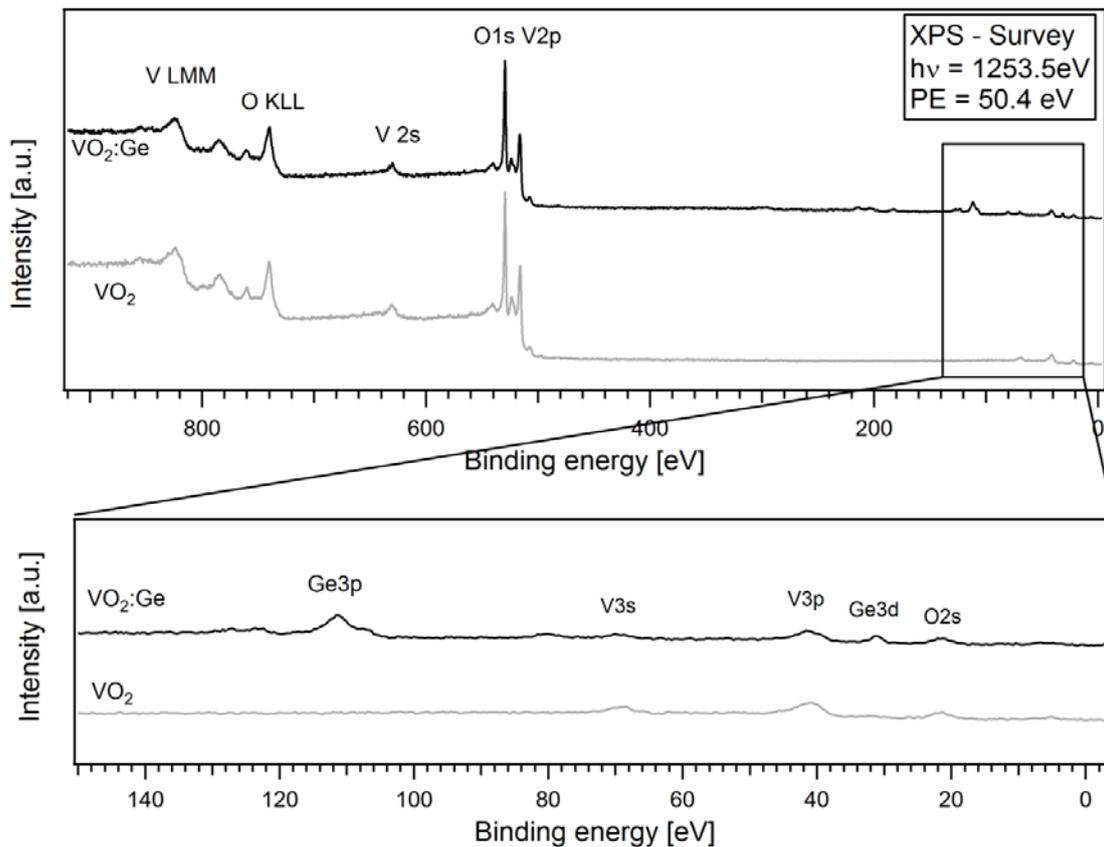


Figure 9: XPS survey spectra of VO<sub>2</sub> and VO<sub>2</sub>:Ge films. Only peaks associated to V, O and Ge atoms are present. C is below the detection limit.

The chemical composition of the analysed films is evaluated from the XPS core-level spectra. The elemental quantification is done from the O1s, V3p and Ge3d core-level peak integration. As expected, Ge3d core level peak is present only in the Ge doped sample. Quantification is performed after background subtraction and satellite correction.

The elemental quantification yields a 31.1 at.% V and 68.9 at.% O concentration for the pure film and 69.7 at.% O, 25.7 at.% V and 4.6 at.% Ge for the doped film. This composition of the pure VO<sub>2</sub> film is not stoichiometric. Although the transfer from the deposition chamber ( $\sim 10^{-6}$  mbar) to the analysis chamber ( $\sim 10^{-9}$  mbar) was done as soon as possible, at  $\sim 10^{-6}$  mbar only 1s is enough to form a monolayer of reactive impurity gas. Therefore a slight oxidation of the surface might occur and the somewhat bigger concentration of oxygen in the switching thermochromic film, compared to that of a stoichiometric VO<sub>2</sub>, might be explained.



## Rutherford Backscattering Spectroscopy (RBS)

An accurate elemental quantification by EDX is limited and XPS being a very surface sensitive technique, the XPS core level quantification, while relatively precise, is limited to the sample surface. Therefore, for a precise quantification of the Ge concentration in VO<sub>2</sub> thin films, Rutherford Backscattering Spectrometry (RBS) is chosen.

Among the many deposited sample series, the one containing the film with the highest recorded transition temperature (~94°C) is of special interest. Five VO<sub>2</sub> based samples – both pure and Ge doped – have been deposited. It is observed that the transition temperature increases proportionally with doping, up to a critical dopant concentration, where the thermochromic behaviour is lost. In order to accurately determine the precise composition of the film with the maximum switching temperature and the critical dopant concentration where the switching behaviour is lost, an RBS investigation is carried out. Besides accurate dopant concentrations, with RBS the precise film thicknesses are determined as well.

The RBS data is collected using a 1.7 MV tandemron accelerator with a 2 MeV He<sup>2+</sup> ion beam. Incident angle of ion beam is 0°, normal to the sample surface, while backscattered particles are detected at 150° scattering angle. Data analysis is done using the Ion Beam Analysis DataFurnace code [Bar97] in order to simulate the experimental RBS spectra.

Sample	Applied power [W]	Thickness [nm]	Ge content [at.%]	T <sub>SMT</sub> [°C]
1	0	478	0.09	66.3
2	5	495	0.48	69.6
3	15	513	4.28	75.8
4	17	534	5.93	93.6
5	20	585	8.65	-

Table 2: The Ge at.% and film thicknesses as determined by RBS measurement and measured switching temperatures.

The RBS results such as film thickness determined from layer areal density measurements and at.% of Ge content are given for each sample in Table II. The energy spectra of the backscattered ions are displayed in Figure 10, where the yield of backscattered He ions is plotted against the channel number (backscattering energy). The height of the peak gives the concentration of backscattered ions, while the width gives the layer thickness. The Ge contribution is seen at high backscattering energies (high channel number) and is partly superposed on the V signal. At lower energies, the oxygen component is superposed on the Si substrate signal.

The simulated spectrum was obtained by modelling a Ge<sub>x</sub>V<sub>(1-x)</sub>O<sub>2</sub> monolayer on Si substrate and it fits the experimental RBS data. As expected, by increasing the applied power on the Ge target, the Ge concentration of the deposited films is gradually increasing. Furthermore, considering the evolution of deposition rate with time linear, layers are normalized to the same deposition time (120 min). It is found that the thickness of the deposited layers increases with the Ge content.

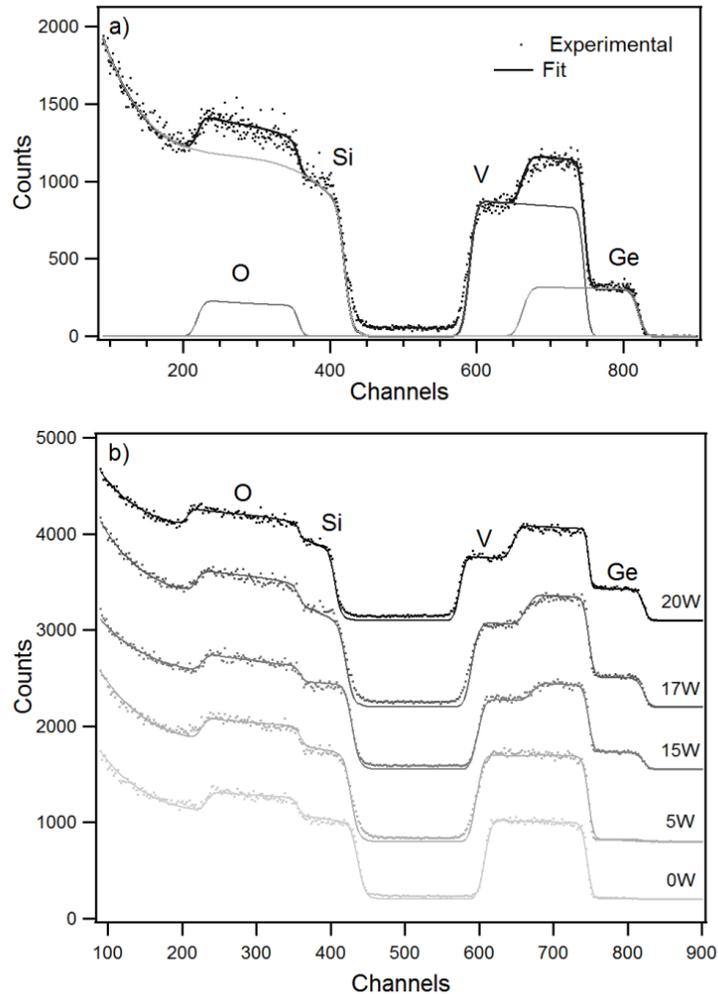


Figure 10: a) Experimental data (points) and simulated RBS spectra (solid line) of the  $\text{Ge}_{0.059}\text{V}_{0.941}\text{O}_2$  film. The result of the simulation agrees well with the experimental RBS spectrum. b) Comparison of  $\text{VO}_2$  and increasingly doped  $\text{Ge}_x\text{V}_{(1-x)}\text{O}_2$  films by varying the applied power on the Ge target. The width of the V and O signals are related to the film thickness, the peak heights give the concentration of backscattered ions. [Kra17]

#### A1.4. Design of a customized heating stage for FTIR spectrometry measurements

Thermochromic vanadium dioxide based films change their optical properties with temperature, especially in the mid-infrared spectral region. In order to have a precise control of the sample temperature during the FTIR spectrometry measurements, a custom made portable heating stage is built. It is adapted to fit the integrating sphere and designed in such way that the back-heated sample is placed very close to the sphere's opening, but without any direct contact with the surface of the sphere's enclosure.

This is important due to the coating of the integrating sphere which oxidizes after exposure to high temperatures. The thermocouple used to monitor the sample temperature is fixed inside the copper heating block. Due to the high thermal conductivity of Cu, the temperature inside the Cu block is considered to be the same as that of the sample fixed on it (samples are usually few hundred nanometers of thermochromic films deposited on 0.5mm conducting Al substrates).



Measuring the temperature inside the Cu block is considered a more suitable approach as opposed to having the thermocouple in direct contact with the sample's back surface. In the latter case, the sample might be not evenly heated and could lead to a temperature gradient inside the film, therefore, not uniform switching. The very small distance between heating stage and integrating sphere does not allow for temperature reading on the front-side of the sample. The photograph and schematic of the heating setup are shown below.

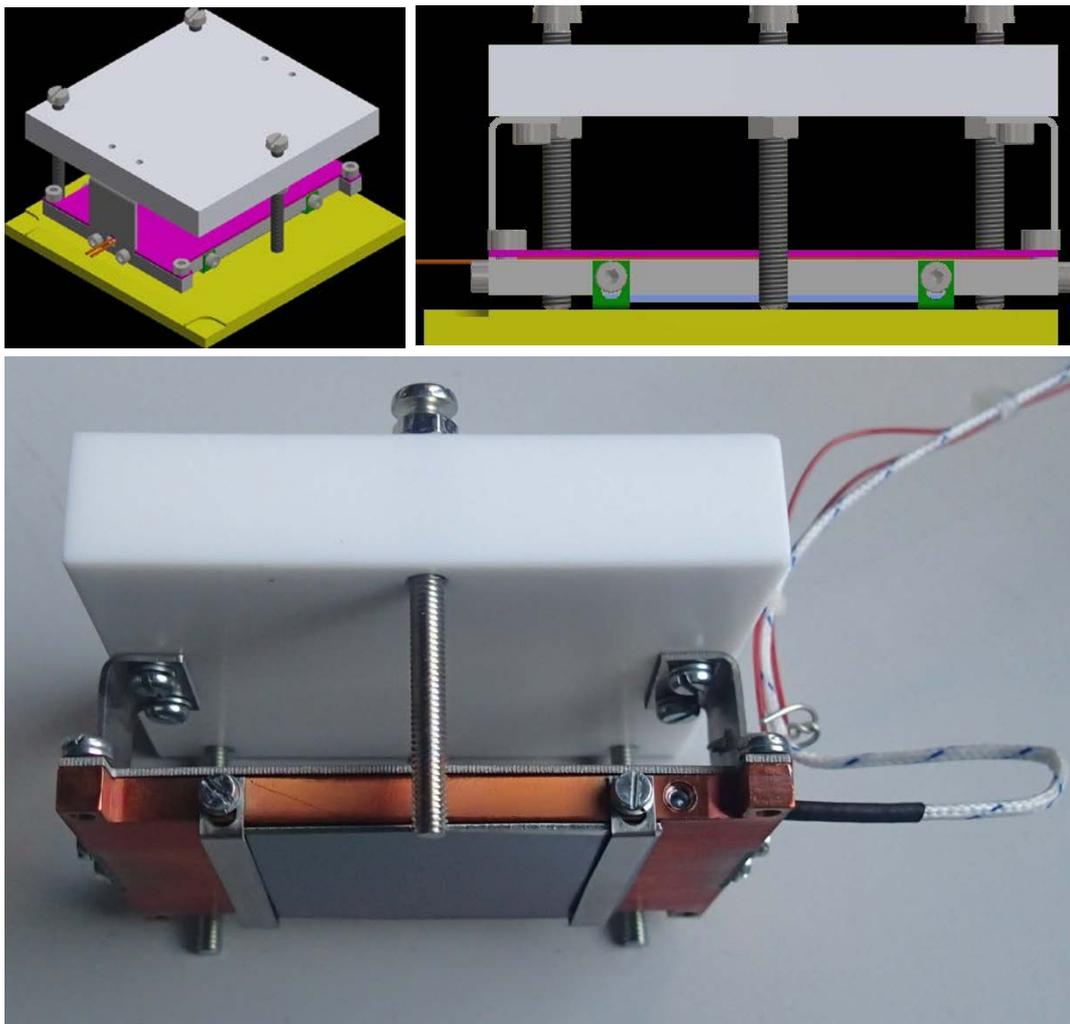


Figure 11: Schematic and photo of the designed heating stage.



#### A1.5. Thermal emissivity switch of pure and Ge doped thermochromic thin films

Mid-infrared reflectance of pure and Ge doped vanadium dioxide thin films on Al substrates is measured. Measurements are done both below and above the thermochromic transition temperature in order to determine the emittance switch at given wavelengths.

##### Vanadium dioxide thin films

The optical switch of thermochromic vanadium dioxide films in the infrared region has been previously captured by thermal imaging (commercial FLIR Systems thermographic camera). A  $\text{VO}_2$  coating has been deposited on reflecting stainless steel (SS) substrate. Below the transition temperature, the semiconducting  $\text{VO}_2$  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  $\text{VO}_2$  becomes opaque to the infrared radiation in its metallic state. On reflecting substrates such as stainless steel, copper or aluminum, the thermochromic coating has a low thermal emittance below and a high emittance above the transition temperature.

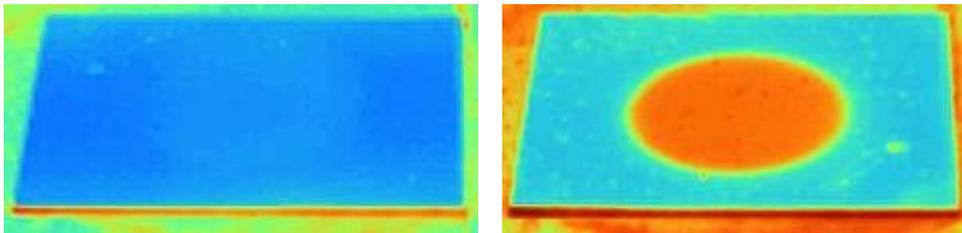


Figure 12: Thermal image of the thermochromic absorber coating in the cold state with low emittance (left) and in the hot state with high emittance (right).

Although easy to visualize, this technique is not suitable for a precise quantitative determination of the thermal emissivity change of the sample. With the upgrade of the existent Bio-Rad FTS-175C Fourier transform infrared spectrometer with a 3" gold coated integrating sphere and a high performance nitrogen-cooled MCT detector for the Mid-IR range (2-20  $\mu\text{m}$ ), coupled with the custom designed heating stage described in the previous section, the temperature dependent spectral reflectance/emittance in the mid-infrared range can be measured precisely.

Films of ~320 – 340 nm estimated thickness have been deposited by reactive magnetron sputtering, at 600°C, on 0.5 mm thick, 50 mm x 50 mm sized commercially available Al sheets (Goodfellow). The total reflectance spectra of the sample have been determined by FTIR spectrometry both before and after the thermochromic transition. Since the sample is opaque, from the measured reflectance spectra, the spectral emissivity can be directly determined (Figure 13). The thermal emittance of the thermochromic absorber in its two states considerably differs.

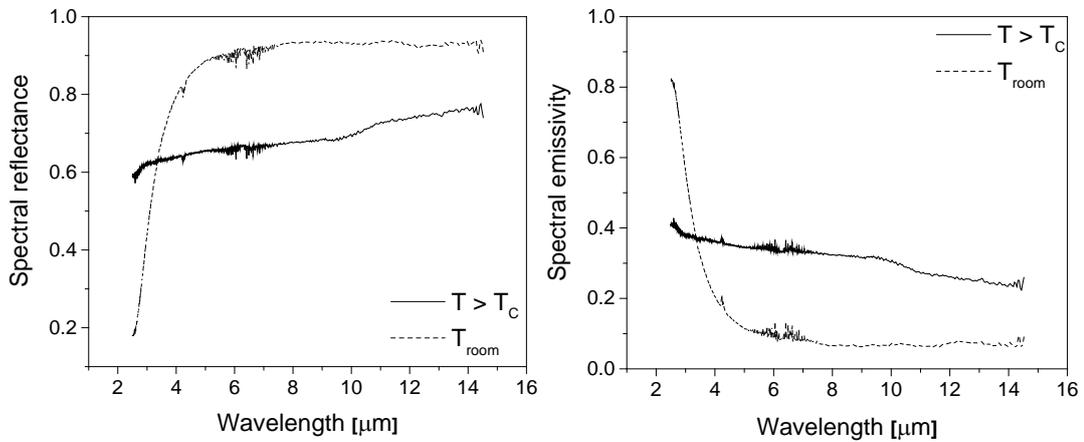


Figure 13: Spectral reflectance and corresponding spectral emissivity of the thermochromic absorber both below and above the transition temperature of vanadium dioxide.

The emissivity switch around 8  $\mu\text{m}$  is of special interest, as the spectral emittance of a blackbody of 100°C peaks at this wavelength. In the case of pure  $\text{VO}_2$  deposited on Al, the emissivity changes considerably from ~6% below the critical transition temperature to ~33% above it.

#### Ge doped vanadium dioxide thin films

It has been determined previously that a novel Ge type doping can significantly increase the transition temperature of  $\text{VO}_2$  based thin films (up to ~ 95°C). This is an important step in the successful integration of the thermochromic function into the new generation of smart solar absorber coatings. However, it is interesting to study the effect of Ge doping on the optical properties – especially thermal emissivity – of the deposited films. Therefore, just as the pure  $\text{VO}_2$  film discussed in the previous section, two Ge doped films - with different Ge content - have been deposited on Al substrate and measured by means of FTIR spectrometry in the mid-infrared range. The different doping content has been achieved by changing the applied power on the Ge target (8W and 12W).

To evaluate the emissivity switch between the two states, the samples have been measured both at room temperature and above the critical transition temperature. For comparison, the emissivity spectra of the doped samples have been plotted together with that of the pure  $\text{VO}_2$  film (Figure 14).

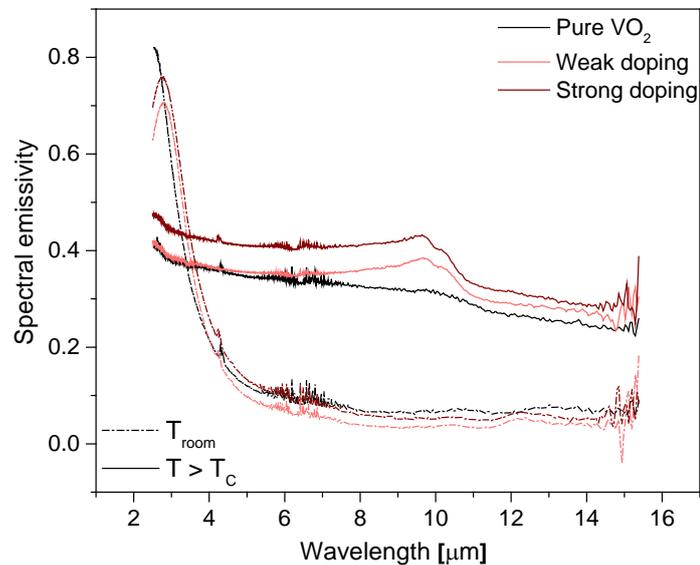


Figure 14: Spectral emissivity change between the low (dashed line) and high temperature state (solid line) of three samples with different composition: pure VO<sub>2</sub>, weakly doped and strongly doped coatings.

It is found that the emissivity switch in the Ge doped samples is higher compared to that exhibited by the pure film. The difference in emissivity is more pronounced in the high temperature state. Furthermore, the emissivity seems to gradually increase with the doping, reaching a roughly 10% emissivity increase at 8 μm for the strongly doped sample. Hence, besides increasing the transition temperature, Ge doping also improves the emissivity of the samples in the high temperature state, making the sample more efficient at radiating off the excess heat.

#### A1.6. Angle dependent IR optical investigation of VO<sub>2</sub> films

The angular dependence of thermal emittance for a thermochromic sample above its critical temperature is determined. Since the coating is supposed to show metallic properties, the emissivity versus angle for a rough oxidized aluminum plate is measured for comparison (Figure 15.a). The measurements are performed at 100°C and 99°C for the VO<sub>2</sub> and the aluminum respectively. Both curves are very similar. 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. This result is in very good agreement with the Fresnel relation where typical results for metals are illustrated in Figure 15.b.

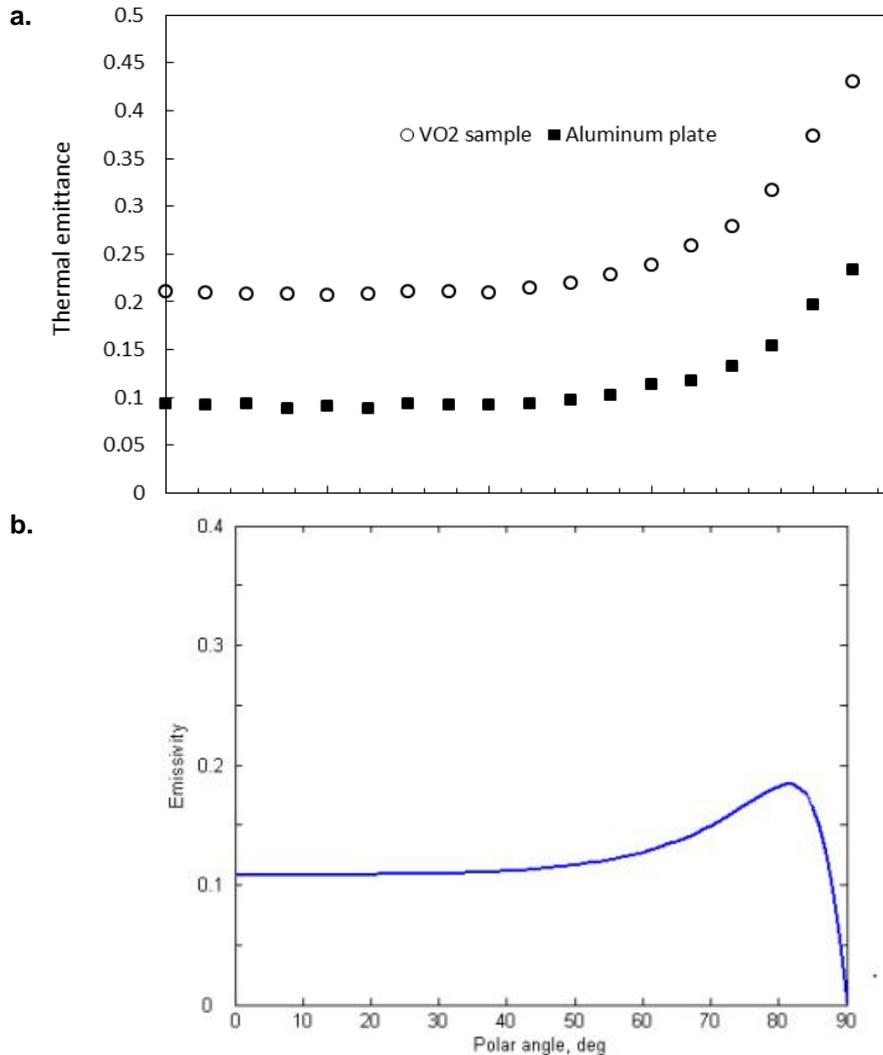


Figure 15: a. Angular dependence of the thermal emittance for VO<sub>2</sub> and aluminum. b. Typical directional emissivity of a metal according to Fresnel's relation with  $n=1.5$  and  $k=7$  [Teo07].

The emissivity values of the VO<sub>2</sub> thin film are higher than the ones from aluminum, which shows that the VO<sub>2</sub> is in a “bad metal state”, and therefore emits more than a typical metal. The emissivity values of the aluminum plate are similar to the ones given in tables. Emissivity of perfectly smooth metals is close to 0 since they reflect almost all light. Most measurements give higher values of emissivity because of oxidation layers, roughening and contamination.

The thermal emittance of vanadium dioxide above the transition temperature is higher at greater angles than at normal incidence. This represents an advantage for solar collector application, since it means that, generally by measuring at normal angles, we underestimate the total thermal emittance of the device. The smart coating is more efficient at dissipating heat via radiation than what is predicted from normal incidence measurements.



#### A1.7. Thermochromic switch in the visible spectral range

During the temperature dependent reflectance measurements of the vanadium dioxide based thermochromic films, visible thermochromism has been observed.

**Further details available in the Confidential Appendix. The corresponding section of the Confidential Appendix contains unpublished data based on which publications are envisaged.**

#### A2. Understand doping mechanism by means of detailed characterization of the films and theoretical considerations

Whether the increase in transition temperature is driven by structural or electronic factors is not well understood. To this end, a detailed study of the electronic properties, on the valence band and core level spectra of doped samples is carried out. The effects of Si doping are analyzed. Silicon, a group 4 element just as Ge, is expected to show similar properties. Optical band gaps of pure and Ge doped films are determined and compared to the results of recent theoretical predictions.

##### A2.1. Study of the electronic properties of pure and Ge doped VO<sub>2</sub> by UPS and XPS

XPS and UPS give valuable information on the electronic structure of the deposited pure and Ge doped films. After the deposition at high temperatures, samples are right away transferred to the photoelectron spectrometer. During cooling, UPS spectra are taken at 2 minute intervals. In this manner the transition from high temperature, metallic phase into the low temperature, semiconducting phase is observed *in-situ*.

The Fermi edge disappears and a shift in the density of states near the Fermi level is recorded. It results in the opening of a band gap and marks the metal-to-semiconductor transition. For the Ge doped film, already in the hot state there is no observable Fermi edge. However, the density of states near the Fermi level shift during cooling and the insulating character of the film becomes stronger. The UPS spectra of the two samples can be correlated with the results of resistivity measurements. The pure sample, which shows a clear Fermi edge in the hot state and a gap opening near the Fermi level in the cold state, exhibits a sudden drop in resistivity of more than 2 orders of magnitude with very low resistivity values in the hot, metallic state. Meanwhile, the doped sample which exhibits only slight changes in the density of states at the valence band edge and lacks a Fermi edge even in the hot state, displays a rather smeared out transition of smaller magnitude than the pure sample. Moreover, the resistivity values in the hot state are considerably higher than in the case of pure VO<sub>2</sub>. This could explain the absence of a true metallic character of the film.

**Further details available in the Confidential Appendix. The corresponding section of the Confidential Appendix contains unpublished data based on which publications are envisaged.**



## A2.2. Investigation of an alternative dopant element, Si with similar valence and electrical properties to Ge

It is not yet established whether the increase in transition temperature is driven by structural or electronic factors. In the periodic table, Si is found in the same group as Ge and both behave as semimetals. Their electronic configuration is similar, having the same number of electrons in the outermost shell, therefore, similar valences. It is then interesting to investigate whether Si doping exhibits the same effect on the thermochromic transition as Ge doping. The found similarities or differences between the two dopant elements, Ge and Si, can be of significant importance in understanding the probable determining factors of the transition and the governing doping mechanisms.

Literature on Si doping is contradictory, with [Zhao14] reporting an increase in the critical transition temperature and [Wu15] results showing the opposite.

Temperature dependent electrical resistivity curves and in situ XPS and UPS spectra of Si doped vanadium dioxide thin films are measured and the results compared with those of the previously characterized Ge doped films.

### Four-point resistivity measurement

Pure  $\text{VO}_2$  film switches at  $67.8^\circ\text{C}$ . Up to 1.2 at% Si doping ( $\text{V}_{(1-x)}\text{Si}_x\text{O}_2$  15W), the  $T_h$  ( $72.3^\circ\text{C}$ ) and hysteresis width increases. At higher doping levels the switching character of films is lost due to possible amorphization of thin films. The resistivity of thin films increases with doping. Hence, there are obvious similarities between the two dopants. Si changes the thermochromic transition properties in a similar way as Ge. The doping efficiency of Si is even comparable to that of Ge, with  $\sim 4^\circ\text{C}$  increase in transition temperature per at.% dopant. However, the transition is lost very early on, at just above 1 at% Si doping. This makes Si a considerably less promising dopant for solar collector application. Nonetheless, it brings interesting new considerations towards the understanding of doping mechanism and selection of efficient new dopant elements.

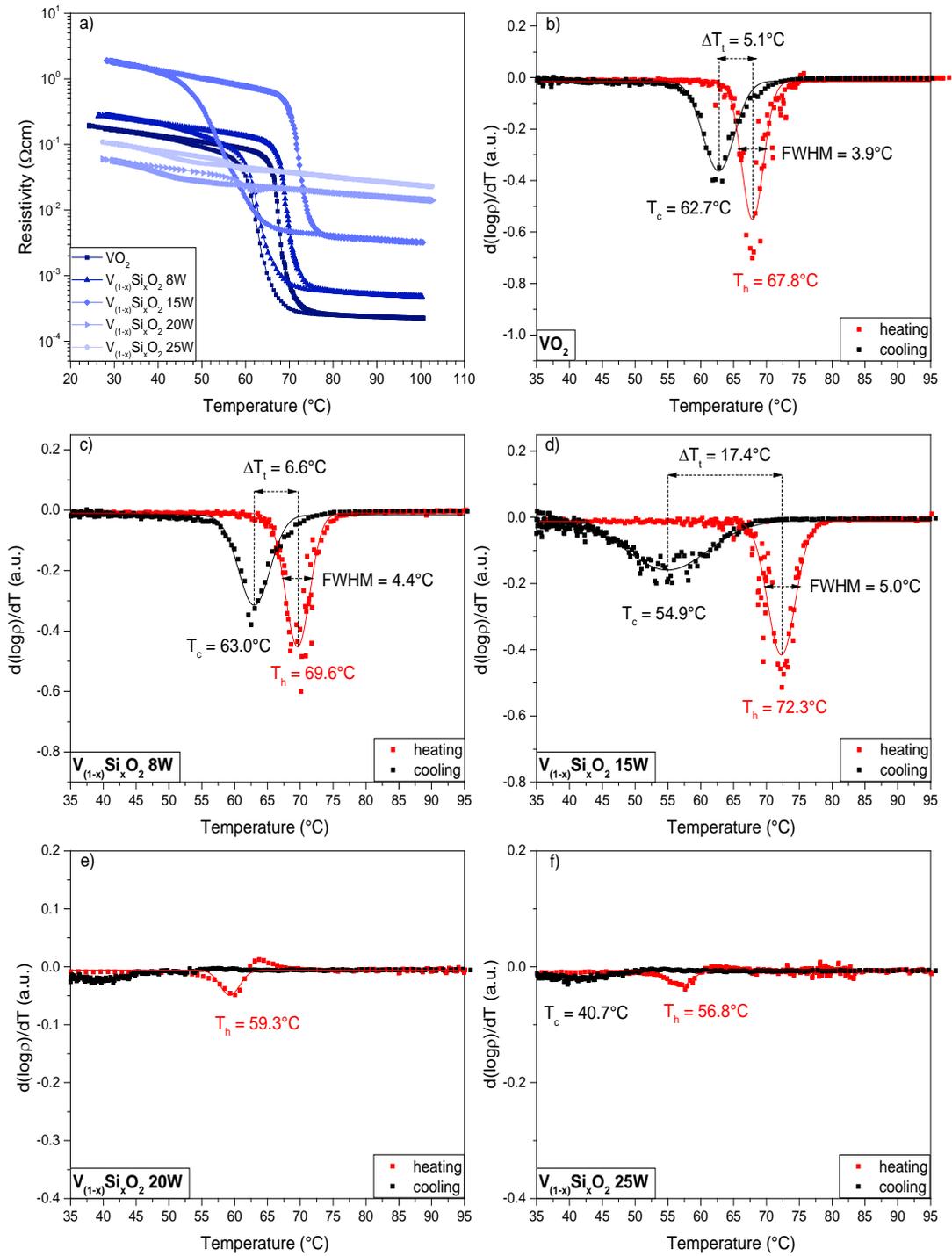


Figure 16: a) Resistivity measurements of doped and pure  $\text{VO}_2$  films. The  $d(\log\rho)/dT$  vs  $T$  plots for b) pure  $\text{VO}_2$  and c) 8W, d) 15W, e) 20W, f) 25W Si doped  $\text{V}_{(1-x)}\text{Si}_x\text{O}_2$  films.  $T_h$ ,  $T_c$ ,  $\Delta T_t$  mark the transition temperature during heating, cooling and the hysteresis width respectively. [Kra17-2]



## UV Photoelectron Spectroscopy

Decrease of DOS at the Fermi level, associated with V 3d states, with Si doping. In  $\text{VO}_2$ , the opening of a band gap during cooling marks the *in-situ* metal-insulator transition. For the sample with  $\sim 1.2\text{at}\%$  Si ( $\text{V}_{(1-x)}\text{Si}_x\text{O}_2$  15W) a vague Fermi edge is detectable. While at  $\sim 1.5\text{at}\%$  Si content ( $\text{V}_{(1-x)}\text{Si}_x\text{O}_2$  25W) the film is completely semiconducting. Broad features centered around  $\sim 7$  eV related to V 3d-O 2p $\sigma$  band hybridization.

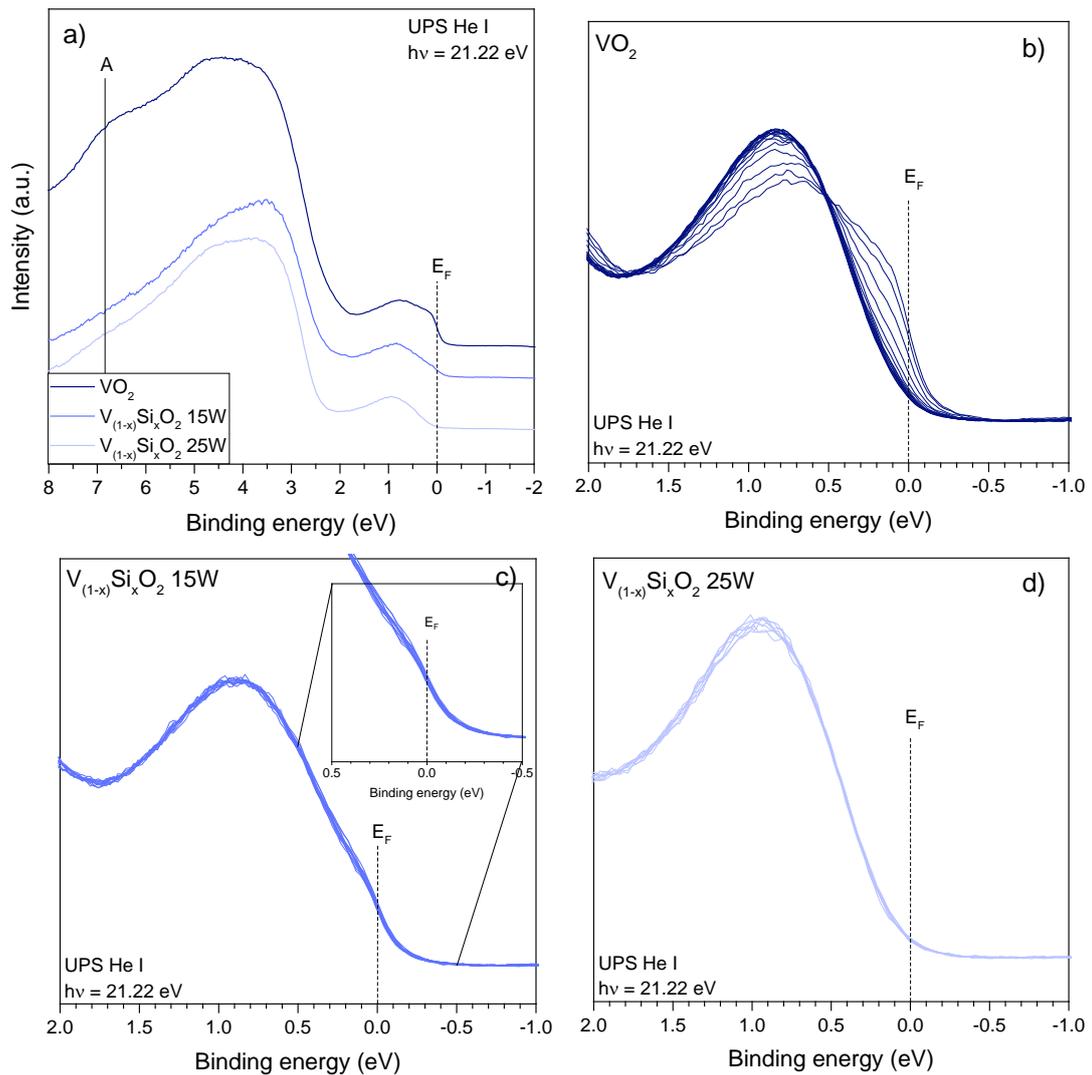


Figure 17: a) He I and valence band spectra of  $\text{V}_{(1-x)}\text{Si}_x\text{O}_2$  and  $\text{VO}_2$  films. A zoomed in view near the Fermi level of the 3 samples is given in b), c) and d). The intersecting straight lines mark the position of the Fermi edge and the bonding of O 2p $\sigma$  orbitals with V d band (A). [Kra17-2]



## X-ray Photoelectron Spectroscopy

Binding energy of core lines shift to higher values with Si doping. V $2p_{3/2}$  core level peak deconvolution shows the fitted components peak at 515.8eV BE and 516.9eV BE. These values are in very good accordance with those reported in literature for V $^{4+}$  and V $^{5+}$ . Hence, V $^{5+}$  states become dominant on the expense of the four-fold oxidized V atoms, as doping levels increase.

A Shirley function was used to subtract the background. The V  $2p_{3/2}$  peaks were fitted with mixed Lorentzian-Gaussian curves. Film composition was evaluated from the O 1s, V  $2p_{3/2}$  and Si 2p core-level peak integration, using Scofield sensitivity factors combined with calibration with pure VO $_2$  sample.

The quantification yielded: ~1.2at% Si for the 15W and ~1.5at% for the 25W doped samples. The ratio between the at% of V and O was 1:2 for all analyzed samples.

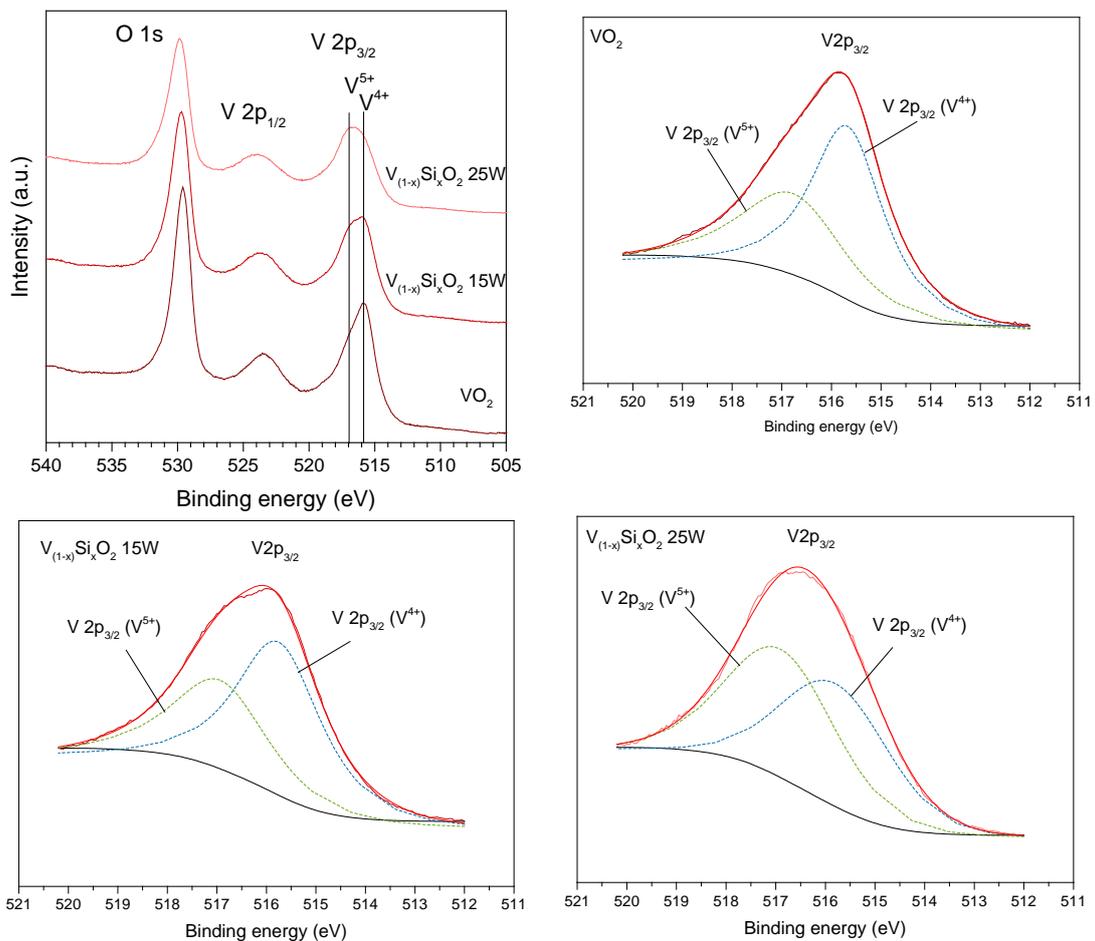


Figure 18: a) O 1s and V 2p core-level spectra of the VO $_2$  and V $_{(1-x)}$ Si $_x$ O $_2$  films. The intersecting straight lines mark the position of V $^{4+}$  and V $^{5+}$  states. b),c),d) Fitting of the V  $2p_{3/2}$  peak for the 3 analysed samples. [Kra17-2]



Based on the above results, it is concluded that Si doping affects the valence band and core level changes of VO<sub>2</sub> thin films similarly to Ge. Moreover, the transition temperature increases with Si doping. Although, the doping efficiency per at.% Si is comparable to that of Ge ( ~4°C increase per at.% dopant for both elements), amorphization in Si doped films occurs early on at slightly above 1 at.%.

A2.3. Optical bandgap determination of pure and Ge doped vanadium dioxide thin films and comparison with the results of recent theoretical predictions.

Reflectance and transmittance measurements in the near-IR range have been performed on pure and Ge doped VO<sub>2</sub> films (deposited on Si and sapphire substrate). From these data the absorption coefficient was calculated according to [1].

$$\alpha(\lambda) = -\frac{1}{d} \ln \frac{T(\lambda)}{1-R(\lambda)} \quad [1]$$

Knowing the absorption coefficient against the photon energy, the optical bandgap of the material is determined (Tauc plot).

The optical bandgap for pure VO<sub>2</sub> film (deposited on sapphire substrate) has been found to be 0.6 eV which is perfectly matching the value reported in literature.

**Further details available in the Confidential Appendix. The corresponding section of the Confidential Appendix contains unpublished data based on which publications are envisaged.**

A3. Doping optimization: How high can be doped? Which maximal transition temperature T<sub>c</sub> can be achieved? Which switching contrast can be achieved?

A3.1. Determination of optimum Ge doping levels for thermochromic vanadium dioxide based thin films with elevated T<sub>c</sub>.

Two sets of pure and Ge doped VO<sub>2</sub> thin films were prepared and, by four point probe measurement, their temperature dependent electrical resistance was determined. It was shown that doping with Ge results in the critical temperature to be increased. However, doping also reduces the magnitude of the resistivity drop upon transition. During the semiconductor-to-metal transition, the electrical resistance of pure films undergoes a change about two orders of magnitude (logarithmic scale). This change is progressively reduced with increasing power on the dopant target. Similar effects have been reported for other dopants before, such as Al and W doping [Pao09]. This could be explained by a progressive amorphization of the films with the increase in dopant concentration, where an excessive doping leads to the loss of the switching character of thermochromic films. Therefore, it is mandatory to find the optimum Ge doping level, where the transition temperature is raised as much as possible while still keeping the switching character of the films.



With regards to costs, the dopant concentration of the films is not sensitive as, at the high purity levels required for the thermochromic thin film applications, metallic V and Ge prices are fairly close.

Chemical analyses by means of EDX, XPS and RBS are performed on the Ge doped samples exhibiting a semiconductor-to-metal transition (SMT) at the highest  $T_C$ . Our results indicate that the atomic dopant concentration must be kept below ~6 at.% in order to prevent the films from losing their semiconductor-to-metal transition. So far, the maximum critical temperature reached is ~96°C for a ~5.9 at.% Ge concentration. Further optimization of the deposition parameters, doping with Ge and additional elements could lead to even higher transition temperatures.

A3.2. Optimization of parameters other than the doping level, for a better control of the thermochromic behaviour of Ge doped vanadium dioxide based thin films.

Deposition parameters other than doping level can influence the transition temperature of doped samples as well. The effect of  $O_2$  partial pressure on Ge doped thin films is investigated. For that, the oxygen partial pressure is slightly changed while keeping the dopant levels constant. The results show that the oxygen content has a clear effect on the resistivity values and it can also influence the transition temperature to some extent.

The values of the PID controller are inversely proportional to oxygen partial pressure: lower the PID value, higher the corresponding oxygen partial pressure. Higher  $O_2$  partial pressures (lower PID) result in higher resistivity values. Interestingly, unlike doping, changing the  $O_2$  partial pressure has almost no effect on the magnitude of transition or on the hysteresis width.

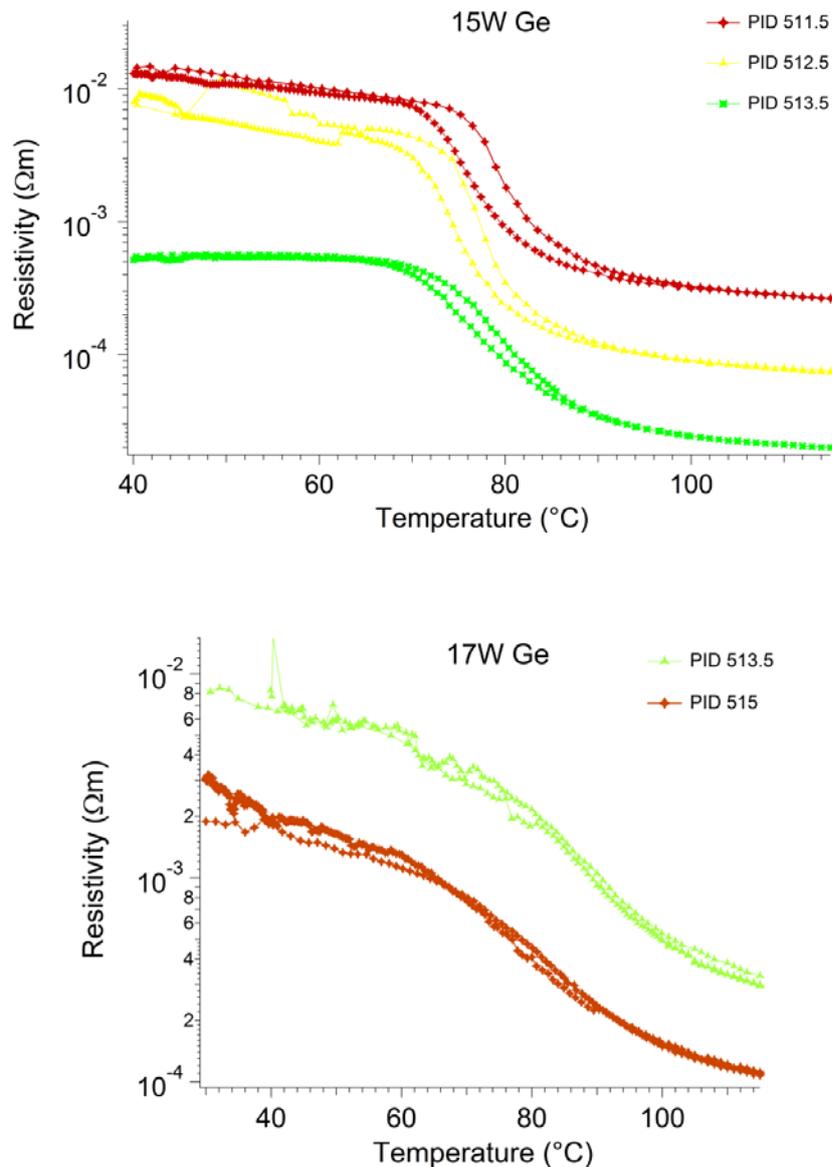


Figure 19: Effect of  $\text{O}_2$  partial pressure on doped  $\text{VO}_2$  films with 15W (top) and 17W (down) applied power on Ge target.

## B. Maximizing switching contrast for multilayers

### B1. Develop concept for multilayered interference thin film stacks

Structures of metallic layers with dielectric spacers between can exhibit enhanced optical reflection or transmission due to interference effects. A multi-layered interference thin film stack has been proposed. The concept has been tested by means of optical simulation. The simulation is based on the optical constants  $n$  and  $k$ , which have been previously determined by ellipsometry.

**Further details available in the Confidential Appendix. The corresponding section of the Confidential Appendix contains unpublished data based on which publications are envisaged.** 41/53



## B2. Determination of the minimum thickness for individual thermochromic coatings with good enough crystallization

### B2.1. Minimum thickness for switching vanadium dioxide based thin films

For some of the proposed interference multilayer designs, rather thin thermochromic films with thicknesses in the range of 20 nm - 100 nm are needed. There are indications in the literature that vanadium dioxide based thin films exhibit thermochromism only above a certain minimum thickness, but there is no obvious fundamental physical reason for this limitation. The minimum thickness for thermochromic behavior of vanadium dioxide based thin films is determined by experiment (variation of deposition time, substrate temperature and oxygen flow).

At the critical temperature, single crystals exhibit a change of 5 orders of magnitude in electrical properties. High quality, epitaxially grown films generally show a 4 order transition, while good quality films on Si substrate undergo a 3 or slightly larger order of magnitude change in its resistivity. It is then clear that the substrate plays a very important role in film quality and, subsequently, in the transition magnitude. Furthermore, thicker the films are, closer their behavior to bulk  $\text{VO}_2$ , therefore stronger their switching properties. In very thin films it is difficult to obtain stark switching contrast. We report that on Si wafer with  $\text{SiO}_2$  top layer, we have successfully deposited  $\text{VO}_2$  films of only 30 nm thickness that still exhibit a 3 order drop in resistivity through the semiconductor-to-metal transition. Films with high switching contrast in this thickness range are suitable for various multilayered designs.

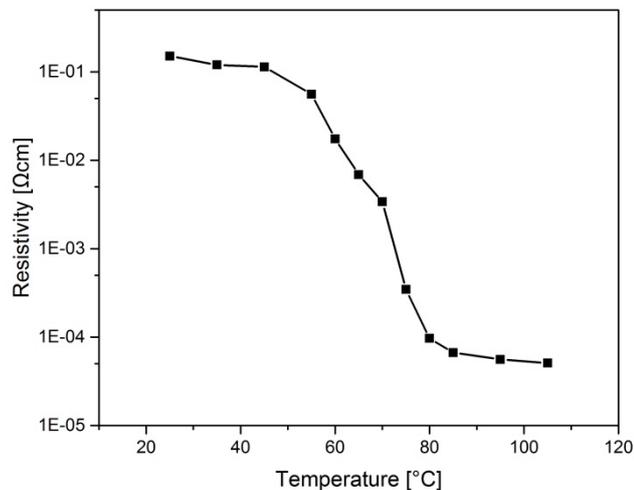


Figure 20: Temperature dependent electrical resistivity of a 30 nm thick  $\text{VO}_2$  film during heating.



## B2.2. Investigation of the dependence of IR behavior of VO<sub>2</sub> thin films with film thickness

Four samples of VO<sub>2</sub> films on tungsten substrate are deposited. The thickness is varied by changing the deposition time. Nominal thicknesses of the films are: 480, 240, 120 and 60 nm. The thickness of the films influences the thermal emissivity of the samples. In the cold state (Figure 21), the 240, 120 and 60 nm thin films all exhibit a reflectance of ~0.97 in the 5.5 – 16.5 μm range. This means a thermal emittance of around 0.03 which corresponds to that of the metallic substrate measured with the emissometer (0.024). The result suggests that for thicknesses up to 240 nm the VO<sub>2</sub> thin film is partly transparent to infrared radiation. However, there is a drop of reflectance for low wavelengths. This drop seems to be thickness dependent as thicker the VO<sub>2</sub> film is, higher the wavelength at which the drop happens. Indeed, an absorption edge in the near infrared range is shifting towards higher wavelengths with higher thicknesses. The 480 nm thick film is slightly less reflective as the others, implying that the sample has a higher thermal emittance.

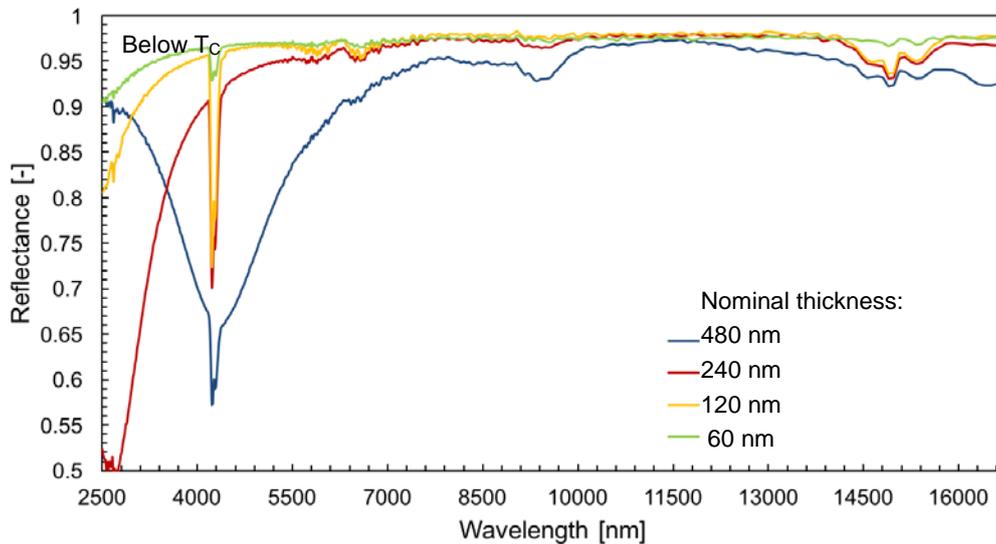


Figure 21: FTIR reflectance spectra of four VO<sub>2</sub> films of different thickness deposited on W substrate and measured below the thermochromic transition temperature.

In the hot state too, the reflectance is decreasing with increasing film thickness. Here the dependence is even stronger than in the insulating state. This suggests that for an efficient thermal emittance modulation, relatively thick films might perform better than very thin ones.

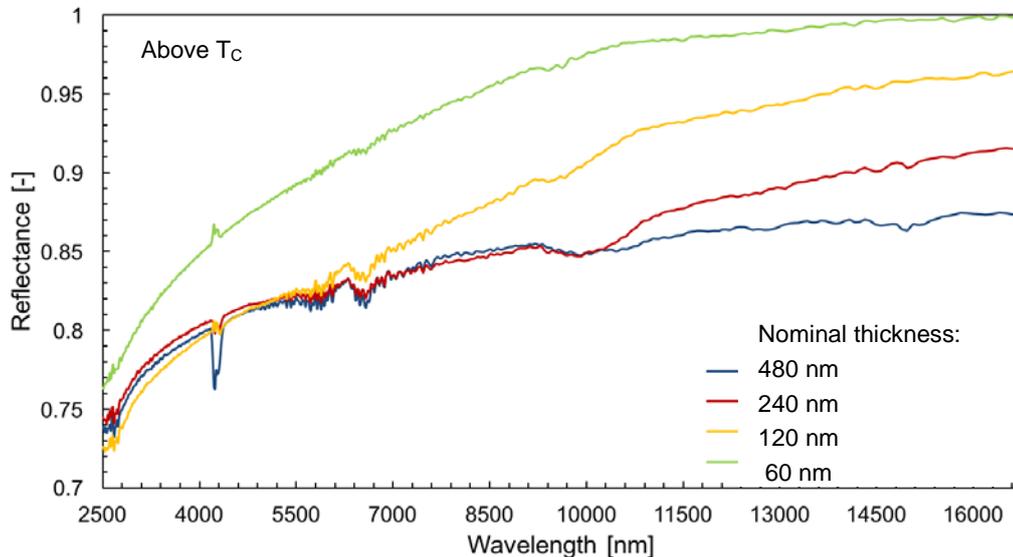


Figure 22. FTIR reflectance spectra of four VO<sub>2</sub> films of different thickness deposited on W substrate and measured above the thermochromic transition temperature.

B3. Simulate and optimize multilayers based on the knowledge of the optical constants  $n$  &  $k$  of individual layers

B3.1. Multi-layered absorber design simulation based on optical constants,  $n$  and  $k$

Starting from an optimized multilayer composed of Al substrate, VO<sub>2</sub> film and SiO<sub>2</sub> antireflection coating, a thin layer of selective absorber coating is introduced in order to reach higher absorption values. A selective absorber has been chosen to complete the multi-layered design. This type of coating has previously demonstrated good potential as selective absorber and additional very high resistance to oxidation – even at very high temperatures.

Simulation of the new four-layered absorber stack is carried out based on the optical constants of each contributing layer. The  $n$  and  $k$  of vanadium dioxide sputtered films have been previously determined by FTIR ellipsometry.  $n$  and  $k$  for the Al substrate and absorber are taken from literature. The  $n$  and  $k$  for SiO<sub>2</sub> top coating are determined by visible ellipsometry measurements.

**Further details available in the Confidential Appendix. The corresponding section of the Confidential Appendix contains unpublished data based on which publications are envisaged.**



### B3.2. Optimization of the deposition parameters for sputtered selective absorber coating.

In order to deposit good quality absorber films, the working sputter parameters are determined. The right target composition, power applied to the target, oxygen flux and the deposition temperature are studied.

**Further details available in the Confidential Appendix. The corresponding section of the Confidential Appendix contains unpublished data based on which publications are envisaged.**

### B3.3. Optical and structural characterization of the sputtered selective absorber coating.

Samples deposited at high temperatures (300°C and 600°C) differed from the samples sputtered at room temperature. It is likely that a different phase is formed at higher temperatures.

**Further details available in the Confidential Appendix. The corresponding section of the Confidential Appendix contains unpublished data based on which publications are envisaged.**

### B3.4. Optical characterization of the deposited multi-layered stacks.

Once good quality selective absorber layer has been obtained, the deposition of the full multi-layered absorber stack was done according to the simulation results. The FTIR reflectance measurements, show that the deposited multi-layered stack behaves very similar to the simulated one in the room temperature state.

**Further details available in the Confidential Appendix. The corresponding section of the Confidential Appendix contains unpublished data based on which publications are envisaged.**

## C. Alternative thermochromic materials

### C1. Deposition of alternative thermochromic oxide films

**Further details available in the Confidential Appendix. The corresponding section of the Confidential Appendix contains unpublished data based on which publications are envisaged.**

### C2. Characterization of the alternative thermochromic oxide films

**Further details available in the Confidential Appendix. The corresponding section of the Confidential Appendix contains unpublished data based on which publications are envisaged.**



## D. Application scouting

Extensive literature study resulted in novel ideas and new concepts have been proposed. Applications of thermochromic thin films in various fields are explored.

### D1. Applications in the field of solar thermal collectors

In 2015, Viessmann has announced their new line of solar thermal collector based on thermochromic thin film technology. Using pure vanadium dioxide (emissivity switch at  $\sim 68^{\circ}\text{C}$ ), it is possible to keep the absorber temperature below  $150^{\circ}\text{C}$ , which at 3 bar pressure in the system is enough to avoid the evaporation of the heat transfer fluid and the degradation of glycol components. A decrease in stagnation time of more than 70% has been also reported.

Therefore, the concept of thermochromic absorber technology has been proven efficient at full collector scale. The EPFL developed smart absorbers have the added benefit of Ge doping which not only raises the transition temperature to above  $90^{\circ}\text{C}$ , but in the same time increases the switch in thermal emissivity.

In 2017, an important contact with a European industrial solar absorber manufacturer has been established. The company manufactures thermal collectors with the highest energy efficiency on the market currently. A sample exchange has been initiated and EPFL developed thermochromic films have been deposited on the commercially used substrates. The company's selective absorber coating will be then deposited on the samples.

### D2. Applications in the field of smart building envelopes

Thermochromic technologies have already impacted the building sector with the advance of vanadium dioxide based smart windows. Due to its considerable emissivity change in the thermal spectral range, vanadium dioxide based films could be deployed in a variety of other applications, e.g. for thermal regulation of roofs or building envelopes. With doping, the temperature ranges over which the emissivity changes occur can easily be adjusted (both for low and high temperature applications).

### D3. Applications in the field of photovoltaics

Multilayers of metal oxides have been deposited on top of CIGS photovoltaic cells. Hereby, the PV cells were not damaged, and their function was maintained. In principle, our thin film deposition processes can thus be compatible with PV technology. However, for PV modules, a maximum solar transmittance and a low operation temperature are desired in most cases. The situations are rare when a thermochromic switching really contributes a major advantage. One probable application could be the use of thermochromic markers for PV modules. In this case, the recent findings on visible thermochromism could be explored.



#### D4. Applications in the field of automotive mobility

As in buildings, radiative thermochromic films for temperature regulation purposes could be employed in the automotive sector for trains or cars (windows and shields). Furthermore, visible thermochromism could have useful applications as markers on motor components.

Thermochromic coatings might become an advantage when mobility shifts to electric traction. Then, waste heat from the motor will no longer be available, and the thermal properties of the envelope become more important. In the cold season, the thermal emissivity of the vehicle body should be low, and in the hot season, the thermal emissivity of the vehicle body should be high, very much like the thermochromic absorber of a solar thermal collector. Such a thermochromic car body could be combined with thermochromic glazing, which allows for high solar gains in winter, and low solar gains in summer. Therefore, applications of thermochromic films can be envisaged for both vehicle envelope and glazing. Thin layers of vanadium dioxide can be deposited on solid or flexible surfaces alike.

Flexible solar cells can be used for vehicle-integrated photovoltaics, which might also become more important when mobility shifts to electric traction. We deposited multilayers of metal oxides on top of flexible photovoltaic cells. The PV cells were not damaged, and their function was maintained.

#### D5. Applications in the field of microelectronics

The fast and reversible semiconductor-to-metal transition (SMT) makes  $\text{VO}_2$  an attractive material for microelectronic applications. The elevated transition temperature of  $\sim 95^\circ\text{C}$  reached by Ge doping, has the potential to advance even more the use of vanadium dioxide thin films in electronic device applications - where higher critical temperatures than  $68^\circ\text{C}$  of pristine  $\text{VO}_2$  are needed. A large variety of  $\text{VO}_2$  based microelectronics devices have been studied recently.

A new principle has been proposed and validated in coplanar waveguide (CPW) bandstop filter tuning [Cas18-2]. The tunable filter is fabricated on a high-resistivity silicon substrate based on a CMOS compatible technology using a  $1\ \mu\text{m} \times 10\ \mu\text{m}$  long and 300 nm thick vanadium dioxide ( $\text{VO}_2$ ) switch by exploiting its insulator to metal transition. The filter is designed to work in Ka band with tunable central frequencies ranging from 28.2 GHz to 35 GHz.

A phase-change tunnel field-effect transistor (PC-TFET) has been proposed as a hybrid design integration of a tunnel FET and a 2-terminal SMT switch. Combining the strengths of the two devices results in the first solid-state  $\text{VO}_2$ -based 3-terminal switch with simultaneous very low  $I_{\text{OFF}}$  current, high  $I_{\text{ON}}/I_{\text{OFF}}$  ratio and ultra-steep subthreshold swing, a performance that cannot be individually achieved by a tunnel field-effect transistor or a MIT switch [Vit17].

With the advent of 2D materials, thin van der Waals (vdW) heterostructures can be made based on a large diversity of materials. The vdW  $\text{MoS}_2/\text{VO}_2$  heterojunction combines the excellent blocking capability of an n-n junction with a high conductivity in on-state, and it can be turned into a Schottky rectifier at high applied voltage or at raised temperature [Oli17]. Furthermore, a tunable photosensitivity and excellent junction photoresponse in the 500/650 nm wavelength range have been obtained. For the first time, a field-effect transistor has been obtained from gated  $\text{MoS}_2/\text{VO}_2$  heterojunctions. The electrostatic doping effect of the gate on the junction results in a subthreshold slope (SS) of 130 mV/dec at room temperature,  $I_{\text{ON}}/I_{\text{OFF}} > 10^3$  and  $I_{\text{OFF}} < 5\ \text{pA}/\mu\text{m}$  at  $V_{\text{D}}=1.5\text{V}$ .



## 5 Discussion of results

For the pure thermochromic material, the transition temperature of 68°C is relatively low and should be increased to approximately 95°C. Using a novel type of Ge doping, we showed and confirmed that it is possible to significantly increase the transition temperature of pure vanadium dioxide films. A ~95°C transition temperature is reached with ~5.9 at.% Ge. By previous computer simulations it could be estimated that the energy losses due to the mismatch of the transition temperature are around 14%. Furthermore, Ge doping is shown to have the added benefit of increasing the thermal emittance of the switching films when in the high temperature state implying a better radiation of the excess heat to the surroundings. Above the critical transition temperature, when the thermochromic film is in its metallic state, the thermal emittance of vanadium dioxide films is angle dependent and it increases with the angle from normal incidence. Again this translates in a better heat dissipation than what the normal incidence measurements predict.

Germanium is not a rare element and is also not known to be toxic. Commercially, germanium is obtained as a byproduct of metal refining and from coal ashes. At the high purity levels required for the thermochromic thin film applications, metallic V and Ge prices are fairly close and the overall production cost is not sensitive with regards to the dopant concentration of the films.

## 6 Conclusions and outlook

Within this project, significant progress has been made in the field of thermochromic solar collectors. All project goals have been achieved.

Our thermochromic solar absorber coatings are inorganic, selective, and show a perfectly reversible phase transition at a critical temperature implying a considerable change of the thermal emissivity. The switch in thermal emissivity is expected to limit the temperature of the absorber to values below the degradation temperature of glycols (160°C-170°C).

- Using a novel type of Ge doping, we showed and confirmed that it is possible to increase the transition temperature. A ~95°C transition temperature is reached with ~5.9 at.% Ge.
- Furthermore, we show that Ge doping has the added benefit of increasing the thermal emittance modulation of the switching films.
- In the high temperature state, the thermal emittance of vanadium dioxide films is angle dependent and it increases with the angle from normal incidence.
- Si doping is also increasing the transition temperature of vanadium dioxide phase transition. However, film amorphization arises already at rather low dopant concentrations.
- Very thin films of only 30 nm thickness with very good electrical switching have been obtained. Thin switching films are important in multi-layered coating designs.
- Full multi-layered absorber coating has been simulated based on n and k optical constants of the constituting individual layers. A multi-layered design, with a solar absorptance,  $\alpha$  ~97% and thermal emittance,  $\epsilon$  ~6% has been selected.



- The sputter parameters for the used selective absorber coating were optimized.
- Finally, important contacts with industry and theoretical physicists have been established.

These scientific findings open up new perspectives for the future of smart materials for solar thermal collectors.

## 6.1 Next steps after end of project

The main goal of this project TARGET95 – reaching a transition temperature of around 95°C – has been achieved through Ge doping. Once the basic principle and the effects of Ge doping are proven, industrial implementation of Ge doping constitutes the new challenge. Doping at a large scale could be relatively easy to implement when starting from alloy sputter targets. Furthermore, steps should be taken towards the employment of room temperature processes instead of the high temperature deposition. Post-annealing of thermochromic films should be studied in depth, in order to determine whether this could be a cheaper industrial alternative for obtaining switching crystalline films.



## 7 Publications

### In peer-reviewed journals:

- [Cas18] E.A. Casu, N. Oliva, M. Cavaliere, A. Müller, A. Fumarola, W.A. Vitale, A. Krammer, A. Schüller, M. Fernandez-Bolanos, A.M. Ionescu. **Tunable RF phase shifters based on Vanadium Dioxide metal insulator transition**, in IEEE Journal of the Electron Devices Society, 2018. DOI: 10.1109/JEDS.2018.2837869
- [Cas18-2] E.A. Casu, A. Muller, M. Fernandez-Bolanos, A. Fumarola, A. Krammer, A. Schuler, A.M. Ionescu, **Vanadium Oxide Bandstop Tunable Filter for Ka Frequency Bands Based on a Novel Reconfigurable Spiral Shape Defected Ground Plane CPW** in IEEE Access 6, Pages 12206-12212, 2018. DOI: 10.1109/ACCESS.2018.2795463
- [Kra17] A. Krammer, A. Magrez, W. A. Vitale, P. Mocny, P. Jeanneret, E. Guibert, H. J. Whitlow, A. M. Ionescu, A. Schüller. **Elevated transition temperature in Ge doped VO<sub>2</sub> thin films**, in Journal of Applied Physics 122, 045304, 2017. DOI: 10.1063/1.4995965
- [Vit17] W. A. Vitale, E. A. Casu, A. Biswas, T. Rosca, C. Alper, A. Krammer, G. V. Luong, Q.-T. Zhao, S. Mantl, A. Schüller, A. M. Ionescu. **A Steep-Slope Transistor Combining Phase-Change and Band-to-Band-Tunneling to Achieve a sub-Unity Body Factor**, in Scientific Reports 7, 355, 2017. DOI: 10.1038/s41598-017-00359-6
- [Oli17] N. Oliva, E. A. Casu, C. Yan, A. Krammer, T. Rosca, A. Magrez, I. Stolichnov, A. Schüller, O. J. F. Martin, A. M. Ionescu. **Van der Waals MoS<sub>2</sub>/VO<sub>2</sub> heterostructure junction with tunable rectifier behavior and efficient photoresponse**, in Scientific Reports 7, 14250, 2017. DOI: 10.1038/s41598-017-12950-y
- [Vit16] W. A. Vitale, L. Petit, C. F. Moldovan, M. Fernández-Bolaños and A. Paone et al. **Electrothermal actuation of vanadium dioxide for tunable capacitors and microwave filters with integrated microheaters**, in Sensors & Actuators: A. Physical, 2016.
- [Vit15] W. A. Vitale, C. F. Moldovan, A. Paone, A. Schüller and A. M. Ionescu. **Fabrication of CMOS-compatible abrupt electronic switches based on vanadium dioxide**, in Microelectronic Engineering, vol. 145, p. 117-119, 2015.

### In conference proceedings:

- [Oli18] N. Oliva, E.A. Casu, C. Yan, A. Krammer, A. Magrez, A. Schueler, O.J.F. Martin, A.M. Ionescu. **MoS<sub>2</sub>/VO<sub>2</sub> vdW heterojunction devices: Tunable rectifiers, photodiodes and field effect transistors** in Technical Digest - International Electron Devices Meeting IEDM, Pages 36.1.1-36.1.4, 2018. DOI: 10.1109/IEDM.2017.8268503



- [Kra17-2] A. Krammer, F. T. Demièrre, A. Schüler. **Infrared optical properties of doped and pure thermochromic coatings for solar thermal absorbers**, in ISES Solar World Congress and Solar Heating and Cooling Conference 2017. DOI: 10.18086/swc.2017.17.04
- [Kra17-3] A. Krammer, O. Bouvard, A. Schüler. **Study of Si doped VO<sub>2</sub> thin films for solar thermal applications**, in Energy Procedia 122, 745-750, 2017. DOI: 10.1016/j.egypro.2017.07.390
- [Cas17] E. A. Casu , W. A. Vitale , M. Tamagnone, M. Maqueda Lopez , N. Oliva , A.Krammer, A. Schüler , M. Fernández-Bolaños , A. M. Ionescu. **Shunt capacitive switches based on VO<sub>2</sub> metal insulator transition for RF phase shifter applications**, at the 47th European Solid-State Device Research Conference (ESSDERC), 2017. DOI: 10.1109/ESSDERC.2017.8066634
- [Kra16] A. Krammer, A. Gremaud, O. Bouvard, R. Sanjines, A. Schüler, *Surf. Interface Anal.* **48**, 440–444 (2016).
- [Cas16] E. A. Casu, W. A. Vitale, N. Oliva, T. Rosca, A. Biswas, C. Alper, A. Krammer, G.V. Luong, Q.T. Zhao, S. Mantl, A. Schüler, A. Seabaugh, A.M. Ionescu. **Hybrid phase-change - Tunnel FET (PC-TFET) switch with subthreshold swing < 10mV/decade and sub-0.1 body factor: Digital and analog benchmarking**, in Technical Digest - International Electron Devices Meeting, IEDM (p. 19.3.1-19.3.4). Institute of Electrical and Electronics Engineers Inc, 2016. DOI: 10.1109/IEDM.2016.7838452

### Oral presentations:

A. Krammer. *Infrared optical properties of doped and pure thermochromic coatings for solar thermal absorbers*, at ISES Solar World Congress and Solar Heating and Cooling Conference 2017.

A. Krammer. *Solar thermal collectors: Doped VO<sub>2</sub> based smart absorbers*, at "Future Buildings and Districts - Energy Efficiency from Nano to Urban Scale" CISBAT Conference 2017.

A. Krammer, *Doped VO<sub>2</sub> thermochromic coatings for overheating protection in solar thermal collectors*, Master defence, October 21<sup>st</sup>, 2015, Technical university of Darmstadt , Germany.

A. Krammer, *Doped VO<sub>2</sub> thermochromic thin films for overheating protection in solar thermal collectors*, 7<sup>th</sup> EMMI/FAME Master Research Workshop, July 19<sup>th</sup> - 21<sup>st</sup>, 2015, Aveiro, Portugal.

### Poster presentations:

A. Krammer. *Effect of Si doping on the transition temperature and electronic properties of vanadium dioxide thin films*. Science and Applications of Thin Films (SATF), Conference & Exhibition, Izmir 2016.

A. Krammer. *In situ photoelectron spectroscopic characterization of reactively sputtered, doped vanadium oxide thin films*, European Conference on Applications of Surface and Interface Analysis (ECASIA), Granada 2015



### Invited talks:

- A. Schüler, *Gläserne Zukunft*, Forum Energie Zürich, 10 April 2018, Zürich, Switzerland
- A. Schüler, *Dynamisch und energieeffizient: Innovatives Architekturglas*, IGE-Planerseminar, 21 March 2018, Hochschule Luzern, Switzerland
- A. Schüler, *Wärmeschutzfenster mit hoher Durchlässigkeit für Mobilkommunikation: Grundlagen und Leistungseigenschaften*, 30 January 2018, Energieforum Lausanne, Switzerland
- A. Schüler, *Nouveaux vitrages solaires: de la lame de microscope à la plus grande façade photovoltaïque au monde*, conférence zéro carbone, 16 November 2017, Fribourg, Switzerland
- A. Schüler, *Kromatix : from the microscope slide to the world's largest solar façade*, 6-8 September CISBAT 2017 International Conference, Future Buildings & Districts, Energy Efficiency from Nano to Urban Scale, Lausanne
- A. Schüler, *Innovative optical coatings for active and passive solar glass façades*, Power Electronics for Plasma Engineering, 16-18 May 2017, Zielonka, Poland
- A. Schüler, *Selective solar absorber coatings on receiver tubes for CSP: From vacuum-deposited carbon based coatings to wet-chemical derived mixed oxide coatings*, 17-21 April 2017, MRS spring meeting, Symposium ES9 - Surfaces, Coatings and Interfaces in Concentrated Solar Energy Applications, Phoenix, USA
- A. Schüler, *Highlights from research on novel materials for dynamic solar heat gains*, Peak Session SCCER FEEB&D, 9 February 2017, Morat, Switzerland
- A. Schüler, *Innovative glazing with dynamic solar heat gains*, SCCER FEEB&D Final Session 14 October 2016, Empa Dübendorf, Switzerland
- A. Schüler, *Innovative glazing with dynamic solar heat gains*, 12th Conference on Advanced Building Skins, 2-3 October 2017, Bern, Switzerland
- A. Schüler, *Nanocomposite optical coatings for solar energy applications*, Conference on Science and Applications of thin Films, 19-23 September, Cesme, Turkey
- A. Schüler, *Smart Materials for Energy-Efficient Glazed Façades*, ENGINEERED SKINS 2016, 1st September, University of Cambridge, UK
- A. Schüler, *Nanocomposite optical coatings for solar energy applications*, Swiss Nano Convention 2016, 30 June – 1 July 2016, Basel, Switzerland
- A. Schüler, *Dynamisches Glas: Wie sieht das Fenster 2020/2035 aus?*, 2. Fachkongress Energie + Bauen, 27.5.2016, St. Gallen, Switzerland
- A. Schüler, Olivia Bouvard, André Kostro, (LESO-PB, EPFL), *Solar protection control scenarios*, invited talk, October 23<sup>rd</sup>, 2015, SCCER, Future Energy Efficient Buildings & Districts, Midterm Session 2015, EMPA Dübendorf, Switzerland



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