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Thermochromic coatings for overheating protection of solar collectors – temperature matching and triggering

(Thermochromie III)

Mandant:

Office fédéral de l’énergie OFEN
Programme de recherche XY
CH-3003 Berne
www.ofen.admin.ch

Mandataire:

Ecole Polytechnique Fédérale de Lausanne EPFL
Laboratoire d’Energie Solaire et de Physique du Bâtiment
LESO-PB
http://leso.eplf.ch/nano_solaire

Auteurs:

Dr. Antonio Paone, EPFL/LESO-PB, antonio.paone@epfl.ch
Olivia Bouvard, EPFL/LESO-PB, olivia.bouvard@epfl.ch
Mario Geiger, EPFL/LESO-PB, mario.geiger@epfl.ch
Dr. Andreas Schüler, EPFL/LESO-PB, andreas.schueler@epfl.ch

Responsable de domaine de l’OFEN: Andreas Eckmanns
Chef du programme de l’OFEN: Jean-Christophe Hadorn
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Summary

Overheating and the resulting stagnation of solar thermal collectors is a common problem even in central European latitudes. The high temperatures occurring during stagnation lead to water evaporation, glycol degradation and stresses in the collector with increasing vapour pressure. Special precautions are necessary to release this pressure; only mechanical solutions exist nowadays. Additionally, the elevated temperatures lead to degradation of the materials that compose the collector, such as sealing, thermal insulation and the selective absorber coating. The goal of this project is to find a new way of protecting solar thermal systems without any mechanical device (e.g. for shading or for pressure release). Novel thermochromic coatings are developed, which exhibit a change in optical properties at a critical temperature T_c.

Undoped, tungsten and aluminum doped samples of inorganic coatings showing thermochromic switching behaviour are produced by magnetron sputtering. A dynamical switching of the thermal emittance ε can be achieved by thermochromic transition metal oxides.

The effects of doping thermochromic oxide films by tungsten or aluminium, respectively, have been studied in great detail. The structural and optical properties of these films have been characterized in by methods such as X-ray diffraction (XRD) for phase identification, and Rutherford backscattering spectrometry (RBS) for determining the doping concentration.

The performance of a solar collector with an absorber based on a thermochromic film has been simulated in order to determine the stagnation temperature and the produced energy as a function of the thermochromic transition temperature.

In parallel, the possibility of using the switch in emissivity of the absorber coating in order to trigger the transition of a thermochromic or thermotropic coating on the glazing of the solar collector has been studied. In a first step, an analytical approach yielded the required transition temperature of such a switching glazing. Subsequently, the availability of thermotropic glass and other kind of smart glass have been studied. Samples of identified commercial products were characterised to know their optical properties and define if they would be suitable for our application.

The fascinating optical properties of these switchable films elucidate the way towards novel “intelligent” thermal solar collector materials.

Project Goals

The main objective of this project is to limit the stagnation temperature of solar collectors to a value below the boiling point of the heat transfer liquid without degrading the optical performance of the selective coating during normal operation.

Advantages:

- Evaporation of the heat transfer liquid due to overheating will be avoided and the hydraulic system can be simplified.
- The lifetime of the collector materials used for thermal insulation, the joints and the selective coating itself will increase.
- The glycol component of the heat transfer liquid will be protected from degradation.

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 α should correspond to 95% and the thermal emittance ε to maximum 5%. The solar collector suffers overheating connected problems and resulting stagnation above the transition temperature. In this temperature range, the input of solar energy has to be reduced. Therefore, the solar absorptance α should correspond to 35% and the thermal emittance ε to above 40%.

Since we have already shown that the durability of organic thermochromic paints is not high enough for the considered application [Huo08], we focus on inorganic materials in this project: thermochromic transition metal oxides.

Project Goals 2013

A. Effect of doping

- Structural investigation by X-ray diffraction (XRD) of undoped and doped by tungsten or by aluminium thermochromic films.
- Chemical investigation by Rutherford backscattering spectrometry (RBS) of undoped and doped by tungsten or by aluminium thermochromic films.

B. Computer simulations of solar thermal energy systems

- Calculations for the estimation of the stagnation temperature of a thermal solar collector adopting a thermochromic coating.
- Determination of the produced energy as a function of the thermochromic transition temperature.

C. Thermal coupling of coating on absorber sheet and glazing

- Modelling heat transfer between solar absorber and specific glazing. Determination of suitable switching temperature.

D. Switchable glazing: Market analysis and characterisation

- Market analysis on dynamic glazing. Identification of manufacturers and distributors. Study of the availability of thermotropic glazing.
- Characterisation of existing products: thermotropic glass and alternative product, e.g. switchable mirror.

Approach

A. Film characterization of doped individual layers

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.
Undoped coatings switch from semiconducting to metallic state at critical temperatures around 68°C.
The transition temperature of these doped films can be altered by suitable doping. Doped thermochromic metal oxide films are deposited by reactive magnetron co-sputtering of metallic targets in argon/oxygen atmosphere.
In order to verify whether the desired thermochromic crystalline phase is obtained, structural analyses of the deposited films are performed by X-ray diffraction (XRD).
Chemical analyses of the deposited films are performed by Rutherford backscattering spectrometry (RBS). The RBS technique allows us to determine precisely the respective atom concentrations of the elements present in the film.

B. Computer simulations of solar thermal energy systems

The optical properties of thermochromic transition metal oxide films for both the low and the high temperature state are inferred by spectroscopic ellipsometry in the VIS-MIR spectral range. These data can be used as basis for computer simulations predicting the solar absorptance and the thermal emittance on an aluminium substrate. The stagnation temperature of a collector adopting as absorber a thermochromic film doped by tungsten deposited on an aluminium substrate is determined using appropriate physical models [Bal08, Vries98, Zon03].
Using the solar absorptance and the thermal emittance determined for our thermochromic solar absorber coatings, the produced energy as a function of the thermochromic transition temperature was determined by PolySun simulations.

C. Thermal coupling of coating on absorber sheet and glazing

In order to further increase the switch in absorptance of the solar collector, it was investigated whether the emittance switch of the thermochromic absorber could trigger the transition of a thermotropic or thermochromic coating on the solar collector glazing.

The heat transfer from the absorber sheet to the glazing is simulated by a finite element approach or directly calculated by an analytical nodal model based on the equivalent electric circuit.

D. Switchable glazing : Market analysis and characterisation

In section C the thermal coupling between the absorber sheet and the glazing is studied. With its change in emissivity, the absorber could trigger the transition of a dynamic glazing such as a thermotropic or thermochromic one.

A study of the commercially available products is performed. Different sources are investigated: market studies and forecasts on smart glass, scientific literature on tested products, companies identified from patents and internet search.

Main manufacturers are stated and samples of identified products are obtained. Characterisations are performed in order to measure transmittance and reflectance in both states. The considered products exhibit a transition of their state implying a change of their optical properties. The aim here is to determine whether the current available products would meet our needs.

Description of Work and Results

A. Film characterization of doped individual layers

A.1. XRD analysis of doped and undoped thermochromic oxide coatings for phase purity confirmation

Structural information was gathered by X-ray diffraction (XRD) of thermochromic samples. Data are shown in Fig. 1 (a-b). Only the best switching films were analyzed by XRD. Fig. 1 shows data obtained from VO_2:W and Fig. 2 data obtained from VO_2:Al.

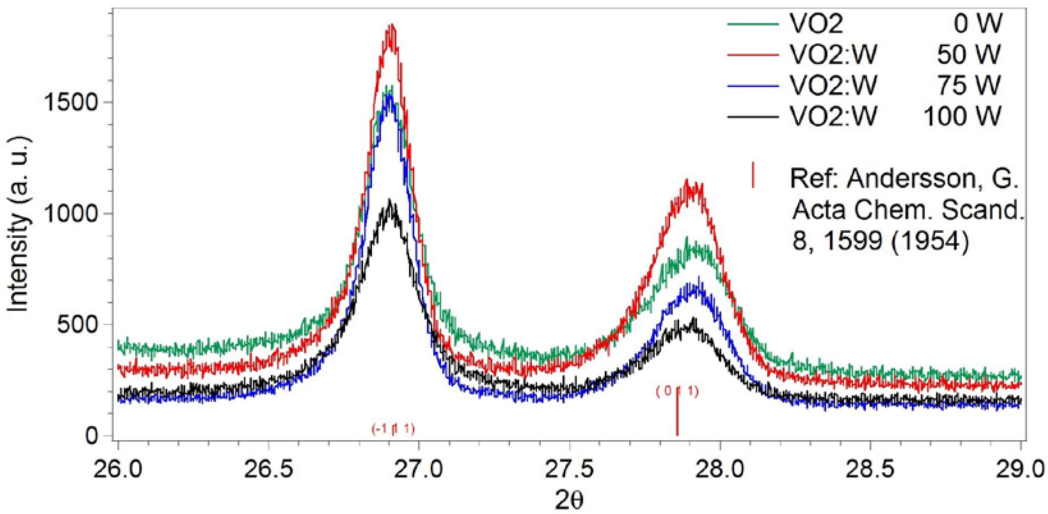


Fig. 1: XRD analysis of undoped-VO_2 and VO_2:W films. In the legend is reported the RF power (in Watt) applied to the tungsten target.

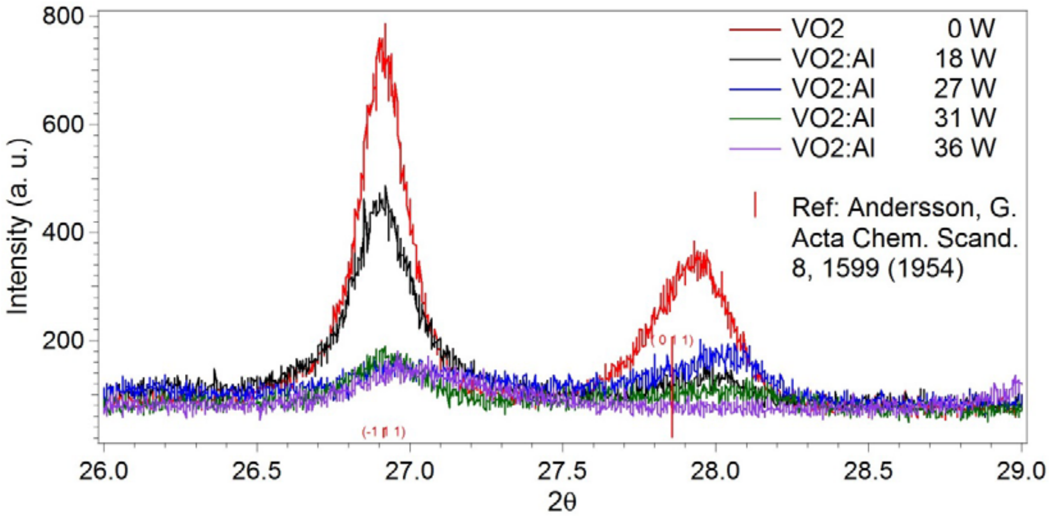


Fig. 2: XRD analysis of undoped-VO_2 and VO_2:Al films. In the legend is reported the RF power (in Watt) applied to the aluminum target.

The analyzed films were deposited on silicon wafers (100). The observed XRD pattern shows a correspondence with the powder diffraction data of some crystal lattice planes ([-1,1,1], [0,1,1]) of VO_2 reported in the literature [And54]. Films are well crystallized. The absence of the other peaks suggests preferential orientation of crystallites. Applying the Scherrer's formula [Cul78], a grain size of 27 nm can be estimated for VO_2.

Aluminium doping makes thermochromic films loosing their special peculiarity of the semiconductor-to-metal transition. This is explained by a progressive amorphization of the film with increasing the aluminium doping. This is confirmed by the XRD results shown in Fig. 2. A progressive amorphization of VO_2:Al films occurs by increasing the aluminum doping because the intensities of these peaks decrease. A similar effect, occurs by excessive tungsten doping (see Fig. 1).

In order to improve the film crystallization and to avoid amorphization the deposition temperature could be increased. Alternative approaches to deposit aluminium doped thermochromic films exist [Pao12].

Futhermore, literature [Goo71] suggests other suitable dopants to raise the transition temperature such as chrome and germanium.

A.2. Rutherford backscattering Spectroscopy (RBS) analysis of the thermochromic transition metal oxide films for a highly accurate measurement of the film thickness and the chemical composition (doping concentration)

In Rutherford backscattering spectrometry (RBS), a sample is exposed to a beam of high energy ions. The energy of the backscattered ions allows to infer the chemical composition and the thickness of a thin film deposited on a substrate. This analysis was performed in order to quantitatively investigate the doping in the VO_2:W and VO_2:Al film deposited by RF-reactive magnetron co-sputtering.

RBS analyses of VO_2:W films produced at LESO-PB were performed at IMA-Arc (Institute of Applied Microtechnologies - La Chaux-de-Fonds) under the supervision of Dr. P. Jeanneret.

Three VO_2:W samples which show the thermochromic transition between 68°C and 49.5°C were investigated. By means of a Van der Graaff generator, a 2 MeV He^{++} beam was generated. The scattered ions were detected with charge-sensitive “surface barrier” detectors. RBS in single shoot mode was performed on these samples. Experimental data are summarized in Tab. 1, where the power applied on the tungsten target, the film thickness and the average atomic concentration of tungsten in the thermochromic films are respectively given (relative error ± 5% at.%).

Power applied on the tungsten target (Watt)	Thickness (nm)	Tungsten (at.%)
50 W	359	0.04
75 W	365	0.12
100 W	368	0.35

Table 1: Power applied on the tungsten target, film thickness and average atomic concentration of W.

The doping concentration is inferred homogenous and reproducible. These films were deposited on a monocrystalline silicon wafer.

A bilayer model was used in order to consider a possible variation in the doping concentration into the films. This model did not improve considerably the fit. In the RBS analysis, a slight gradient in the tungsten doping is evidenced. A higher W-doping appears at the interface between the Si substrate and the VO_2:W film.

As for the results of the chemical analyses of the thermochromic film deposited by thermal evaporation in 2010, these findings suggest that tungsten doping of our VO_2 films is more effective (doping efficiency of -55°C/at.% ± 12%) than previously reported in literature (doping efficiency of -23°C/at.%) [Sol06]. Instead of occupying the sites in the crystal lattice where they contribute to lowering the transition temperature, most of the tungsten atoms might segregate into an eventual second tungsten-rich phase.

The atomic concentrations of Al was estimates less than 2% in every VO_2:Al film. A precise quantitative determination of this doping is not possible by RBS analyses due to the detection limits of this technique. By RBS, a heavier dopant into a lighter matrix can be more precisely determined instead of a lighter element into a heavier matrix because the probability of interaction between the dopant and the ions of the beam is related to their atomic masses.

B. Computer simulations of solar thermal energy systems

B.1. Stagnation temperature of a collector adopting a switching thermochromic absorber

The optical properties of a thermochromic transition metal oxide film for both low and high temperature states have been previously inferred by spectroscopic ellipsometry in the VIS-MIR spectral range. These data are used as basis for computer simulations predicting solar absorptance and the thermal emittance on an aluminium substrate.

The model of the solar collector which was adopted for this simulation is reported in Fig. 3 (a). In Fig. 3 (b), the stagnation temperature for a thermochromic film mixed with a 40% volume fraction of SiO_2 is reported. This figure clearly shows the doped thermochromic film becomes highly emissive in the metallic state. The thermal emittance is depending on the aluminium substrate at low temperature and on the metallic state of the thermochromic film after switching. The optimum layer thickness has been identified. The emittance is evaluated by integration of the absorbance spectra weighted with the thermal spectrum of a black body at 100°C. This integration was performed in the range from 2000 to 20000 nm.

Baldi *et al.* [Bal08] calculated this stagnation map on the method described by de Vries [Vries98] and Zondag *et al.* [Zon03]. They considered the absorber as a single layer without taking into account the substrate. A solar absorptance of about 0.75 was obtained in the semiconducting state by using the thermochromic film mixed with a 40% volume fraction of SiO_2. The absorbance increase in the metallic state is not negligible. A solar absorptance of about 0.86 was obtained in the metallic state.

The glycols used in solar thermal collectors start to degrade above 170°C, the use of this coating as solar absorber lowers the stagnation temperature below this critical point. In this simulation the antireflective coating of SiO_2 was not considered.

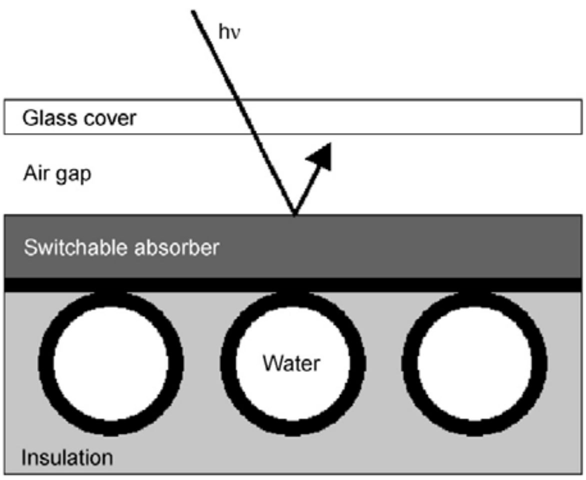


Fig. 3 (a): Model of the solar collector.

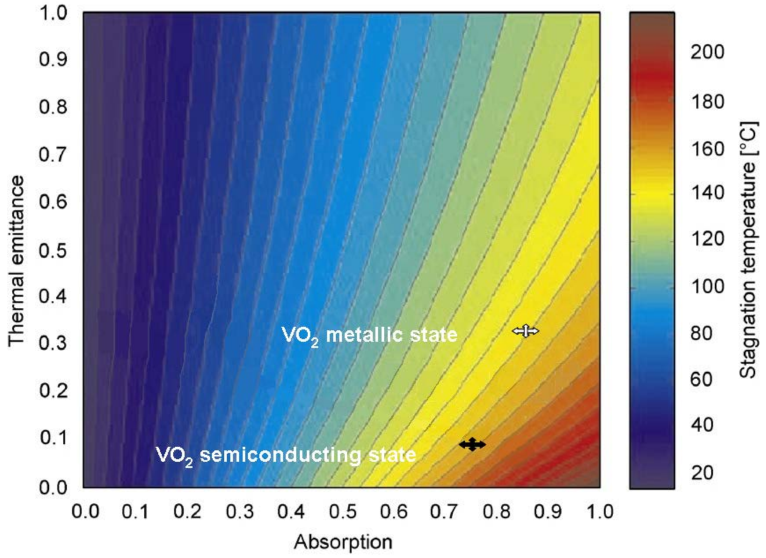


Fig. 3 (b): Stagnation temperature map as a function of solar absorptance and thermal emittance of a VO_2 based absorber of the model of the solar collector showed in [Bal08]. The arrows indicate the stagnation temperature for a thermochromic film mixed with a 40% volume fraction of SiO_2, both in the metallic (white arrows) and semiconducting (black arrows) states.

B.2. Determination of the produced energy as a function of the thermochromic transition temperature

In order to evaluate the influence of the switching temperature of a thermochromic absorber on the total energy produced by a dynamic collector, a thermal system including the COBRA Soltop panel was considered. The loss of energy due to two switching temperatures, 68°C and 95°C, was estimated in the "worst case scenario" considering an ideally perfect thermochromic absorber with a solar absorption switching from 95% to 0%.

The maximum daily temperature of the COBRA Soltop collector was determined by PolySun simulations according to the requirements summarized in the following figure:

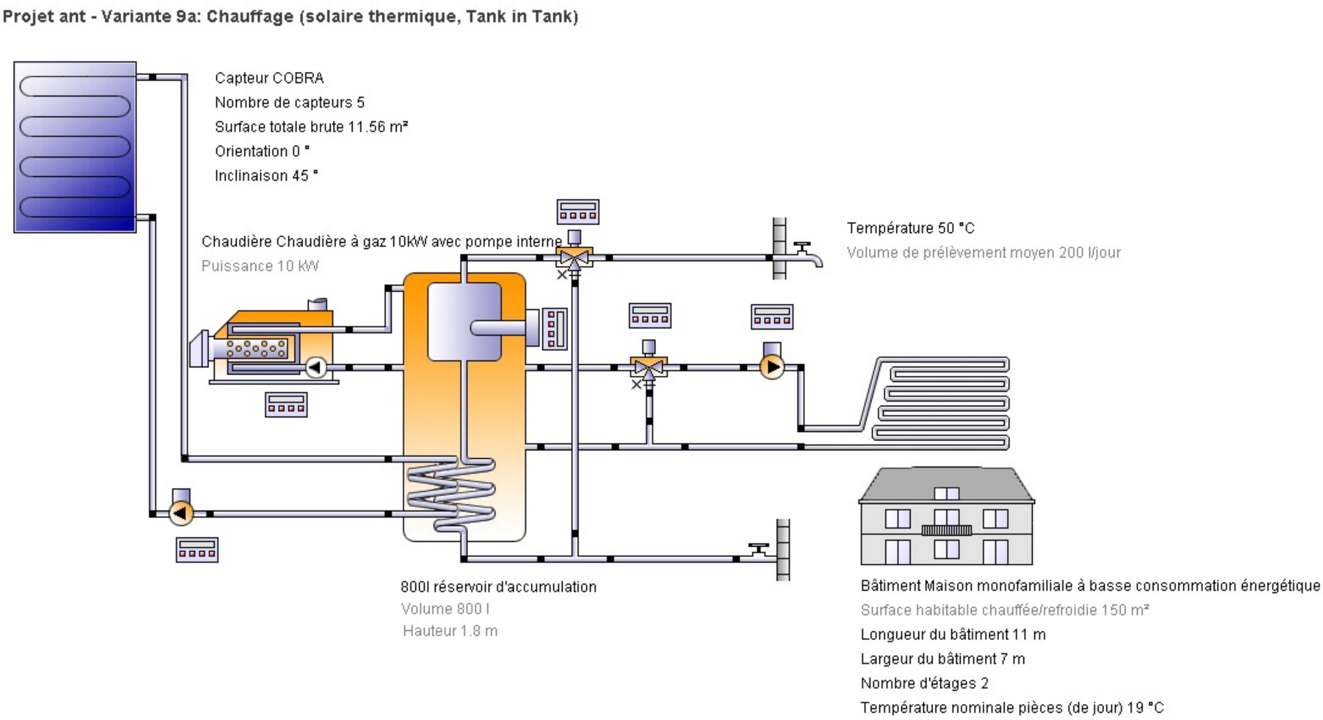
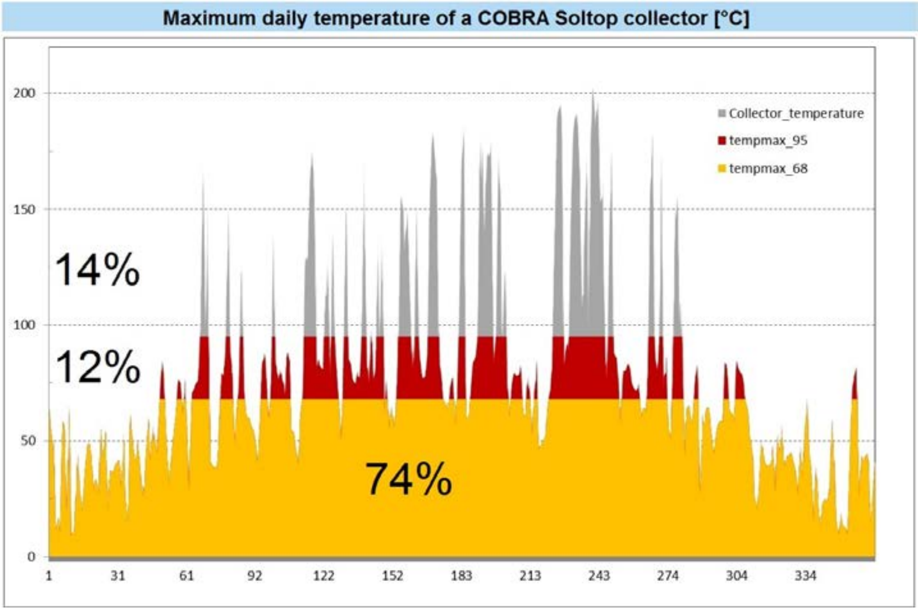


Fig. 4 (a): Thermal installation located in Lausanne. 5 solar panels COBRA type were simulated in combination with a 10 kW gas boiler in order to provide 200 l/day at 50°C for domestic use and to heat a 150 m^2 residential building.

COBRA : total collector output : 4496 kWh



$$\alpha = 0.99$$
$$\varepsilon = 0.01$$

(b)

Fig. 4 (b): The maximum daily temperature of a COBRA Soltop collector. The yellow and the red area represent the energy produced when the temperature of the absorber is respectively below 68°C and between 68°C and 95°C.

The thermal installation is located in Lausanne. Fig. 4 (b) shows the performance of this collector. The yellow, the red and the grey area indicate respectively the energy produced by the absorber when its temperature is below 68°C, between 68°C and 95°C, and above 95°C.

In Fig. 4 (b), the solar absorption and the thermal emittance of the simulated absorber are written on the right side of the figure.

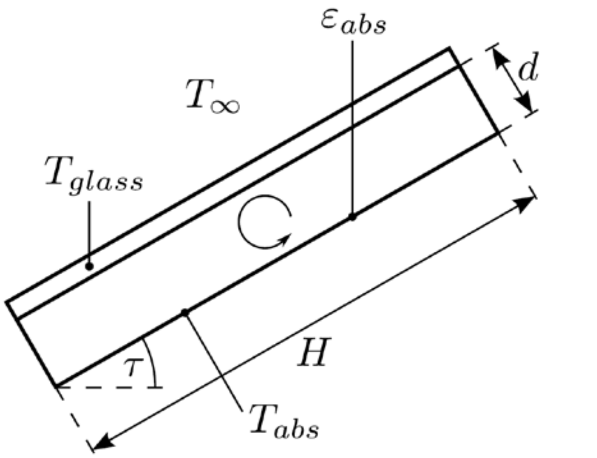
If a hypothetic thermochromic absorber with a solar absorptance α switching between 95% and 0% would be used instead of a static absorber, the produced energy depends on the switching temperature, T_C. Such a thermochromic solar absorber would lower the stagnation temperature below the critical degradation temperature of the glycols (170°C), and also below the temperature of water evaporation (100°C).

The thermal energy which would be transferred to the thermal energy system corresponds to either the yellow area of Fig. 4 (b) (for T_C = 68°C) or to the red + yellow area (for T_C = 95°C). The yellow, the red + yellow and the grey areas comprise respectively 74%, 86% and 14% of the total area. Using such thermochromic absorber with a complete switch in the solar absorptance and a transition temperature of 68°C, 12% of the total energy would be lost with respect to a transition temperature of 95°C. However, this comparison is an overestimation of the losses, because it is based on the assumption on a complete shutdown of delivered energy. For real thermochromic absorber coatings, the delivered energy is not shut off completely (as is e.g. the case for coatings switching predominantly in thermal emissivity).

C. Thermal coupling of coating on absorber sheet and glazing

Combining a thermotropic glazing with a thermochromic absorber could protect the solar thermal collector more efficiently from overheating. In this section, the possibility to trigger a dynamic glazing by of the rise of emissivity of the absorber will be discussed.
Thermotropic glasses change transmittance when their temperature rises by increasing opacity. For our thermochromic absorber coatings, the thermal emissivity increases as soon as the transition temperature is reached. In this situation, we expect that the temperature of the thermotropic glass rises, too, triggering thereby the thrmochromic or thermotropic transition which causes a decrease in solar transmittance.
The aim of this study is to calculate the temperature change of the covering glass pane. The temperature rise of the thermochromic/thermotropic glazing has to be sufficiently high in all weather conditions. The wind speed and the ambient temperature have to be taken into account as they affect the heat transfer towards the surroundings.

C.1. Thermal coupling with single glazing



T_∞	ambient temperature
T_{glass}	cover glass temperature (thermotropic)
T_{abs}	absorber temperature
ε_{abs}	absorber emissivity (will vary with T_{abs})
τ	roof slope

Fig. 5: Schematic drawing of the solar thermal collector.

For this study we fill fix the following parameters:

$$\begin{aligned} H &= 2 \text{ meters} \\ d &= 2 \text{ centimeters} \\ \tau &= 30\text{deg} \\ \varepsilon_{glass} &= 0.837 \end{aligned}$$

The absorber is thermochromic. So the emissivity changes with the temperature. Following parameters have been considered:

$$\begin{aligned} T_{abs} < 64°C \quad &\Rightarrow \quad \varepsilon_{abs} = 0.05 \\ T_{abs} > 95°C \quad &\Rightarrow \quad \varepsilon_{abs} = 0.5 \end{aligned}$$

These conditions correspond to the modes of normal low temperature operation and overheating. In the temperature range between 64°C and 95°C the thermochromic absorber coating might already have been switched, but the additional transition of the thermochromic/thermotropic glazing is not yet necessary.

The goal is to estimate how the glass temperature is correlated with the ambient temperature and external heat transfer coefficient h_{ext}.

2D simulations

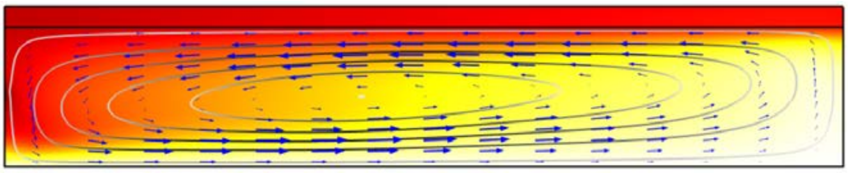


Fig. 6: Simulation of convection in tilted rectangular enclosure with COMSOL Multiphysics.

Finite element computer simulations of complex fluid dynamics were performed with COMSOL Multiphysics in order to evaluate the heat transfer between to absorber sheet and the glazing.

In the complex simulations of a full solar collector, the following difficulties were encountered:

- Long computing times
- Problems of convergence of the computing algorithm (occasionally)
- Varying number of convection loops leading to uncertainty in the results

However, the external heat transfer coefficients were determined with COMSOL. The values chosen for the rest of the study are given in Table 2.

$h_{ext}[\frac{W}{m^2K}]$	wind speed $[\frac{m}{s}]$
8	0
23	5
46	10

Table 2: External heat transfer coefficients as a function of wind speed.

1D simplification

A node model was used to describe the system. The diagram in Fig. 7 shows the equivalent electrical circuit of the system:

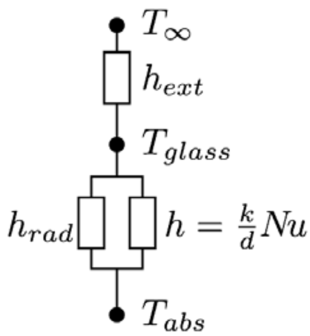


Fig.7: simplified 1D thermal model of the solar collector.

Radiation, convection and conduction heat transfer coefficient were determined using the corresponding formulas [FAI91]. Convection formula was chosen in accordance to the geometry of the design, e.g. tilted rectangular cavities [IDW].

An analytical approach allowed us to determine the glass temperature by iteration.
The thermal flux is constant through the system therefore it is equal at the nodes before and after the glass.

$$h_{ext} \cdot (T_{glass} - T_{\infty}) = (h_{rad} + h) \cdot (T_{abs} - T_{glass})$$

therefore

$$T_{glass} = \frac{T_{\infty} \cdot h_{ext} + T_{abs} \cdot (h_{rad} + h)}{h_{ext} + h_{rad} + h}$$

In order to solve this equation, an iterative method is adopted. Firstly, an estimation of T_{glass} is necessary, then a new T_{glass} is calculated. Reusing the last result of T_{glass} as improved approximation, this iteration is repeated until the value converges.

In each of the three cases of external heat transfer coefficient h_{ext}, the glass temperature T_{glass} was calculated in two configurations. For a low absorber temperature with T_{abs} = 64°C and ε_{abs} = 0.05 and for a high absorber temperature with T_{abs} = 95°C and ε_{abs} = 0.5.
The switching temperature of the thermochromic/thermotropic glazing has to lie in the interval between the glazing temperatures obtained for these two cases.
The range of suitable transition temperatures of the thermochromic/thermotropic glazing has been identified for this situation. The detailed results are given in the confidential annex of this report.

D. Switchable coatings on the collector gazing

D.1. Study of available products on the market

Dynamic glazing - also called smart glazing or smart glass – changes its properties depending on different parameters. This project deals mainly with a thermochromic coating; it changes its colour with the increase of temperature in order to switch absorptance and emissivity. Other types of dynamic coatings include, electrochromic and electrotropic glazing, changing respectively its colour or opacity, depending on the applied current. As the aim is to implement this coating on the glazing of a solar collector, a passive solution would be preferable. Having this purpose in mind, thermotropic coatings were investigated. Thermotropic coatings change opacity when their temperature rises above a given threshold. Therefore, an increase of the temperature of the solar absorber and its switch in emissivity would trigger the thermotropic coating, which would prevent the solar collector from overheating by increasing opacity.

The development of smart glass sector is currently at its early stage. More and more types of products appear or are improved but the market volume is low. Due to their price and questions about longevity, reliability and system integration, they are not yet in everyday use. On the other hand, buildings and even automotive use more and more glass and energy demand is a major concern. More recently, switchable mirrors using Chiral Liquid Crystals have been developed. This technology is emerging but its commercialization is still in progress. A study made by Navigant Research in 2013 [NAV13] estimates an important growth of the market volume for electrochromic, suspended particles, thermochromic and photochromic glass by 2022. Nevertheless, the latter study does neither consider thermotropic glass nor switchable mirror.

Even if sales volumes are small, electrochromic and electrotropic glazing already exists quite widely on the market. Due to the ease of changing the state with an electrical switch, they are used in a small domain for light control or privacy. Therefore, this type of glazing is often called privacy glass.

Main manufacturers include:

- o SageElectrochromics, SageGlass™
- o Innovative glass, LC Privacy glass
- o Polytronix, Polyvision™ switchable privacy glass
- o Research Frontiers, SPD SmartGlass

A thermotropic glass becomes opaque when the temperature rises above a given threshold. A Japanese company called Affinity developed a product called Thermotropic Smart Windowpanes. Some windows have been produced with the Technical University of Munich for a research project as shown in Fig. 8 [WAT13], [NIT05].

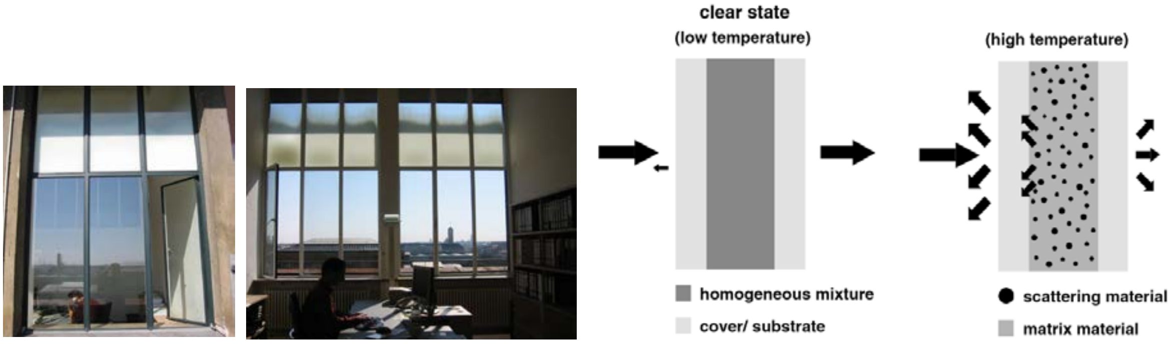


Fig. 8: Thermotropic glazing, Technische Universitat München, Affinity's intelligent windows.

Developped by Okalux and the Fraunhofer institute, the thermotropic shading system T-OPAL® consists of a polymeric layer in the glazing elements [FRA13], [SEE10]. The method for producing this thermotropic casting resin has been patented in 2000 [BIC00].

The only commercially available thermotropic glazing to our knowledge is Solardim® Eco. It is made by the German company Tilse [TIL13] produces a thermotropic glazing called Solardim® Eco. This glazing is used in energy saving self-regulating windows [SEE12].

D.2. Characterisation of commercially available thermotropic glass

The optical properties in visible and near-infrared ranges of a commercially available thermotropic glass pane have been measured using an integrating sphere. Thus, it was possible to measure the total and diffuse transmittance and reflectance as shown in Fig. 9.

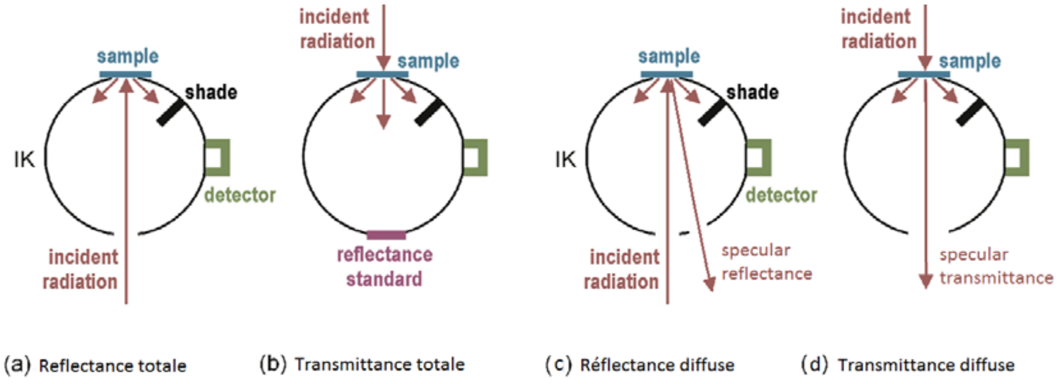


Fig. 9: Principle of measurement of the total and diffuse transmittance and reflectance measurements.

The total transmittance $T(\lambda)$ and reflectance $R(\lambda)$ in the VIS-NIR range were measured for the clear and hazed states. Using this data, the total solar energy transmittance and reflectance were calculated (according to EN 410) (see Table 3).

The absorptance $A(\lambda)$ is calculated using $T(\lambda)+ R(\lambda)+ A(\lambda)= 100\%$.

State	Total energy transmittance factor	Total energy reflectance factor
Clear	43.47%	5.2%
Hazed	30.32%	5.9%
Difference	13.16pp	0.7pp

Table 3: Total solar transmittance reflectance, and absorptance for the measured thermotropic glazing.

Even in the clear state, the measured thermotropic glazing exhibits less than 50% transmitted energy. This would reduce considerably the efficiency of a solar collector and is therefore not sufficient. There is no significant change in reflection, which is around 5-6%. It is only a bit more than a single glass to air interface (~4%). Because reflection does not change, and transmission is reduced by only 13pp, it means that mainly the absorbance is increasing in the hazed state. Details on the measured spectra are given in the confidential annex of this report.

The product tested in this study does not offer a transition large enough to allow the use as a protection for overheating. Doping can change the properties of thermotropic glazing. Muehling et al. have investigated how the particle size can increase back scattering: “Samples containing particles of high median diameter (4800 nm) primarily scatter in the forward direction. However, with smaller particles (300–600 nm) a higher backscattering (reflection) efficiency was achieved.” [MUE09]. Yet, the total transmittance in the clear state is still reduced and would decrease the efficiency of the collector.

Therefore, the characterized product is in its current form not suitable for our application. Thermotropic resins and the nanometric/micrometric components for thermotropic glazing have to be improved. It would be more interesting to have a layer able to reflect most of the energy.

D.3. Characterisation of a commercially available switchable mirror

In the previous part, a thermotropic glass has been studied. The product transition can be adjusted with the level of doping of the embedded resin; however it seems that it would still not be responding in a way suitable for our application. More reflection would be preferable. Following this we had the opportunity to test a switchable mirror. Although, this is an electric device and would not be a passive solution, characterisation was performed in order to evaluate the potential of this kind of product.

The switchable glass is composed of a single layer Chiral Liquid Crystal (CLC, also called Cholesteric Liquid Crystal) mixture between two Indium-Tin-Oxide (ITO) electrodes coated with a polyimide layer and two optically transparent substrates. When no current is applied, CLC forms a planar structure which naturally reflects light. The clear state occurs with all CLC helices unwounded and aligned with the electric field.

The product received at EPFL/LESO-PB effectively demonstrates quick transition. In addition, as illustrated by Fig. 10, it showed a highly reflective state and a clear transmitting state.

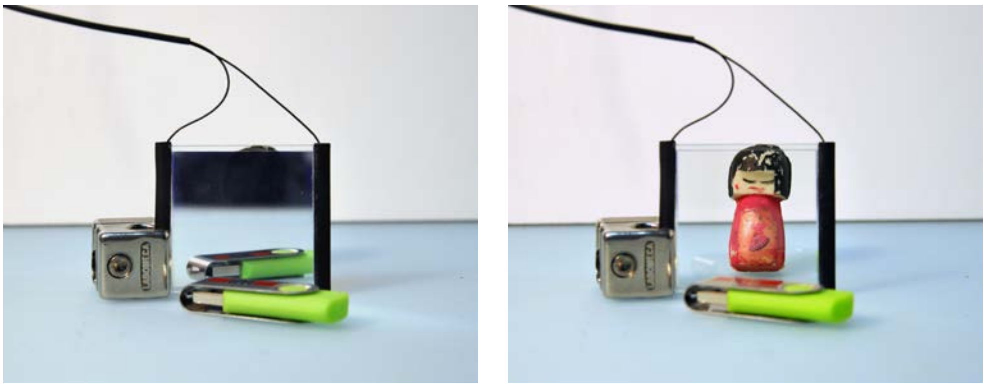


Fig. 10: Switchable mirror: left, in mirror state (power OFF) and right, transparent state (power ON) (photography: Olivia Bouvard, EPFL/LESO-PB).

The direct transmittance was measured in the UV-VIS-NIR range (350-2100 nm) in the clear and the reflective state. This product exhibits high value of transmittance in the visible range in the clear state and very low transmittance in reflective state.

As presented in Table 4, the fraction of solar spectrum transmitted is 41.2%, while the part of the visible light (according to human sensibility) is only 1.4%. This switchable mirror has been designed to reflect the visible light. Visible transmittance is reduced to 1.4% in the mirror state and in the clear state transmittance is superior to 87%. More details are given in the confidential annex of this report.

State	**Solar transmittance factor**	**Visible transmittance factor**
Mirror	41,2%	1,4%
Clear	82,8%	87,7%
Difference	41,6pp	86,3pp

Table 4: Total solar transmittance reflectance, and absorptance for the measured switchable mirror.

The measured switchable mirror exhibits interesting optical properties. For further improvement, the spectral properties of chiral liquid crystals can be tuned depending on the properties of the crystals.

However, when no tension is applied, the glazing stays in the mirror state. Furthermore, there is still no information on long-term longevity under heat and UV-light. If this kind of product is to be applied for solar collector, the lifetime in harsh conditions should be at least 25 years.

Evaluation 2013 and Outlook 2014

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. However, the transition temperature of 68°C is relatively low and should be increased to 95°C. By computer simulations it could be estimated that the energy losses due to the mismatch of the transition temperature are below 14%.

Literature studies suggested that it might be possible to increase the transition temperature by doping the coatings with aluminium. However, aluminium doping has led so far to an amorphisation of the film structure leaving the transition temperature unchanged. On the other hand, a stronger switch in thermal emittance might likewise be achieved. In the future, further attempts shall be made in order to increase the transition temperature by suitable doping. Possible approaches might be a variation of the process parameters such as the substrate temperature, or doping by other elements.

The switch in thermal emissivity limits the temperature of the absorber to values below the temperature of degradation of glycol (160°C-170°C).

However, it would be preferable to limit the temperature to approx. 100°C, avoiding likewise the formation of the used water-glycol mixture. In order to limit the temperature of the absorber below 100°C, the primary switch in thermal emissivity might trigger a secondary switch in the solar transmittance of a thermochromic or thermotropic collector glazing.

The thermal coupling between the solar absorber sheet and the glazing of the collector has been studied by numerical computations, and the range of preferable transition temperatures has been identified. The optical properties of a commercially available thermotropic glazing have been characterized. These investigations showed that in its current form the product is not yet satisfying, and would have to be improved for the envisaged application. As an alternative, switchable mirrors have been considered. Their optical properties are more promising, but open questions remain concerning e.g. cost and durability. Our thermochromic coatings could also be used on the collector glazing, and are therefore a promising alternative. In the future, this approach shall be considered.

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Industry Contacts

- Interaction and discussions with ALCAN that shows a general interest in our research development
- CTI project on sol-gel deposition of nanostructured selective solar absorber coatings in collaboration with the Swiss solar collector manufacturer ENERGIE SOLAIRE SA
- ASULAB (SWATCH GROUP) donated equipment for vacuum deposition of thin films, suitable for multilayer deposition
- Partnership with SWISSINSO: technology transfer of magnetron sputtering and research on novel coatings for innovative solar collector glazing

National scientific collaborations

- Active participation of Dr. Rosendo Sanjines and Henry Jotterand, Laboratory of Thin Films Physics, Prof. Laszlo Forro, Institute of Complex Matter Physics, EPFL. Experiments on magnetron sputtering and X-ray diffraction analysis
- Within EPFL, access to electron microscopes and to the facilities of TEM sample preparation is provided by the Interdepartmental Center of Electron Microscopy CIME.
- The research group of Prof. Libero Zuppiroli (LOMM at EPFL) provides access to their new ellipsometer. This contact will be useful for future measurements of the optical properties of thermochromic coatings.
- Collaboration with the research group of Prof. Peter Oelhafen, Institute of Physics, University of Basel.
- The research group of Prof. S. Mikhailov (IMA-Arc) provided access to their Van der Graaff accelerator for the RBS analyses.
- The research group of Prof. F. Bussy at UNIL in the Mineralogy and Geochemical Institute provided access to their EPMA JEOL 8200 super probe equipment for WDS analyses.

International scientific collaborations

- An informal scientific collaboration exists with the Polymer Competence Center Leoben (PCCL) in Austria.
- Informal scientific collaboration with the Department for Energy at Politecnico di Torino with Prof. M. Perino and Prof. V. Serra and Dr. L. Bianco.

Invited Presentations 2013

A. Paone, **Switchable selective absorber coatings for overheating protection of solar thermal collectors**, group seminar, November 26th, 2013, Poltecnico di Torino, Italy.

O. Bouvard, **Diffuse and total transmittance and reflectance of a thermotropic glass**, group seminar, November 26th, 2013, Politecnico di Torino, Italy.

S. Coccolo, **Bioclimatic Design of Sustainable Campuses using Advanced Optimisation Methods**, group seminar, November 26th, 2013, Politecnico di Torino, Italy.

Andreas Schüler, **Nanocomposite optical coatings for solar energy conversion**, group seminar, November 26th, 2013, Politecnico di Torino, Italy.

Dissemination

A. Paone, public thesis defense, **Switchable selective absorber coatings for overheating protection of solar thermal collectors**, December 6th, 2013, EPFL, Lausanne, Switzerland.

Award

<u>**Solar Energy Journal Best Paper Award**</u> to Martin Joly and co-authors for novel selective coatings :

"**Novel black selective coating for tubular solar absorbers based on a sol-gel method**"
by Martin Joly, Yannik Antonetti, Martin Python, Marina Gonzalez, Thomas Gascou, Jean-Louis Scartezzini, Andreas Schüler, Volume 94, August 2013, Pages 233-239,
http://dx.doi.org/10.1016/j.solener.2013.05.009.

Publications

A. Paone, PhD thesis, **Switchable selective absorber coatings for overheating protection of solar thermal collectors**, EPFL thesis No. 5878, Lausanne, Switzerland, 2013

A. Paone, R. Sanjines, P. Jeanneret, H. Whitlow, G. Guibert, S. Mikhailov, F. Bussy, J.-L. Scartezzini, A. Schüler, **Improved doping efficiency in VO_2:W films deposited by thermal evaporation and magnetron co-sputtering and influence of doping on the metal-semiconductor transition in VO_2:Al films**, in preparation.

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