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Ph.D. Thesis

Design, Simulation and Optimization of Selective Solar Absorbers for High Efficiency Solar Collectors.

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List of symbols and abbreviations

Symbols

Symbol	Description	Unit
α	Total absorption coefficient	
α_{λ}	Spectral absorptivity	
as	Solar absorptance	
α_{LED}	Absorptance at LED illumination	
a	Attenuation coefficient	m^{-1}
A	Area	<i>m</i> ⁻²
Βλ	Spectral irradiance of a blackbody	$Wm^{-2} \mu m^{-1}$
b	Wien's displacement constant	μm·K
С	Speed of light in a medium	ms^{-1}
C ₀	Speed of light in vacuum	ms^{-1}
<i>C</i> _p	Specific heat capacity	$Jkg^{-1}K^{-1}$
С	Solar concentration ratio	
Δη	Efficiency variation	
Δ	Phase difference	
$d_{i,opt}$	Optimal thickness of the i^{th} layer of a multilayer coating	nm
E_{BB}	Total emitted power, Stefan-Boltzmann law	Wm ⁻²
E_{λ}	Spectral irradiance of a body	$Wm^{-2} \mu m^{-1}$
<i>ε(T)</i>	Spectrally averaged emittance at temperature T	
Et	Temperature dependent spectrally averaged emittance	
Esub	Equivalent substrate emittance of a solar absorber	
ξλ	Spectral emissivity	
e	Maximum percentage error on the layer thickness of a multilayer selective coating	
ϵ_{0}	Dielectric constant of free space	Fm^{-1}
Er	Complex relative dielectric constant	
ϵ_1	Real part of the relative dielectric constant	
<i>€</i> 2	Imaginary part of the relative dielectric constant	
G	Irradiation	Wm^{-2}
h	Plank constant	Js
H	Irradiance On the solar absorber	Wm^{-2}
hconv	Convective heat transfer coefficient	$Wm^{-2}K^{-1}$
Ι	Intensity of a light wave	Wm ⁻²
k	Boltzmann constant	JK^{-1}
λ	Wavelength	<i>m</i>

λ _{cut-off}	Cut-off wavelength	т
т	Mass	kg
п	Refractive index	
ñ	Complex refractive index	
N	Average Number of Solar Rays Reflections onto Mirrors of a concentrating solar system	
ητ	Thermal transfer efficiency at temperature T	
η _{abs}	Efficiency of a solar absorber	
η_{coat}	Coating efficiency of a solar absorber	
η_{all}	Overall efficiency of a solar absorber in a high vacuum envelope	
 <i>µСРС</i>	Thermal efficiency of a CPC collector in high vacuum envelope	
η _{max}	Overall efficiency related to the optimal thickness package	
η _{min}	Minimum efficiency value of a multilayer coating caused by given errors on layer thickness	
η' _{min}	Minimum value of the efficiency related to the thickness values of two fixed layers of a multilayer stack and all the possible combinations of the remaining layers	
Pin	Incident illuminating power per unit area	Wm ⁻²
PLED	Light Power Provided by A Calibrated LED System	Wm ⁻²
Ψ	Amplitude ratio	
q_h	Heat Flux to the thermal system	Wm^{-2}
ρ	Total reflection coefficient	
ρλ	Spectral reflectivity	
<i>r</i> _p	Fresnel reflection coefficient for p- polarization	
r _s	Fresnel reflection coefficient for s- polarization	
σ_{SB}	Stefan-Boltzmann constant	$Wm^{-2}K^{-4}$
t	Time	S
T	Temperature	K
τ	Total transmission coefficient	
$ au_{\lambda}$	Spectral transmissivity	
Tamb	Ambient temperature	K
T_h	Absorber temperature	K
$ au_{glass}$	Glass transparency	
T _{hS}	Stagnation Temperature	K
μ_0	Magnetic permeability	Hm^{-1}
v	Frequency	Hz
W	Weighting factor	

Abbreviations

Abbreviation	Definition
СРС	Compound Parabolic Concentrator
CSP	Concentrating Solar Power
DCMS	Direct Current Magnetron Sputtering
DCRMS	Direct Current Reactive Magnetron Sputtering
EFPC	Evacuated Flat Plate Collector
ETC	Evacuated Tube Collector
FIR	Far Infrared
FP	Standard Flat Plate Collector
FTIR	Fourier Transform Infrared Spectroscopy
GA	Genetic Algorithm
НТЕ	Heat Collection Element
HVFP	High Vacuum Insulated Flat Plate Collector
IR	Infrared
МТВ	Mini Test Box
NEG	Non-Evaporable Getter
NIR	Near Infrared
OSA	Optical Spectrum Analyzer
PVD	Physical Vapour Deposition
RF	Radio Frequency Sputtering
RFMS	Radio Frequency Magnetron Sputtering
RFRMS	Radio Frequency Reactive Magnetron Sputtering
SSA	Selective Solar Absorber
UV	Ultraviolet light
VIS	Visible Light

1.Introduction and aim

Many scientific societies and academies have released statements and studies that highlight the fact that climate change is a real issue. The IPCC (Intergovernmental Panel on Climate Change) for example, predicts a temperature rise of about 1 to 5 °C over the next century, and states that "the range of published evidence indicates that the net damage costs of climate change are likely to be significant and to increase over time"[1]. Human activities and in particular greenhouse gases emissions are the dominant cause of global warming. To limit some of the effects of the climate change the first step is "mitigation", i.e. reducing the flow of greenhouse gases in the atmosphere: the transition to renewable energy resources will be of fundamental importance in global sustainable development and solar energy will play a key role in this process. The goal is to reduce the use of fossil fuel and consequently the greenhouse gas emissions, thus mitigating climate change issues [2][3]. A non-negligible part of the energy resources employed by the developed countries is nowadays used for heating and cooling [4][5]. The industrial sector deserves particular attention [6] since it comprises the largest portion of global energy consumption among the major energy-consuming sectors [7]. Globally, the industrial sector is responsible for over one third of total energy consumption and a quarter of global CO_2 emissions [8]. Figure 1.1.1 shows the share and breakdown of heat demand in industry: as anticipated, industry accounts for about 30% of the total worldwide energy usage. Heat constitutes about 75% of industrial energy demand and half of it is at low and medium temperature. It is important to note that industrial processes still rely on fossil fuel combustion for process heat (only 9% of the thermal energy is supplied by renewable sources).



Figure 1.1.1 Share and breakdown of heat demand in industry: heat represents three quarters of the energy demand of industries world-wide, and half of it is low to medium temperature heat, that could be easily supplied by renewable heat. Source: Solar Payback (2017), based on IEA statistics and calculations by IRENA.

Solar energy could be easily integrated in industrial plants as a renewable energy source, offering two possibilities: concentrating and non-concentrating solar collection [9]. Concentrating Solar Power (CSP) devices are suitable for process heat supplying because of the considerably high working temperatures (up to 500 °C), but their usage is limited by the fact that they can only collect direct solar radiation, and by the added extra costs deriving from the need of a complicated tracking system and maintenance.

Non-concentrating technologies such as flat-plate (FP) collectors or evacuated tubes are considerably cheaper and they can be installed almost anywhere, as they use both direct and diffuse solar irradiance, but they do not deliver heat above 100 °C with adequate efficiency.

At the moment, the vast majority of projects use non-concentrating technologies since solar heating is economically competitive with fossil fuels at low-medium temperatures. Food and beverage industry, service industry, and textile industry, are examples of industries that need low to medium temperature heat, and it is no coincidence that they represent the main areas in which solar heat has been deployed. Hence, solar collectors could be a gamechanger in industrial transitioning to renewable energy sources, but at the present state of technology they cannot yet provide mid-temperature heat on a large scale, and therefore are unable to replace a significant portion of industrial process heat. A potential solution to overcome the limits of the conventional solar collectors comes from the High Vacuum Evacuated Flat Plate Solar Collectors (EFPC). EFPC could be considered as a third category of solar collectors competing in the thermal energy market, as they keep all the advantages of a flat plate solar collector, while being able to supply mid-temperature output with high efficiency. Vacuum insulated flat plate collectors concept is known since 1970's [10], but just recently EFPCs have been introduced on the market by a relatively young company, TVP Solar [11][12], due to the technical challenges involved in the production of a quality product [13]. High vacuum insulation allows for the elimination of the gas induced thermal losses, while an accurate design could limit to a negligible value the conductive losses, moving the operating temperature from about 80 °C (standard flat-plate solar collector) to 200 °C, without concentration. Since the solar absorber is suspended in a high vacuum envelope the thermal radiation remains the only loss mechanism, that rapidly rises with increasing temperature. For this reason, to efficiently use the thermal energy derived from the solar radiation using flat plate solar collectors, an optimized (and low-cost) Selective Solar Absorber (SSA) is required [13]. A selective solar absorber is a surface which is able to discriminate between solar spectrum and infrared spectrum, being able to capture as much solar light as possible, while emitting as little thermal energy as possible, taking advantage of the difference between the wavelength ranges of the solar spectrum and the thermal radiation emitted by a heated body.

Commercial solutions of solar selective coatings are unavoidably developed and optimized for the most widespread solar collection technologies, justifying the lack of selective coatings optimized for high vacuum insulated collectors. For EFPCs in fact, the high working temperatures reached without concentration require special attention to be given to the radiative parameters of the selective coating. The two most used solar thermal devices (Concentrating solar power (CSP) and flat plate solar collectors) justify the lack of interest by both the SSA manufacturers and the researchers in fine-tuning the thermal emittance against solar absorptance. In fact, for CSP the solar absorptance is dominating over thermal emittance because of the high value of the concentration ratio, while for the flat plate collectors the greater importance of solar absorptance over thermal emittance is justified by the low temperature output [14]. The emerging technology of EFPCs places itself in a new field where the high working temperatures without concentration require special attention to be given to both solar absorptance and thermal emittance in the design of the selective coatings. Recently, a growing number of papers have been published on this topic and it is a clear indication of its importance. However, the literature still lacks articles that propose valid SSA coatings optimized for EFPC technology.

The main purpose of this research is to develop a method to optimize solar selective coatings well suited for the emerging technology of the high vacuum insulated flat plate collectors, focusing on a simple-to-realize, industrially feasible and robust selective coating, for both low and medium temperature applications. For this purpose, the current state of the art regarding the selective solar absorbers was reviewed to assess which are the solutions that can meet the required criteria. Once the architecture of the SSA was established, the selection of the right materials represented the first part of the designing stage. Among the possible designs inspected, multilayer selective absorbers based on chromium and chromium oxide appeared to be the best suited for the purposes of this work. The selected materials were deposited via electron beam and sputtering physical vapour deposition, which represent the most used coating techniques in industrial field. Standard instrumentation was used to characterize the materials. Optical constants of the materials were extrapolated, validated, and used to perform numerical simulations of the SSAs.

The key parameters which rule the performances of the solar coatings were defined along the thesis, focusing the attention on the requirements of the high vacuum insulated flat plate collectors and the mid-temperature application. These considerations represented the basis for the introduction of the methods to optimize a selective solar absorber, in a process that led to a custom algorithm especially thought for the emerging EFPC technology. The algorithm was perfected to maximize the performances for any desired target temperature, ensuring at the same time the robustness of the performances, aiming at mass industrial production. In fact, the performances of multilayer solar absorbers are strongly affected by the thickness of the various layers. To take into account the unpreventable errors on thickness of the film that can occur during industrial processes, the robustness of the performances of the coatings in terms of error on the layer thickness of each layer are discussed for the optimized coatings giving interesting insights on the limits of the coatings in terms of performances of the coatings.

To concretize the work and validate the results of the optimization process, the investigated coatings were fabricated via electron beam and sputtering physical vapour deposition. The radiative properties of the fabricated selective coatings were characterized both via standard optic characterization techniques and a custom calorimetric instrument to evaluate the performances in operating condition. Since the PhD project is funded by CNR-Confindustria ("Dottorati di Ricerca Industriali" program XXXIV cycle) and TVP Solar is part of the project, there was the possibility to fabricate the solar coatings via roll-to-roll industrial machinery. The excellent values of solar absorptance and thermal emittance validated by measurements on the fabricated samples promise unparalleled performances for the emerging technology of EFPCs, while the excellent results of the analysis on the robustness of the optimized coatings is a plus when aiming at mass industrial production.

2. Solar thermal collectors

2.1. Electromagnetic propagation

Electromagnetic waves are characterized by a parameter, called wavelength λ which represents the distance covered by the radiation in a period, or the frequency v, which represents the number of cycles in the time unit. Velocity of the propagation *c* can be expressed as:

$$c = \lambda v \tag{2.1.1}$$

In Figure 2.1.1 electromagnetic radiation spectrum has been reported. The wavelength range is divided into separate bands, and the electromagnetic waves within each band are called by different names: radio waves, microwaves, infrared, visible light, ultraviolet, X-rays, and gamma rays.



Figure 2.1.1 Electromagnetic radiation spectrum [15].

Speed of light in vacuum is $c_0 = 2.9979 \cdot 10^8$ m/s. This velocity is linked to the dielectric constant of free space ϵ_0 and magnetic permeability μ_0 :

$$c_0 = 1/\sqrt{\mu_0 \epsilon_0} \tag{2.1.2}$$

In a medium the speed of light is lower than c_0 and it depends on the material:

$$c = 1/\sqrt{\mu\epsilon} \tag{2.1.3}$$

Being ϵ and μ the dielectric constant and magnetic permeability of the medium. We can define:

$$n = \frac{c_0}{c} = \frac{\lambda_0}{\lambda} = \sqrt{\frac{\mu\epsilon}{\mu_0\epsilon_0}} = \sqrt{\epsilon_r\mu_r}$$
(2.1.4)

Being *n* the refractive index and ϵ_r and μ_r the relative dielectric and magnetic constant of the medium. The refractive index depends on the frequency of the radiation. Equation 2.1.4 shows the physical phenomenon that the speed of light becomes slower in a medium with high *n*. Frequency ν is unaltered when passing from a medium with refractive index n₁ to another with refractive index n₂, while velocity of propagation varies:

$$\frac{c_1}{c_2} = \frac{n_2}{n_1} \tag{2.1.5}$$

And so does the wavelength:

$$\frac{\lambda_1}{\lambda_2} = \frac{n_1}{n_2} \tag{2.1.6}$$

When the electromagnetic radiation (defined as irradiation, *G*) hits the surface of a body, part of the radiation is reflected, while the remaining part enters the body and propagates through. If the body is an absorbing medium the light that enters the body will be absorbed and converted into energy. On the contrary, if the body is transparent, or its thickness is lower than the thickness that is needed to absorb all the radiation, the light that enters the body is transmitted reaching the back surface where it can be reflected again and/or transmitted to the other side. To quantify these phenomena, it is useful to introduce the absorption, reflection and transmission coefficients, respectively equal to the absorbed, reflected and transmitted fraction of the incoming irradiation *G*. These coefficients are wavelength dependent, and their spectrally averaged value defines the total absorption, reflection and transmission coefficients, α , ρ and τ respectively. According to the energy conservation principle:

$$\alpha G + \rho G + \tau G = G \tag{2.1.7}$$

The attenuation coefficient *a* (also called absorption coefficient) is defined as the amount of energy absorbed per unit length and it quantifies the absorption of light by a medium. The attenuation coefficient *a* must not be confused with the total absorption coefficient α , being α a dimensionless parameter which quantifies the fraction of the incoming radiation *G* absorbed by the medium. If *z* is the direction of propagation and the intensity (power per unit area) at position *z* is *I*(*z*), the decrease of the intensity in *dz* is:

$$dI = -adz \cdot I(z) \tag{2.1.8}$$

That integrated results in the Beer's law:

$$I(z) = I_0 e^{-az} (2.1.9)$$

Being I_0 the intensity at z=0.

Absorption and the refraction can be incorporated into a single quantity named complex refractive index, \tilde{n} . The complex refractive index allows to calculate the reflectivity *R*, and hence the transmissivity *T*. \tilde{n} is usually defined as:

$$\tilde{n} = n + ik \tag{2.1.10}$$

The real part of \tilde{n} (n) is the refractive index as defined in equation 2.1.4. The imaginary part (k) is called extinction coefficient. The extinction coefficient is directly related to the attenuation coefficient a:

$$a = \frac{4\pi k}{\lambda} \tag{2.1.11}$$

Fresnel equations describe the behaviour of the electromagnetic radiation when it crosses an interface dividing two materials with different refractive index [16]. These equations can be used to evaluate reflection, absorption and transmission coefficients depending on wavelength, angle of incidence and polarization of the incoming light radiation.

We can relate the refractive index of a medium to its relative dielectric constant ϵ_r through the following relationship:

$$n = \sqrt{\epsilon_r} \tag{2.1.12}$$

Where ϵ_r is a complex number, we therefore define the complex relative dielectric constant $\tilde{\epsilon_r}$ as in the following equation:

$$\epsilon_r = \epsilon_1 + i\epsilon_2 \tag{2.1.13}$$

Using Equation 2.1.12 we can write:

$$\tilde{n}^2 = \epsilon_r \tag{2.1.14}$$

Now we can derive the relationship between the real and imaginary parts of the relative dielectric constant and the refractive index:

$$\epsilon_1 = n^2 - k^2 \tag{2.1.15}$$

$$\epsilon_2 = 2nk \tag{2.1.16}$$

2.2. Solar and thermal radiation

Solar radiation

Solar radiation is the definition for the electromagnetic radiation emitted by the sun. As the solar radiation passes through the atmosphere, part of it is absorbed, reflected or scattered. Direct radiation is defined as the radiation that reaches Earth's surface without being scattered, travelling on a straight line from the sun, down to the surface of the earth, whereas the radiation having experienced scattering processes in the atmosphere is defined as diffuse radiation. The total radiation that reaches Earth's surface is given by the sum of the direct and diffuse irradiation. The orientation of a surface is a fundamental parameter when dealing with direct irradiance, on the contrary the maximum amount of diffuse radiation can be gathered when the surface is laying down horizontally, since diffuse radiation is generally equally distributed throughout the sky. Because the solar spectrum varies according to geographic location, time of the day, season etc., standard reference spectra have been defined to be used as reference for the performance comparison of photothermal devices from different manufacturers and research laboratories. Figure 2.2.1 shows the two standards defined for terrestrial use [17].



Figure 2.2.1 Standard solar spectra for terrestrial use and black body radiation spectra.

The AM1.5 Global spectrum is intended for flat plate collectors and has an integrated power of 1000 W/m^2 . The AM1.5 Direct plus circumsolar spectrum includes the direct beam from the sun plus the circumsolar component. It has an integrated power density of 900 W/m² ant it is intended for solar concentrator. It is worth to notice that terrestrial solar radiation is limited to the range of wavelength between 0.3 µm and approximately 2.5 µm, i.e. ultraviolet, visible and near-infrared ranges (UV/VIS/NIR).

Thermal radiation

All the materials with a temperature higher than 0 K are constantly emitting electromagnetic radiation, defined as thermal radiation. At high temperature the electromagnetic radiation represents an important mechanism of thermal loss, that significantly affects the performances of the collectors. To properly define the thermal radiation of a body, blackbody radiation should be introduced first. Blackbody radiation is defined as the thermal radiation emitted by an idealized physical body, which is called a blackbody. A blackbody in thermal equilibrium is both a perfect absorber and a perfect emitter, in the sense that it both absorbs end emits the same or more energy than any other object at the same temperature, for all the wavelengths. The spectral irradiance $B_{\lambda}(T)$ (Wm⁻³) of a blackbody is described by Plank's radiation law [18], in SI units:

$$B_{\lambda}(T) = \frac{2\pi hc^2}{\lambda^5 (\exp\left(\frac{hc}{k\lambda T}\right) - 1)}$$
(2.2.1)

Being λ the radiation wavelength (m), T the blackbody temperature (K), h (J·s) the Plank constant, c (m/s) the speed of light in vacuum, k (J/K) the Boltzmann constant. Nevertheless, the conventional unit used for blackbody spectral irradiance is in Wm⁻²µm⁻¹.

The total emitted power $E_{BB}(Wm^{-2})$ is obtained by integrating the blackbody spectral irradiance over all the wavelengths:

$$E_{BB} = \sigma_{SB} T^4 \tag{2.2.2}$$

Being σ_{SB} (Wm⁻²K⁻⁴) the Stefan-Boltzmann constant.

The intensity and peak wavelength of the thermal radiation depend on the temperature, according to Wien's displacement law [19]:

$$\lambda_{peak} = \frac{b}{T} \tag{2.2.3}$$

Being T (K) the absolute temperature and b ($\mu m \cdot K$) the *Wien's displacement constant*. Wien's law indicates an inverse relationship between wavelength and temperature: higher the temperature, shorter the wavelength at which the peak is placed. Figure 2.2.1 shows how, for increasing temperature, the peak of blackbody radiation has higher intensity and shift towards shorter wavelengths, according to Wien's law.

The thermal radiation spontaneously emitted by an object is called thermal emittance and it can be defined as the ratio between the power emitted by the object itself and the power emitted by a blackbody at the same temperature. For the majority of the solar thermal applications the thermal radiation spectrum is generally limited in the infrared range between approximately 1 μ m and 50 μ m.

2.3. Solar collectors

A solar collector is a device used to collect solar radiation converting it in thermal energy, through a heat transfer fluid (or more in general a transport medium). Solar thermal collectors can be generally outlined as shown in Figure 2.3.1: they usually consist of a chamber, closed by a transparent cover to let solar radiation in, a solar absorber, and thermal conducting pipes which circulate the heat transfer fluid (HTF) that are connected to the absorber. The solar absorber itself is usually composed of a solar selective thin film coating deposited on a metallic sheet substrate. The thin film coating is designed to absorb as much solar light as possible while minimizing the thermal radiation losses. Solar thermal devices are mainly divided into two categories: concentrated and unconcentrated Solar Thermal devices [9]. Concentrators mainly collect direct solar radiation and a small portion of the diffuse light that fall within the acceptance angle. They enable high temperature outputs, but the need of a tracking infrastructure can add to the expense and complication of the devices themselves. Unconcentrated solar thermal collectors on the other hand, are able to collect both diffuse and direct irradiance, and they are considerably cheaper, but their use in industrial process heat suppling is limited by the low temperatures output. Losses in a solar collector are to be identified with:

- Reflection losses due to both the glass cover and the solar absorber surface. They can be reduced by using anti-reflective glass and optimized coatings.
- Conduction losses, due to the necessary connections between the high temperature components and the collector frame. They can be reduced by using the right insulating materials and a careful design.
- Losses due to the internal gases: at ambient pressure the main mechanism is represented by convection losses, at moderate vacuum pressures gas convection becomes negligible while gas conduction losses are still present. For high vacuum pressures (<10⁻² Pa) both convection and conduction losses due to the internal gases are negligible.
- Radiative losses due to the thermal radiation coming from high temperature components (mainly the solar absorber). They can be reduced by acting on the selective coating and the substrate properties.



Figure 2.3.1 Solar collector conceptual drawing.

The main types of solar collector devices are presented in this section.

2.3.1. Flat plate collectors

Flat plate solar collectors (FP) (Figure 2.3.2) are made of a metallic chamber closed on the top side by a transparent glass, this box houses a solar absorber sheet. Solar radiation is transmitted by the transparent cover and hits the solar absorber plate, which transfers the absorbed thermal energy to the thermal fluid (oil, air, water...), usually circulating in pipes directly soldered to the absorber plate. Absorbers plates are usually made out of good thermal conducting metals (copper or aluminium) and can be coated with special materials designed to absorb as much solar light as possible while minimizing the thermal radiation losses. The sides and bottom of the box hosting the absorber to the ambient. Flat plate solar thermal collectors are able to collect both diffuse and direct sunlight, and they are considerably cheaper with respect to the other commercial alternatives, but their use in industrial process heat suppling is limited by the low temperatures output.



Figure 2.3.2 Standard flat plate solar collector [20].

2.3.2. Gas filled or partially evacuated flat plate collectors

The thermal losses from the absorber to the ambient significantly affect the flat plate collector efficiency. A simple way to reduce the losses is to partially evacuate the panel. Figure 2.3.3 shows how partial evacuation, down to 10^3 Pa (regime of gas heat conduction independent from pressure) allows to get rid of conductive losses. To further reduce the thermal losses a gas more appropriate than air can be used to reduce the thermal conductivity, introducing a sealed and gas-filled flat collector. Gas like Argon, Xenon or Krypton have been studied to serve to this purpose (see Figure 2.3.3) [21]. The typical employed pressures are in the range of 10^2-10^4 Pa. This sealed design guarantees to the collector a longer service lifetime because the solar selective coating is protected against environmental agents.



Figure 2.3.3 Heat losses by gas heat conduction from the hot absorber to the casing in a flat-plate collector in dependency of the gas pressure in the collector casing for different filling gases. The typical operation pressure ranges in the plateau between 100 and 10⁴ Pa (adapted from [21]).

2.3.3. Evacuated tubes collectors

A way to enhance the performances of a solar collector is to evacuate the space between the absorber and the external box, taking advantage of the vacuum as an efficient isolation mechanism to eliminate the convection losses. We already discussed how partial evacuation, down to 10^3 Pa (regime of gas heat conduction independent from pressure) allows to get rid of conductive losses. Further reducing the gas pressure down to about 10^{-2} Pa allows to eliminate the gas conduction losses too, as shown in Figure 2.3.3.

Evacuated tubes solar collectors (ETC) use a series of sealed glass tubes equipped with an inner solar absorber (Figure 2.3.4). The absorber can be either a metallic fin with a selective coating and attached to a metal (or glass) pipe that circulates the heat transfer fluid, or the pipe itself can be 'painted' with a solar coating. An anti-reflective coating can be deposited on the inner and outer surfaces of the glass tubes to improve transparency. Vacuum help preserving both the selective and the inner anti-reflective coating. Glass-metal evacuated tubes need a highvacuum tight seal at one or both sides of the evacuated tube. The glass-to-metal seal connects the brittle glass material to a metal with usually different thermal expansion coefficients. Hence, temperature differences lead to thermal stresses in the seal itself putting the vacuum tightness at risk [22]. Glass-glass evacuated tubes are a way to solve glass-metal seal issues because glass-to glass seal is very reliable. They are made with two borosilicate glass tubes fused together at one or both ends, vacuum is made between the two concentric tubes and the absorber is placed in the inner tube. The drawback of this configuration is that two glass layers reduce the transparency leading to higher optical losses. To avoid this issue the selective coating could be deposited directly on the inner glass tube, but the poor glass heat conduction would affect the thermal exchange.

Vacuum pressure used are of the order of 10^{-2} Pa [23]. A getter pump¹ is commonly evaporated inside the high vacuum tubes to keep a good vacuum pressure over the time. Life of the vacuum lies between 5 to 15 years depending on the type of collector.

As shown in Figure 2.3.5, evacuated tube collectors can achieve high temperatures (above 200 °C) with high efficiencies, taking advantage of the high vacuum insulation [24].

However evacuated tube collectors have a discontinuous absorbance area and cover only a fraction of their occupied area (gross area), because of the space between the glass tubes and the vacuum gap between each tube and its absorber inside. ISO 9806 standard states that the efficiency of solar thermal collectors should be measured in terms of gross area, and this might favour flat plates type collectors.



Figure 2.3.4 Evacuated tube collector



Figure 2.3.5 Collector efficiency vs (Tm-Ta), being Tm and Ta the absorber and ambient temperature, respectively. (Adapted from [25]).

2.3.4. Parabolic troughs

Parabolic trough collectors consist of concave parabolic shaped high reflecting mirrors that concentrate solar light onto a receiver pipe located in the focus of the parabola as shown in Figure 2.3.6. A single-axis tracking mechanism is used to angle both solar collectors and heat receivers toward the sun, ensuring that all the solar radiations fall parallel to mirrors axis. The heat collection element (HTE) consists of a solar absorber pipe insulated by an evacuated glass

¹ Getters pumps are metallic compounds designed to absorb the gas molecules (such as hydrogen, water and other gases) that permeate into the vacuum envelope over time.

tube. Because of the high temperature outputs of the concentrating technologies, the solar absorber is usually made of a stainless-steel pipe equipped with a selective solar coating. The operating temperature of the system is in the range of 200-500 °C and the geometric concentration ratio of the parabolic-trough system is in the range of 30–100 [26]. The heat transfer fluid used is generally synthetic oil, but molten salts can be used when there is the need to reach high temperatures [27]. Large scale power plants need a storage system to overcome the inconsistency of the solar energy source. Although these collectors guarantee high temperature outputs as discussed, with relatively high efficiency, their use is limited by the fact that they only collect direct-beam sunlight requiring high cleaning standards for the mirrors and tracking systems to efficiently harness solar energy in day-light hours, resulting in high maintenance costs and installation issues.



Figure 2.3.6 Parabolic trough collectors.

2.3.5. Power tower

In a power tower sunlight is concentrated by a large number of flat sun-tracking mirrors, called heliostats, on the receiver placed at top of a tall tower (Figure 2.3.7 [28]). The heat transfer fluid can exchange heat with a working fluid powering a turbine generator to produce electricity. Newer designs that use molten salts or liquid sodium as working fluids allow to store energy before using it accounting for the instability of the solar source. This kind of technology can reach temperatures as high as 600-700 °C, however its usage is limited by the expensive equipment costs, the need for large areas of land, the high maintenance costs for the heliostats and tracking mechanism and the negative impact on the wildlife.



Figure 2.3.7 Solar power tower [28].

2.3.6. Point focus collectors

Point focus collectors use a large parabolic dish of mirrors to focus solar rays onto a receiver (Figure 2.3.8, [29]). The heat generated is usually used to run an engine/generator and produce electricity. Stirling engines are always used to convert the solar power into electricity. Typical parabolic dish collectors are equipped with a two-axis tracking system. Concentration ratios range from 500 to 3000, allowing for high operating temperatures (up to 450 °C) [30]. Due to limitation in size, they are suitable only for small power generations (they are rarely connected together in a solar field), while being ideal for modular use.



Figure 2.3.8 Parabolic dish schematic. EuroDish system [29].

2.3.7. CPC

Compound Parabolic Concentrator (CPC) is an example of non-imaging concentration of sunlight that could be designed for stationary or passive tracking thus having acceptable concentration ratio (Figure 2.3.9). A CPC can collect both direct-beam sunlight and part of diffuse light (only rays within the acceptance angle) [31] and concentrate them on an absorber tube. Compound parabolic concentrators gained increasing attention from researchers and industrial developers as they offer the possibility to reach high temperatures keeping high conversion efficiencies without incurring in the expenses of complicated tracking systems and high maintenance costs.



Figure 2.3.9 Schematic diagram of 2D trough CPC a) 3D model of glazed PV-CPC system b) cross section of glazed PV-CPC system with/without cooling pipes. Adapted from [31].

2.3.8. High vacuum evacuated flat plate solar collectors.

High vacuum Evacuated Flat Plate Collectors (EFPC) (also known as High Vacuum Insulated Flat Plate Collectors (HVFP)) combine the advantages of Evacuated tubes and flat plate collectors. EFPCs are evacuated down to 10⁻² Pa or lower pressure, allowing to eliminate both convection losses and gas conduction losses. For this reason, EFPC should not be confused with partially evacuated collectors. The first collector making use of high vacuum insulation was developed at CERN [32], while TVP SOLAR SA was the first company to commercialise Solar Keymark certified collectors in 2012 [33]. EFPC are more complicated to realize than ETC, as they need to support the external structure against the atmospheric pressure and a glass-metal seal to join the glass cover and the metallic part of the vacuum envelope. To support the glass against atmospheric pressure an array of pins is used, so the absorber plate is provided with holes to properly accommodate the pin structure (also considering thermal expansion issues) (Figure 2.3.10, [34]). To prevent outgassing that will inevitably raise the internal pressure affecting the performances, only materials with low vapour pressure should be used for the collectors. To efficiently keep high vacuum insulation EFPCs make use of Non-Evaporable Getter pumps (NEG), which can be regenerated in situ by exposure to solar light. EFPC technology offers the highest efficiency among the other non-concentrating technologies [13], but their practical realization is a technical challenge.



Figure 2.3.10 Conceptual design of a 0.25 m² Evacuated Flat Plate Solar Collector (Henshall et al. [34])

TVP Solar

TVP Solar is a young company that designs, develops, and manufactures high vacuum evacuated flat plate collectors. They successfully overcame the technical challenges in the production of a high vacuum collector, and patented special technologies such as an efficient glass-metal seal and a proprietary NEG getter pump that allows to maintain high vacuum (10⁻² Pa to 10⁻⁷ Pa) throughout the entire service life of the collector [12]. A careful design and material choice allow to reduce to a minimum the conduction losses, while a selective absorber and an Anti-Reflective coated glass contribute to performances higher than the ones of evacuated-tube solar thermal collectors and even higher than those obtained by compact parabolic concentrating solar collectors [35].

Figure 2.3.11 shows the efficiency of MT-Power high vacuum collector produced by TVP Solar. Such collectors are optimized to operate within the range 80–180 °C. They are Solar Keymark certified by ITW Stuttgart (see certificate N. 011-7S1890 F). It is clear from the graph in Figure 2.3.11 how these collectors can achieve an efficiency as high as 45% at T_m - T_a =160 °C (being T_m and T_a the absorber and ambient temperature respectively), while stagnation temperature is higher than 300 °C. Stagnation temperature describes the state of a solar thermal system in which the flow of the Heat Transfer Fluid is interrupted and the system reaches a temperature for which the absorbed energy equals the losses. In other words, stagnation temperature could be described as the temperature for which efficiency is zero. Such performances are achieved without solar concentration, featuring zero maintenance and avoiding the added extra costs deriving from the need of a complicated tracking system as well as cleaning of the reflectors, resulting in reduced system costs [11,12].



Figure 2.3.11 Left) TVP Solar High Vacuum Evacuated Flat Plate Collector. Right) Efficiency of MT-Power v 4.0 high vacuum insulated collector by TVP Solar (adapted from [12]).

The industrial field of solar thermal flat panel working at mid temperature is new and not deeply investigated, so there is extensive room for improvement in performances: the scope of this PhD project is to explore ways to improve the efficiency in solar to thermal energy conversion of these new generation of solar thermal collectors. As mentioned before, high vacuum insulation reduces the internal gas convective and conductive losses to a negligible level, keeping high conversion efficiency at high working temperature (Figure 2.3.12). In this case the thermal radiation is the main loss mechanism, and the radiative properties of the solar absorber are an aspect of primary importance. Figure 2.3.12 right) shows how, by acting on the radiative properties of the solar absorber, radiative losses could be further reduced (orange dash line) resulting in a performance increase (green dash line). Selective coatings optimized for the new working temperature range, introduced by the new high-vacuum insulated flat-panels, are not developed or sold yet. There are commercial solutions of solar selective coatings that still result in excellent performances up to 150 °C, but for higher temperatures no marketed alternatives neither research studies that propose valid SSA coating optimized for EFPC technology are released. Hence, the main purpose of this research will be to develop a method to optimize solar selective coatings well suited for EFPCs emerging technology, focusing on a simple-to-realize, industrially feasible and robust selective coating, for both low and high temperature applications.



Figure 2.3.12 Effects of high vacuum insulation on the performance of a flat plate solar collector. Left) Efficiency and losses in a standard flat plate solar collector without vacuum insulation. Right) Efficiency and losses of a high vacuum insulated flat plate solar collector. Dash red lines identify the efficiency at 100 °C of both a standard flat plate collector and a high vacuum insulated flat plate collector.

3.Solar absorbers

3.1. Selectivity

Selectivity is defined as the property of a solar absorber to differentiate between the wavelengths of the solar spectrum radiation and the infrared wavelengths that are characteristic of the blackbody radiation temperature. Since solar radiation spectrum is limited to relatively short wavelengths UV/VIS/NIR, whereas a realistic terrestrial application is in the range of infrared wavelengths, an effective Selective Solar Absorber (SSA) should be able to discriminate between solar spectrum and infrared spectrum, being able to capture as much solar light as possible, while emitting as little thermal energy as possible.

The selectivity of an absorber can be characterized introducing the solar absorptance and the thermal emittance. The spectral emittance ε_{λ} could be defined as the ratio between the radiation energy emitted by the object itself $E_{\lambda}(T, Surface)$ that depends by the temperature T and the surface, and the energy emitted by a blackbody at the same temperature $B_{\lambda}(T)$ dependent by the temperature T:

$$\varepsilon_{\lambda}(T, Surface) = \frac{E_{\lambda}(T, Surface)}{B_{\lambda}(T)}$$
(3.1.1)

The total emittance $\varepsilon(T, Surface)$ or thermal emittance is obtained by integrating over all the wavelengths:

$$\varepsilon(T, Surface) = \frac{\int_0^\infty \varepsilon_\lambda(T, Surface) B_\lambda(T) d\lambda}{\int_0^\infty B(\lambda, T) d\lambda}$$
(3.1.2)

When radiative energy interacts with a given surface, part of it could be reflected, while another fraction could be absorbed and the remaining fraction could be transmitted, defining the spectral absorption, reflection and transmission coefficients, α_{λ} , ρ_{λ} , and τ_{λ} respectively. The sum of the three coefficients is 1 (see Equation 2.1.7):

$$\alpha_{\lambda} + \rho_{\lambda} + \tau_{\lambda} = 1 \tag{3.1.3}$$

For opaque surfaces transmittance is equal to 0, resulting in the following relationship:

$$\alpha_{\lambda} = 1 - \rho_{\lambda} \tag{3.1.4}$$

According to Kirchhoff's law, for a given surface in thermal equilibrium, spectral absorptivity and emissivity are equal:

$$\alpha_{\lambda}(T, Surface) = \varepsilon_{\lambda}(T, Surface)$$
(3.1.5)

Where α_{λ} and ε_{λ} are defined as the spectral absorptivity and spectral emissivity respectively, and they should both be considered as dependent on the temperature and the surface type. Even if, according to Kirchhoff's law, α_{λ} and ε_{λ} are equal at the equilibrium, α_{λ} is conventionally intended for the solar spectrum range while ε_{λ} is conventionally intended for infrared blackbody emission range.

This formulation let us define the spectral absorptivity and spectral emissivity as dependent by the reflectivity:

$$\alpha_{\lambda}(T, Surface) = \varepsilon_{\lambda}(T, Surface) = 1 - \rho_{\lambda}(T, Surface)$$
(3.1.6)

This allows us to write spectrally averaged solar absorptance and the thermal emittance as follows (for convenience dependence from the surface will be omitted from now on):

$$\alpha_{S}(T) = \frac{\int_{0\,\mu m}^{\infty \mu m} [1 - \rho_{\lambda}] S(\lambda) d\lambda}{\int_{0\,\mu m}^{\infty \mu m} S(\lambda) d\lambda}$$
(3.1.7)

$$\varepsilon(T) = \frac{\int_0^\infty [1 - \rho(\lambda)] B_\lambda(T) d\lambda}{\int_0^\infty B_\lambda(T) d\lambda}$$
(3.1.8)

Being $S(\lambda)$ (Wm⁻³) the spectral solar irradiance.

Because of α_{λ} negligible dependence on the temperature, the spectrally averaged absorptivity will be simply identified with the nomenclature α_s [36].

Thermal transfer efficiency η_t is defined as the solar irradiation converted into thermal energy at a certain temperature T and solar concentration C:

$$\eta_t = \alpha_s - \frac{\varepsilon(T)\sigma_{SB}T^4}{CS}$$
(3.1.9)

Being S (Wm⁻²) the integrated solar spectrum. Thermal transfer efficiency η_t allows to derive important energetic considerations as regarding the selective solar absorbers.

3.2. Ideal Selective Absorbers and cut-off wavelength

The ideal selective solar absorber is a reference point when dealing with selective absorbers. The ideal SSA spectral emissivity is assumed to be a step function which flips from 1 to 0 and the wavelength at which the transition happens is commonly named cut-off wavelength (λ_{cutoff}) [37,38]. In other words, an ideal SSA exhibits a spectral curve like the black line in Figure 3.2.1: $\alpha_{\lambda} = 1$ where $\lambda < \lambda_{cutoff}$ and $\varepsilon_{\lambda} = 0$ where $\lambda < \lambda_{cutoff}$. The formal definition of λ_{cutoff} descends from energetic considerations: it is the wavelength that maximizes the absorber thermal performance, and it depends on the working temperature and on the solar incoming power (i.e., solar concentration ratio) [14]. It was generally verified that λ_{cutoff} is the wavelength at which the blackbody emission curve crosses the solar radiation spectrum [14,38]. As shown in Figure 3.2.2, at low temperature, blackbody emission and solar spectrum barely overlap, allowing for a cut-off wavelength that allows $\alpha=1$ for almost all the solar spectrum wavelength range. When the operating temperature increases over 200 °C, the blackbody emission starts to overlap the solar spectrum and λ_{cutoff} is such that a significant part of the solar spectrum is in the range for which $\alpha_{\lambda} = 0$, which means that part of the incoming solar radiation will be lost in favour of reduced thermal radiation losses (Figure 3.2.2).

It is clear from equation 3.1.9 that, in absence of concentration (concentration factor C = 1), the thermal efficiency η_t has a strong temperature dependence due to the Stephan Boltzmann emission term that can be mitigated by a very low value of the thermal emittance. The presence of concentration C >1 reduces the radiation loss term, and the emittance loses importance with respect to the solar absorptance term. Since the blackbody irradiance is temperature dependent, also the ideal λ_{cutoff} that maximizes the thermal efficiency, depends on the absorber operating temperature and as well as on the concentration factor, as illustrated in Figure 3.2.3.

The ideal selective solar absorber neglects important aspects related to the non-ideal characteristics of an actual SSA, as the non-null thermal emittance, non-unitary solar absorption and the slope width of the reflectivity curve in the transition from low to high spectral reflectivity. These characteristics are well summarized in Figure 3.2.1 by a generic commercial SSA (in red line). Yang et al. [39] studied the effect of non-ideal SSA properties

on the performances of a Concentrated Solar Power (CSP) system: their simulated SSA has a finite constant slope in the transition from high solar absorptance to high reflectance (instead of the ideal step function) and a not null thermal emittance. The conclusion is that when dealing with a real SSA, the relative importance of solar absorptance and thermal emittance to enhance the absorber efficiency has to be taken into account.



Figure 3.2.1 On the left axis, spectral emissivity curve of real SSA (red line) and of an ideal SSA (black line). On the right axis the spectral irradiance of the sun (red area) and of a blackbody at a temperature of 250 °C (purple area).



Figure 3.2.2 Ideal Selective Solar Absorber spectral emissivity (left axis) and blackbody emission (right axis) for 100 °C working temperature (blue) and 300 °C working temperature (orange) vs Solar Spectrum (red, left axis). An ideal SSA presents α =1 in Solar Spectrum region and ε =0 in IR region. Transition between two regimens happens at the cut-off wavelength. Cut-off wavelength depends on both the operating temperature and solar concentration ratio and it is a key parameter to take into account in the design of a SSA optimized for mid-temperature application.



Figure 3.2.3 Ideal cut-off wavelength as function of the absorber temperature for different concentration factors.

Figure 3.2.4, shows a commercial solar absorber (Mirotherm 1300® from Alanod [40]) operating at 100 °C and 300 °C, respectively on left and right graphs. The commercial absorber under investigation is optimized for low temperature output. Despite the non-null thermal emittance and the slope width of the reflectivity curve in the transition from low to high spectral reflectivity, the absorber will result in excellent performances at 100 °C operation (Figure 3.2.4, left), because it will allow for high solar absorption while thermal emittance $E_{BB} \cdot \varepsilon_{\lambda}$ (dash blue line) is minimum, according to the fact that blackbody spectrum ranges in an interval of wavelengths for which ε_{λ} reaches its minimum values. On the contrary, the same solar absorber operating at 300 °C (Figure 3.2.4, right), shows high thermal losses (dash orange line) as the blackbody emission peak is situated where the commercial absorber still exhibits high α_{λ} values (or ε_{λ} according to Kirchhoff's law).



Figure 3.2.4 Emissivity of commercial SSA (Mirotherm 1300® from Alanod [40], black dotted curve, right axis), Solar Standard ASTM G173-03 (red line, right axis), 100 °C and 300 °C blackbody spectral emission (blue and orange curve respectively, left axis), SSA spectral irradiance at 100 °C and 300 °C (blue and orange dash curve respectively, left axis).

3.3. Relative importance of α and ε

Another important aspect that will be considered in the design of a real Selective Solar Absorber is the relative importance of solar absorptance and thermal emission. Efficiency equation for a solar absorber could be written as follows:

$$\eta_{abs} = \frac{q_h}{CH} = \alpha_s - \frac{\varepsilon_t \sigma_{SB} (T_h^4 - T_{amb}^4)}{CH} - \frac{h_{conv} (T_h - T_{amb})}{CH}$$
(3.3.1)

 η_{abs} = absorber efficiency, $\alpha_{S=}$ Solar absorptance, ε_t =thermal emittance, q_h =heat flux to the thermal system (Wm⁻²), H=Irradiance on the absorber (Wm⁻²), T_h=Absorber temperature (K), T_{amb}= temperature of the environment (K), σ_{SB} =Stefan-Boltzmann Constant (Wm⁻²K⁻⁴), h_{conv} =convective heat transfer coefficient (Wm⁻²K⁻¹) [14].

In a high vacuum envelope convective term is negligible and we can write:

$$\eta_{abs} = \frac{q_h}{CH} = \alpha_s - w\varepsilon_t \tag{3.3.2}$$

Where the weighting factor *w* is given by:

$$w = \frac{\sigma_{SB}(T_h^4 - T_{amb}^4)}{CH}$$
(3.3.3)

When weighting factor w is higher than 1, this means that thermal emission is more important than solar absorptance for the overall efficiency of the absorber. Figure 3.3.1 shows that in the case of high vacuum insulated flat panels (no concentration, high working temperatures), weighting factor is always higher than 1, meaning that thermal emittance is more important than solar absorptance in terms of performances.



Figure 3.3.1 Weighting factor versus Absorber temperature $T_h(^{\circ}C)$ for different solar irradiation (different concentration ratios) (black, red and blue lines). The red dot indicates the operating temperature (150°C) and the green arrow the increasing importance of thermal emittance with working temperature. The region for which weighting factor>1 is highlighted in yellow, and it is associated with high vacuum flat plate solar collectors.

Because high vacuum insulation reduces the internal gas convective and conductive losses to a negligible level keeping high working temperature, the thermal radiation is the main loss mechanism and the radiative properties of SSA are an aspect of primary importance. It is worth noting that thermal emittance gains weight over the absorptance as the working temperature increases (green arrow in Figure 3.3.1) and that HVFPs represent the only commercial product with w > 1. At present, several absorbers are commercially available, and when tested in unconcentrated solar panels under high vacuum they do not differ in a significant way from each other with a stagnation temperature of about 310 °C [41]. Currently the EFPC collector developed by TVP Solar includes the absorber Mirotherm® from Alanod [40], a commercial SSA optimized for low working temperatures (up to about 150 °C). It results in excellent performance up to 180 °C, but at higher temperatures the low selectivity of the absorber increases the thermal radiation losses, affecting the panel efficiency and limiting the stagnation temperature at about 320 °C with an illumination of 1000 W/m². The increased panel efficiency due to high vacuum has been studied also from other researchers [42] and the superior performance up to 250 °C have been predicted [13], if an optimized SSA was mounted in EFPC. However, the authors did not give any indication on how to produce such optimized SSA.

3.4. Spectrally selective absorbers

At present, the possible designs of the Selective Solar Absorbers could be classified in six major design types [38,43,44]: intrinsic absorbers, semiconductor-metal tandem absorbers, multilayer absorbers, ceramic-metal composites (cermet), surface texturing and photonic crystals. In this section the design architecture and working principles that characterize the main types of selective absorber will be reviewed.

3.4.1. Intrinsic selective absorbers

For the Intrinsic selective absorbers, the selectivity is an intrinsic property of the material. Even if there are some naturally occurring intrinsic solar absorbers, their selective properties are far from being optimal for these materials to be used as solar absorbers. Intrinsic solar-selective properties could be found in transition metals and semiconductors, but they need to be significantly altered to be useful as selective solar absorbers. [45]

For the typical metal the plasmon frequency, above which absorptivity gradually increases, is located at the ultraviolet wavelengths, as shown in Figure 3.4.1 a). From this figure is possible to notice how the cut-off wavelength is well below the ideal cut-off wavelength. In just few cases, such as for tungsten, absorptivity can reach acceptable values in the visible and near-IR, as shown in Figure 3.4.1 b) [38].

Between intrinsic absorbers, Hafnium carbide (HfC, Figure 3.4.1 b)) is a compound of particular interest because of its resistance to high temperatures, linked to its high melting point. However, to reach the desired properties, Hafnium carbide needs structural and compositional modifications and an antireflective (AR) layer [45].

Other examples of intrinsic absorbers which show a proper solar selectivity are the highly degenerate semiconductors such as Cu_2S (Figure 3.4.1 b)). However, also this kind of coatings requires additional features to achieve acceptable performance. In general, they function best as primary layers for more complex selective absorber designs, such as multilayer stacks or cermets [38].

In conclusion, intrinsic absorbers are stable and easy to fabricate but their non-optimal selective properties limit their commercial applications [46].



Figure 3.4.1 a) Reflectance of an ideal selective absorber compared to that of a metal and a heavily doped semiconductor. b) Spectral reflectance for the some intrinsic materials as HfC, tungsten and Cu₂S [38].

3.4.2. Semiconductor-metal tandem absorbers

In this kind of solar absorber, a semiconductor coating is deposited over a metal reflector as shown in Figure 3.4.2. Semiconductors and doped semiconductors are characterised by a particular electronic band structure. In a semiconductor a relatively small bandgap allows for a significant number of the valence electrons to cross the band gap and to move into the conduction band if excited with a certain amount of energy. The photons with a wavelength shorter than the bandgap of the semiconductor are absorbed by the valence electrons, while photons with a wavelength greater than the bandgap will be transmitted and reflected by the metal layer. The semiconductor will efficiently absorb the solar light while being transparent to the long-wavelength radiation that will be reflected by the low emissivity metal reflector. The wavelength region of the transition from absorber to reflector is dependent on the bandgap of the semiconductors show a high refractive index in the visible wavelengths, which results in high reflection losses, so an antireflection coating is required to enhance the performances of this kind of absorbers.

This coatings can withstand temperatures as high as 500 °C while keeping their optical stability [47]. However, the performances of this kind of coating are particularly sensitive to layer thickness variation, so they require an accurate control on deposition parameters. Diffusion barriers could be necessary to prevent the diffusion of the semiconductor into the substrate,

while buffer layers could be required to prevent the thermal mismatch between the substrate and the coating [48]. At mid-temperature applications the performances of this coating are affected by the high radiation losses that could be generated by electron hole pair generation and free carrier emission [37].



Figure 3.4.2 Schematic cross section of a semiconductor-metal tandem selective absorber[38].

3.4.3. Multilayer absorbers

Multilayer absorbers, also known as interference stacks, consist in a stack obtained alternating a dielectric layer (high absorptance in solar range, transparent in Infrared region) and a metal layer, thin enough to allow for partial transparency (Figure 3.4.3). The thickness of the various layer is chosen so that light in the solar spectrum wavelengths which is transmitted through a layer is reflected at the metal-dielectric interfaces. Multiple reflections happening at the layers interfaces (as shown in Figure 3.4.3) enhance the absorption of a specific range of the incoming solar spectrum wavelengths [38]. As long as the proper thickness is chosen for the layers, the stack results transparent to the longwave thermal radiation preserving the low emittance properties of the low-emissive metal substrate. An antireflective layer is often used to reduce the reflection due to the generally high refractive index of the dielectrics composing the interference stack, further enhancing the performances of the coating. The thickness of the dielectric determines the shape and position of the reflectance curve. Multilayer absorbers allow to control thermal emittance while guaranteeing high solar absorption and excellent thermal stability [49]. Several multilayer absorbers using different metals and dielectric layers have been studied over the years: some recent examples of multilayer coatings could be found in the works of Khelifa et al. that studied a Cr₂O₃/Cr/Cr₂O₃ multilayer absorber [50], Tsai et al. that presented a CrN/CrON/Al₂O₃ coating [51], and Khoza et al. With a $ZrO_x/Zr/ZrO_x/Al_xO_y$ multilayered coating [52].



Figure 3.4.3) Multilayer absorber scheme: multiple reflections happening at the interfaces enhance the absorption of a specific range of the incoming solar spectrum wavelengths while spectrally averaged emissivity is mainly due to the lowemissive metal substrate

3.4.4. Ceramic-metal composites (Cermet)

Ceramic-metal composites are also known as Cermet. Cermets consist of metal particles of nanometric size dispersed in a dielectric matrix. As shown in Figure 3.4.4, a cermet based solar absorber is usually constituted by one or more cermet layers deposited on IR metallic reflector, and an antireflective coating to reduce the reflection in the solar spectrum wavelengths enhancing the coating performances. Absorption is guaranteed by the cermet layers while spectrally averaged emissivity is mainly due to the low-emissive metal substrate. Cermet allows for high design flexibility, because their solar selectivity can be properly modified by acting on different parameters: materials of the dielectric and metal particles, particles concentration, shape, size, and orientation [38]. A single and homogeneous cermet layer is not usually able to guarantee ideal selective properties, so more complex structures have been studied over the years. A good example of advanced cermet structure is the graded cermet, which is characterized by a metal concentration that gradually decreases from the bottom of the film to the top [53] (Figure 3.4.4, left). The graded Cr–Cr₂O₃ cermet [54] is one of the most used selective coatings. A second example for an advanced cermet structure is a multilayer cermet structure in which each layer has a lower or higher metal volume fraction as shown in Figure 3.4.4, right [55].

Ceramic-metal composites selective absorbers have seen the most commercial success (being used in essentially all commercial vacuum tube receivers) due to their compatibility with inexpensive manufacturing techniques and reliability at temperatures up to 500 °C. Mirotherm® and Sunselect® from Alanod [56], and several types of TiNOx® from Almeco [57] are the most used coating of this type. However the optical properties of the cermet structure are still not fully understood [58,59], and their performance are hard to predict and be optimized.



Figure 3.4.4 Schematic of a cermet with a graded metal concentration (left) and a double cermet composed of low and high metal volume fraction layers (right) [38].

3.4.5. Textured Surfaces

Surface texturing is an alternative approach used to enhance the solar absorption of a surface, leaving its thermal emittance practically unaltered. To achieve high solar absorption, dendrite or porous microstructures (Figure 3.4.5) are used to generate multiple internal reflections, 'trapping' the incident light. The feature sizes of the used microstructures are chosen to be comparable to the wavelengths of the incident solar radiation to efficiently trap light in solar spectrum while resulting as a flat surface for the longer wavelengths (infrared range) [38].

Obviously by selecting an intrinsic material as the base surface, the performances of textured absorbers are further improved.

Textured absorbers are not very sensitive to environmental effects such as oxidation, interdiffusion or thermal shocks which significantly affect the lifetime of conventional multilayer selective

coatings [60]. To be employed as solar absorbers, textured surfaces need be protected from external damage deriving from contacts and abrasion and withstand high temperatures limiting their industrial applications.



Figure 3.4.5 (a) Schematic representation of a dendritic selective surface. Incoming sunlight can be internally reflected up to 50 times to enhance absorption. (b) SEM image of copper textured via an ion beam. [38]

3.4.6. Photonic crystals (PhC)

Photonic crystals consist of periodic arrangements of micro/nanostructures which affect electromagnetic wave propagation. They are fabricated by regularly repeating structures with high and low dielectric constant [61,62]. Reflection and emission spectra of the selective absorbers could be modified using one-, two-, or three-dimensional (1D, 2D, or 3D) micro/nanostructures (1D and 2D structures respectively in Figure 3.4.6 and Figure 3.4.7). Periodicity of the same characteristic dimension of the wavelengths to be controlled can give rise to bands of allowed and forbidden electronic energy bands. Highly efficient solar absorbers could be achieved by using photonic crystals with allowed states in the solar spectrum and forbidden states in the IR spectrum. Photonic crystal's ability to control the radiative properties of a surface promises unprecedented thermal efficiencies, however their use as solar absorber is still limited, because of the relatively complex process of fabrication and because of the technical challenge in realizing structures that are stable at high temperatures. The combination of repeating structure using different materials used to create a photonic device implies many interfaces between the various layers, usually resulting in delamination and thermal stability issues.



Figure 3.4.6 Schematic of a binary 1D tungsten grating. The geometry of the binary grating is determined by its period (Λ), filling ratio (f), and ridge height (h). Adapted from [61].



Figure 3.4.7 SEM images of two fabricated 2D single crystal tungsten PhC samples. Adapted from [62]

3.5. Substrates

Many of the presented selective solar absorbers make use of a metallic IR reflector substrate, because they take advantage of the properties of the coating that will efficiently absorb the solar light while being transparent to the long-wavelength radiation, that will be reflected by the low emissivity metal reflector. With that said, the thermal emittance of the metallic substrate is a parameter of primary importance in terms of overall efficiency of the absorber. This is particularly true for high vacuum insulated collectors. In fact, for standard flat plate collectors the absorber uncoated side is insulated by rock wool, while the coated side is in air or inert atmosphere, plus they will not reach high temperatures and so and it is not useful to provide a low emissivity surface finishing to further reduce substrate emissivity. In high vacuum insulated flat collectors the solar absorber exchange heat mainly in form of thermal radiation with the surroundings. For this reason, together with the high temperatures reached thanks to the high vacuum insulation, it is extremely useful to provide a low emissivity substrate to reduce the thermal losses. The ideal substrate, in addition to good optical properties should be cheap, chemically stable and have high temperature resistance.

Table 3.5.1 (adapted from [63]) lists the thermal emittance of some typical metals that can be used as substrates for solar absorbers. Copper and aluminium have the best trade-off between cost of the bulk and optical properties, and they are the most used substrates. Stainless steel has a thermal emittance of one order of magnitude higher than the lower emissive metals as copper, but its use is almost mandatory for absorbers that should resist to high temperature applications, thanks to its superior mechanical properties and thermal stability.

Emittance	Material
0.01-0.03	Pure silver (Ag), polished
0.02-0.03	Pure copper (Cu), polished
0.02-0.03	Pure gold (Au), polished
0.03	Pure tungsten (W)
0.02-0-06	Pure aluminium (Al), polished, unoxidized
0.05	Wrought commercially pure aluminium (Al)
0.05	Pure iron (Fe), unoxidized
0.05-0.07	Pure nickel (Ni), polished
0.04-0.09	Commercially pure nickel (Ni), cleaned
0.07	Pure molybdenum (Mo)
0.06-0.1	Pure chromium (Cr)
0.1	Carbon steel, polished
0.2-0.3	Austenitic stainless steel, cleaned
0.2-0-4	Ferritic stainless steel, polished

 Table 3.5.1 Thermal emittance for some typical metals in increasing order. Approximate range to 500 °C, from lowest to highest value. (Adapted from [63])

3.6. Thermal stability

Thermal stability is a rather important parameter for selective solar absorbers, because a stable absorber guarantees its performances all along its service lifetime (that should be superior or at least equal to the lifetime of the solar collector itself, usually 20-25 years). The thermal stability is defined as the capacity of the materials to withstand performance degradation due to changes of the properties of the material generated by high temperature activated processes and thermal shocks.

Thermal shocks could affect the performance of multiphase solar absorbers because the difference between the expansion coefficients of the various phases generate thermal stress among the phases leading to microcracking, peeling, bulging [64].

Solid state diffusion mechanisms between the different phases of the coating and between the coating and the substrate involve alteration of the optical properties and a deterioration of the performances of the coatings [65]. Diffusion barriers are used to limit or slow down interdiffusion phenomena.

Exposure to air, humidity, water, and pollutants are another cause for deterioration of the absorber, but not in the case of high vacuum insulated collectors, where thermal stress and diffusion are the main important mechanisms in terms of performance deterioration.

Short duration heat treatment

Short duration heat treatments consist in heating the solar absorber in a vacuum furnace at temperatures usually higher than the operating ones, for short periods of time (order of 10^1 hours). Preliminary information about the thermal stability of the coating could be collected by measuring the optical properties of the coating before and after the heat treatment. Example of this kind of treatment could be found in [14] or [66].

Accelerated ageing

The accelerated ageing test methods are used to predict the service lifetime of the solar absorbers. The International Energy Agency (IEA) formulated an accelerated thermal stability testing and service life prediction method for solar absorber coatings. This method is currently the standard, named ISO/CD 12592, 2 "Solar Energy - Materials for flat-plate collectors -Qualification test procedures for solar surface durability" [67]. Such standard is developed for standard collector working in air at low temperature. The standard assumes that the degradation is caused by diffusion processes according to the Arrhenius' law. The activation energy E_T, according to Arrhenius' law, is the fundamental coating parameter that determines the ageing resistance at the operating temperature. The exponential temperature dependence of the Arrhenius law allows to perform accelerated aging tests using a temperature higher than the operating temperature and to estimate the failure time (the time at which the absorber efficiency is reduced more than the value defined according to the reported standard). However, the absorber temperature changes during the normal working conditions. Such temperature variations can be summarized by a temperature frequency function f(T) that represents how many hours the absorber is at temperature T during one-year operation. It is possible to replace the function f(T) with an effective constant temperature T_{eff} that produces the same aging effect than the real f(T). The degree of aging of a coating can be evaluated through the Performance Criterion (PC), which can be evaluated by measuring the optical characteristics of the absorber.

The PC value is periodically measured during the tests, and the ageing test is stopped when a measurement returns a PC value higher than the one defined as the maximum degradation for a service lifetime of 25 years (Standard ISO/CD 12592, 2). The time when the PC reaches its maximum acceptable value during testing is not experimentally accessible and it is usually extrapolated from the different measurements and used to evaluate the service lifetime. Because this method has been developed for collectors working in air at low temperature, it is not adequate to evaluate the service lifetime of solar absorber in evacuated flat collectors. A different performance criterion has been proposed in [68] especially intended for high vacuum insulated collectors, and some of the absorber that will be proposed in this thesis have been tested, forecasting a service lifetime >25 years.

3.7. Summary

The radiative properties of the Selective Solar Absorbers are an aspect of primary importance to achieve high solar-to-thermal conversion efficiency, especially when the thermal radiation is the main thermal loss mechanism, as in the case of high vacuum evacuated solar collectors. At present, the possible designs of the Selective Solar Absorbers could be categorized in six major design types [38,43,44]: intrinsic absorbers, semiconductor-metal tandem absorbers, multilayer absorbers, cermet, surface texturing and photonic crystals. Bermel et al. in [38] reported some of the best performing SSA for each design found in literature in terms of both experimental and simulated results. Some of the best performing selective coating have been reported in Table 3.7.1 (adapted from [38]). New recently proposed structures and the most recent journal publications could be found in [69][70] for nano-multilayers, [50-52] for multilayers, [71] for photonic designs, [72] for structured graphene metamaterial, [73] for multi-layered cermets. According to the literature data, it could be found that at present the best performing designs built and tested are multilayers and ceramic-metal composites. Among these two design multilayer coatings appear to be the best suited for the purposes of this work, because it allows to control thermal emission still guaranteeing high solar absorption and excellent thermal stability, they have a flexible design, and they are easy to be realized at industrial level.

Except for the photonic crystals which require particular techniques to achieve the micro/nanometric 2D or 3D structures and to guarantee the stability at high temperatures, the remaining solar coatings designs are comparable in terms of production costs because the costs are mainly chargeable to the metal substrate, since the materials used for the coatings are usually very cheap, and the coatings themselves are thick only few nanometres (order of 10^2 nm), making the cost of the coating material negligible with respect to the cost of the bulk substrates.
			Experi	ment				
Туре	Material	α	ε	Measurement temperature (°C)	α	ε	Measurement temperature (°C)	Thermal stability (°C)
Intrinsic	Si3N4/ZrB2[74]	0.93	0.09	102				527
Semiconductor	SiO ₂ /TiO ₂ /α-Si/Al [75]	0.79– 0.81	0.12– 0.14	400				400
/metal	4 FCs**+ Ge + 1 BC*** + Ag [76]				0.907	0.016	127	
	SiO2/Ti/SiO2/Al [49]	0.95	0.063	327				
Multilayer	11 layers of W, TiO ₂ , and MgF ₂ [77]				>0.95	<0.06	447	
	AlxOy/Al/AlxOy [78]	0.95– 0.97	0.05– 0.08	82				300
Cermet	SiO2/Ni:Al2O3(f = 0.61)/Ni [79]	0.94	0.07	100				500
	SiO2/Mo:Al2O3(f = 0→0.5)/Mo [80]	0.96	0.1	350				650
	AlN/Al:AlON(f = 0.143)/Al:AlON(f = 0.275)/Al [81]	0.96	0.08	80	0.958	0.035	80	400
	FC + 4 layers of W:SiO2 + Reflector [82]				0.979	0.042	127	
	Cu surface texture	0.978		427				
Surface texture	[83]	0.983		627				
	α–Si nanocones [84]	>0.93						
PhC	2D W square array cylindrical air holes [62]	>0.8	<0.1					
	2D W hexagonal array cylindrical air holes [85]				>0.95	<0.1		

Table 3.7.1 Performance and thermal stability of some solar selective coatings for the six major SSA designs. (Adapted from [38])

*ARC: anti-reflection coating ** FC: front coating [76] ***BC: back coating [76]

4. Experimental setups & measurements

Thin film and coatings that are the basis of selective solar absorber designs and architectures are usually fabricated using Physical Vapour Deposition techniques (PVD). PVD defines a variety of vacuum-based deposition methods, for which the target material is evaporated from a solid (or liquid) source and then condensed in solid phase on the substrate [86]. Most used PVD techniques are sputtering and evaporation.

A variety of techniques are used to characterize the properties of the fabricated coating like surface composition, depth distribution, film thickness, structure, roughness. These techniques are based on probing methods as scanning probe methods, photon, electron, and ion methods [87]. This chapter briefly introduces the PVD fabrication methods and thin film characterization instrumentation used in this work. A custom made calorimetric instrument developed in collaboration with TVP Solar [11] and CNR-ISASI [88] of Naples is also described in this chapter.

4.1. Sputtering

Sputtering deposition is a type of physical vapour deposition technique based on the sputtering phenomena: when a solid surface is bombarded with energetic ions, surface atoms of the solid are scattered backward due to collisions between the surface atoms and the energetic particles as shown in Figure 4.1.1 [89].



Figure 4.1.1 Sputtering process, scheme of concept. (Adapted from [89]).

Sputtering deposition technique allows to deposit film coatings of thickness that ranges from a few Angstroms to micrometres. There are several types of sputtering systems including Direct Current (DC) diode, Radio Frequency (RF) diode, DC Magnetron Sputtering (DCMS) and RF Magnetron sputtering (RFMS), DC Reactive Magnetron Sputtering (DCRMS) and RF Reactive Magnetron sputtering (RFRMS).

The simplest system is the DC diode, shown in Figure 4.1.2, left. The system is composed of two planar electrodes (a cathode and an anode). The surface of the cathode is composed by the material to be sputter-deposited, while the substrates are placed on the anode. To sustain the sputtering process, the vacuum chamber is filled with an inert gas (usually Argon), at pressure of the order of 1-5 Pa. By applying a DC voltage between the electrodes, a glow discharge (plasma) is generated. The Ar^+ ions generated in the glow discharge are accelerated by the potential difference towards the cathode where they hit and sputter the target material that leaves the cathode and ends on the substrates. In DC sputtering systems the target needs to be an electrical conducting material to ensure the current flow (thus the glow discharge) between

the electrodes. If the target is an electrical insulator the sputtering discharge cannot be sustained because positive surface charges will build up on the target insulator material. For insulating materials Radio Frequency (RF)s puttering is used. RF technique works alternating the electrical potential between the electrodes to avoid a charge building up the target. Figure 4.1.2, right shows an RF system [89].

A sputtering process is defined as reactive sputtering when the atoms sputtered from a target (usually a metal target) and reactive molecules introduced in the system during the deposition chemically react to form and deposit on the substrate a compound thin film. As a reactive source is usually used a gas. The gas source can be a pure reactive gas or a mixture of pure gases or a mixture inert gas – reactive gas [89]. The introduction of reactive processes complicates inevitable the deposition because control over the new additional parameters is needed. Usually sputtering processes are subject to hysteretic behaviours that may affect the deposition. Parameters like partial pressure of the reactive gas or the pumping speed are of fundamental importance to control the reactive process and the quality of the film [90]. Reactive sputtering process can be carried on all the standard sputtering equipment like (DC), (RF), (DCMS) and (RFMS), and it is widely used in coating industry.



Figure 4.1.2 Sputter deposition systems: DC and RF diode. (Adapted from [89]).

Lowering the pressure in the chamber could increase the deposition rates of the sputtering process, and it could avoid process gas molecules being included in the growing film, affecting the film properties. Due to the low working gas pressure, the sputtered particles traverse the discharge space without collisions, which results in high deposition rate and a film with less impurities. If the pressure is too low however, the plasma discharge cannot be sustained as too few positive ions can be generated (few particles per unit volume due to the low pressure will result in few collisions between electrons and process gas particles). To lower the pressure magnetron sputtering is introduced (Figure 4.1.3). In magnetron sputtering systems a magnetic field is used to trap electrons in the glow discharge, by driving them along drift paths in closed loops. The electron trapping effect increases the collision rate between electrons and inert process gas molecules allowing to sustain the plasma. So, the magnetic field increases the plasma density, which leads to increases of the current density at the cathode target, effectively increasing the sputtering rate at the target [89].



Figure 4.1.3 Sputter deposition systems: magnetron sputtering. (Adapted from [89]).

Experimental Setup

The sputtering system used to deposit the multi-layer coating samples presented in this thesis is shown in Figure 4.1.4. The system has a cylindrical vacuum chamber equipped with four sputtering targets of 10 cm diameter placed at 90 degrees from each other, Figure 4.1.4 b). A rotating supporting disc with four sample holders allows to place the substrates under the desired cathode and deposit up to four different materials without breaking the vacuum, Figure 4.1.4 c). The distance between the cathodes and the substrate is set to 10 cm, and the substrate is static during deposition. Flow rates are controlled by means of flowmeters and mass flow controllers. Pressure in the chamber, during the sputtering process, is measured by a capacitance gauge (Pfeiffer CMR 364). All samples are loaded in the chamber the day before and pumped down overnight by a 1500 l/s turbomolecular pump to obtain the same base pressure of about $2x10^{-5}$ Pa. Before gas injection, the pumping speed is reduced by a throttle valve without affecting the base pressure. A rotating shutter placed at few cm from the cathodes (Figure 4.1.4 b)) is used to control the deposition time and, as consequence the layer thickness.



Figure 4.1.4 Sputtering deposition system. The sputtering apparatus a). Sputtering targets b). Rotating supporting disc with four sample holders c). Plasma discharge during deposition process d).

4.2. Electron beam

Electron beam evaporation (e-beam) is a physical vapour deposition technique, useful to produce thin film coatings. Using e-beam technique we are able to deposit film coatings of thickness that ranges from a few Angstroms to micrometres. Figure 4.2.1 shows the basics of electron beam deposition technique. An electron beam is usually generated by thermionic emission. The generated beam is accelerated thanks to a potential difference of the order of 10 kV. Using focusing magnets the high kinetic energy electron beam is focused on the material to be evaporated. Part of the kinetic energy of the electrons is converted into thermal energy, causing the material evaporation. Vapours of the target material will deposit on the substrates

properly arranged in the upper part of the vacuum chamber. The evaporating material could be in form of ingots or pellets, and a crucible is usually used to contain the pellets. The filament that generates the beam and the target material are placed in a way that they don't see each other, to prevent the filament to be covered with the evaporating materials. A magnetic field provided by the so-called 'deflecting magnets' is used to bend the beam and direct it to the target. Additional magnetic fields could be used to steer the beam over a larger surface of the evaporation material. In electron beam systems the pressure in the vacuum chamber needs to at least lower than 10^{-2} Pa to allow the passage of the electrons from the electron cannon to the target material and avoid arcs generation. Rotating sample holders are often used to guarantee thickness uniformity of the deposited film on the substrate. To monitor the thickness of the deposited film during the deposition thickness monitors are used. Thickness monitors are usually based on an exposed oscillating quartz crystal whose frequency decreases as material accumulates. Because the thickness monitor is positioned at a certain distance from the substrate to avoid interferences, it measures a thickness that will be different from the actual thickness on the substrate, so a tooling factor (geometry dependent) is used to correct the reading output of the thickness monitor, so that it corresponds to the actual thickness of the coating on the substrate.



Figure 4.2.1 Electron beam physical vapour deposition technique, scheme of concept.

Experimental Setup

Figure 4.2.2 shows some details of the electron beam apparatus used to deposit some of the presented multilayer absorbers. The deposition chamber is equipped with an electron beam evaporation source and four routable crucibles, Figure 4.2.2 d): it is possible to deposit the desired number of layers alternating the four materials without breaking the vacuum. The ebeam system used is equipped with a rotating planetary that guarantees the samples thickness uniformity and the deposition of several substrates in the same conditions, Figure 4.2.2 c). A thermocouple allows to monitor temperature during the whole process: samples temperature never exceeds 80 $^{\circ}$ C.

Prior to depositions, the vacuum chamber is pumped down to a base pressure of 10^{-5} Pa and the materials are slowly outgassed to remove unwanted trapped gases (impurities). The deposition is controlled by a thickness monitor (Inficon model XTC/3). The tooling factor of the thickness monitor was calibrated depositing a thicker layer (about 500 nm) that was measured using a profilometer (KLA Tencor P-15). The step to be measured was obtained by lift-off procedure in acetone, using standard photolithographic technique. The thickness monitor automatically controls the e-beam current, to keep the evaporation rate constant, as

well as a shutter that stops the deposition once the desired thickness has been deposited. A careful calibration allowed us to obtain a thickness control in the order of 1 nm. All the depositions shown in this work have been carried out on smooth unheated glass substrates (roughness 1 nm).



Figure 4.2.2 E-beam deposition system. The electron beam apparatus a). Vacuum chamber b). Glass substrates mounted on the rotating planetary (thickness monitor sensor is also visible) c). Multiple crucible e-gun and copper crucible.

4.3. Mini Test Box

The Mini-Test-Box (MTB) is a custom experimental apparatus used to measure the absorptance and the thermal emittance of SSA in operating conditions (high vacuum, high temperatures). Figure 4.3.1 and Figure 4.3.2 show the Mini Test Box apparatus: it consists of a stainless steel high-vacuum chamber, closed by an extra-clear float glass, which can host a flat absorber suspended by four springs of negligible thermal conductivity (Figure 4.3.1 and Figure 4.3.2 c). The internal pressure is kept below 10^{-3} Pa by a turbomolecular pump in order to suppress convection and to reduce residual gas thermal conduction down to a negligible level. A thermocouple fixed to the sample measures the temperature of the absorber under investigation. Additional thermocouples record the temperature of the vessel and the glass.



Figure 4.3.1 CAD of the custom experimental apparatus used to measure the absorptance and the thermal emittance of SSA in operating conditions. The Mini Test Box apparatus consists of a stainless-steel high-vacuum chamber, closed by an extraclear float glass, which can host a flat absorber suspended by four springs of negligible thermal conductivity.

An array of LED lights is used to perform indoor measurements (Figure 4.3.2 b, c). The LED system has been calibrated to precisely control the supplied power per unite area and guarantee the spatial uniformity of the light irradiance. Details about LED system are described in [91]. The Mini Test Box is also equipped with a tilting support and a pyranometer to carry on outdoor measurements with solar irradiation spectrum [92] (Figure 4.3.2 a).



Figure 4.3.2 Mini Test Box apparatus under direct solar illumination (a) and under LED light illumination (b and c).

The Mini Test Box measures the actual absorptance and thermal emittance using a calorimetric approach. The variations of the temperature of the sample are strictly related to the absorbed power and the radiative power losses through the following power balance equation:

$$mc_p \frac{dT_a}{dt} = \alpha AP_{in} - \sigma_{SB}\varepsilon(T_h)A(T_h^4 - T_{amb}^4) - \sigma\varepsilon_{sub}(T_h)A(T_h^4 - T_{amb}^4)$$
(4.3.1)

Being *m* the sample mass, c_p the specific heat, α the absorptance, *A* the sample Area, P_{in} the incident Power per unit area, $\varepsilon(T_h)$ the absorber emittance, ε_{sub} the equivalent substrate emittance. During cooling down phase illumination is stopped and $P_{in} = 0$: Equation 4.3.1 allows to evaluate the thermal emittance of the tested sample $\varepsilon_{sample}(T_h) = \varepsilon(T_h) + \varepsilon_{sub}(T_h)$, because the only unknown term is $\varepsilon_{sample}(T_h)$ itself. Once $\varepsilon_{sample}(T_h)$ has been calculated Equation 4.3.1 can be used during heating up phase data to evaluate α . A detailed description of the measurement can be found in [36,93]. The behaviour of an absorber mounted in the MTB has also been numerically simulated using COMSOL Multiphysics [94].

The Mini Test Box also allows to perform experimental measurements of the efficiency of a solar coating at different temperatures through stagnation measurements. To perform the efficiency measurements the absorber is illuminated with different light power using the calibrated LED illumination system described in [91] and the absorber stagnation temperature is recorded. In such configuration the power losses are equal to absorbed power:

$$\varepsilon(T_{hS}) \cdot \sigma_{SB}(T_{hS}^4 - T_{amb}^4) + \varepsilon_{sub}\sigma_{SB}(T_{hS}^4 - T_{amb}^4) = \tau_{glass}\alpha_{LED}P_{LED}(T_{hS})$$
(4.3.2)

where α_{LED} is the absorptance α evaluated as in Equation 3.1.7, where the solar spectrum is replaced by the spectrum of the LED lump used to illuminate the absorber [91], $P_{LED}(T_{hS})$ is the light power provided by the calibrated LED system and T_{hS} is the absorber stagnation temperature at the given LED power. As consequence, at $T = T_{hS}$ the efficiency can be calculated, as reported below:

$$\eta(T) = \tau_{glass} \cdot \alpha_s - \frac{\tau_{glass} \alpha_{LED} P_{LED}(T_{hS})}{H}$$
(4.3.3)

where *H* is the irradiated power chosen as reference and set to 1000 Wm⁻², $\tau_{glass} = 0.91$, $\alpha_S = 0.95$ in the case of Mirotherm® coating (section 2.3.8) actually mounted on TVP Solar high vacuum flat collectors.

Figure 4.3.3 reports the Mirotherm® overall efficiency (as from Equation 5.1.2, chapter 5.1) when mounted in the MTB (blue solid line), the numerical simulation of the experimental setup (red dash-dot line) and the overall efficiency experimentally measured using Equation 4.3.3 (black dots).



Figure 4.3.3 Overall efficiency versus Absorber temperature T_h (°C): Mini-Test-Box (MTB) simulated efficiency (red, dash dot), Led Measured MTB efficiency (black dots), Mirotherm® overall efficiency calculated using Equation 5.1.2 (blue solid line).

4.4. Ellipsometry

Spectroscopic ellipsometry is a technique that allows to characterize thin film coatings in terms of thickness and optical constants.



Figure 4.4.1 Spectroscopic ellipsometry technique working principle.

Figure 4.4.1 shows the working principle of ellipsometry measurement [95]. A linearly polarized light beam hits the sample being reflected or transmitted. After the reflection the light becomes elliptically polarized, from here the name 'ellipsometry'. Ellipsometry measures the

change in polarization as defined by an amplitude ratio, Ψ , and the phase difference, Δ . The measured response depends on optical properties and thickness of the materials. The change in polarization in the ellipsometry measurement is commonly written as:

$$\rho = \frac{r_p}{r_s} = \tan(\Psi) e^{i\Delta}$$
(4.4.1)

Being r_s and r_p the Fresnel reflection coefficient respectively for s- and p- polarization. The incident light is linear with both p- and s- components. The reflected light has undergone amplitude and phase changes for both p- and s- polarized light, and ellipsometry measures their changes.

Ellipsometry is an indirect technique, because Ψ and Δ cannot be directly converted into the optical constants of the material. A flow chart that summarizes ellipsometry data analysis steps is reported in Figure 4.4.2 [96]. After a sample is measured, a model that describes the sample is constructed. In the case of a multilayer coating the model indicates the substrates, the layers which compose the coating positioned in the right order, an expected thickness and a dispersion model² which best describes the material for each layer (other information could be included as the roughness of the surface or the graded properties). This model is used to calculate the predicted response of the measured sample using Fresnel's equations [97], thickness of the layers and optical constants of each material. If the thickness and/or the optical constants are unknown, an estimation is used for the preliminary calculation. The calculated values are compared to experimental data. Any unknown material properties will be varied to improve the match between experiment and calculation. Fitting methods such as the least squares regression analysis are used to reduce the difference between experimental and theoretical curves. The unknown parameters of the material are varied until the best fit is reached. Some control parameters like the χ^2 are used to define the quality of the fitting.



Figure 4.4.2 Flow chart for ellipsometry data analysis [96].

Experimental Setup

Measures of the samples in this work were carried out using a phase modulated spectroscopic ellipsometer by Horiba Jobin Yvon – UVISEL [98]. The ellipsometer is equipped with a xenon

 $^{^{2}}$ A dispersion model defines the complex refractive index in function of the wavelength, using parameters with physical significance which are dependent on the material.

lamp and two detectors: it can analyse the optical response in the wavelength range from 190 nm to 2100 nm. A picture of the ellipsometer setup is shown in Figure 4.4.3.



Figure 4.4.3 Spectroscopic ellipsometer Horiba Jobin Yvon – UVISEL, used for ellipsometric measurements.

To obtain reproducible and reliable results all the films to be analysed were deposited on aluminium film, thick enough to be considered optically infinite, and grown on a glass support to be optically flat. An optically flat substrate allows to neglect the roughness parameter in the models that describe the fabricated thin film sample. Incidence angle of the incoming polarized light could be varied, and it is set so 70° for aluminium substrates.

Software DeltaPsi from Horiba allows to perform data analysis of the measured samples. Figure 4.4.4 shows the ellipsometric measured quantities Ψ and Δ (dotted) and the relative fitting (lines) for a Cr₂O₃/Cr bilayer on Aluminium substrate, model in Figure 4.4.4, inset. Forouhi-Bloomer formula was the dispersion model used for the chromium oxide [99,100], while for chromium and titanium metals Drude-Lorentz [101] dispersion relation has been used (details in section 5.1).



Figure 4.4.4 Ellipsomertric measured quantities Ψ (red, dotted) and Δ (blue, dotted), and the same fitted theoretical quantities Ψ (red line) and Δ (blue line). Al substrate is optically infinite, thickness for Al₂O₃, Cr and Cr₂O₃ is of 7, 15 and 70 nanometres.

Typically, ellipsometers do not measure ψ and Δ directly. Instead, they measure functions of ψ and Δ . In the case of phase modulated ellipsometers, such as the UVISEL PLUS and UVISEL 2, the three measurables are: Is, Ic, and Ic', which are functions of ψ and Δ according to Is = $\sin 2\psi \sin \Delta$, Ic = $\sin 2\psi \cos \Delta$, and Ic' = $\cos 2\psi$ [102].

4.5. Integrating sphere and OSA

An integrating sphere, coupled with an optical spectrum analyser has been used to carry out hemispherical reflectivity measurement on the test samples over visible and near-IR range (350-1750 nm). As the test samples are opaque, we can easily derive spectral absorption from reflectivity measurement (Equation 3.1.4). Figure 4.5.1 shows the working principle of an integrating sphere. Integrating spheres consist of a hollow sphere which is designed to achieve homogeneous distribution of optical radiation by means of multiple Lambertian reflections at the sphere inner high reflective surface, in such a way that the effects of the original direction of light are minimized. An integrating sphere preserves power information but destroys spatial information. A light source id used to illuminate the sample. The light reflected by the sample is collected by an optical fibre after being distributed homogeneously (multiple Lambertian reflections). The collected light is sent to an Optical Spectrum Analyser (OSA), to measure the distribution of power over a specified wavelength span. The output of the measurement is a spectral power intensity (W/nm) which depends on sample reflectivity, sphere properties, type of optical fibre, lamp used. Spectral reflectivity can be estimated by comparing the light power reflected by the test sample with that reflected by a reference sample of known spectral reflectance. Reflected power is defined by the ratio of reflected and incident power. From Equation 4.5.1, it is clear how we can measure the reflection ρ of the sample by simply measuring the measured spectral power reflected by the sample R_{sample} and the measured spectral power reflected by reference sample (and $R_{reference}$) of known reflectivity $\rho_{reference}$.

$$\rho = \frac{R_{sample}}{I_{incident}} = \frac{R_{sample}}{I_{incident}} \frac{R_{reference}}{R_{reference}} = \frac{R_{sample}}{R_{reference}} \rho_{reference}$$
(4.5.1)

Being $I_{incident}$ light power intensity incident on the sample. Equation 4.5.1 shows how the use of reference samples of known reflectivity $\rho_{reference}$, it is not necessary to measure $I_{incident}$.



Figure 4.5.1 Integrating Sphere working principle.

Experimental Setup

In the present project, ISP-REF integrating sphere coupled with an Optical Spectrum Analyzer (ANDO AQ-6315B) for the measurement of reflected light intensity have been used to measure the spectral reflectance of the test samples in the range 350-1700 nm. To correctly measure the reflectance of the test samples, calibrated references have been used. Spectralon® WS-1-SL diffuse reflectance standard from Labsphere (99% reflectivity in the range 400-1500 nm; >96% in the range 250-2000 nm, uncertainty < 2%), and STAN-SSL from Ocean Optics (~4% reflectivity from 200-2500 nm, uncertainty < 2%) are the reference standard used.

4.6. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy has been used for reflectivity measurement in near to far infrared range (1.5 μ m to 30 μ m). As the test samples are opaque, we can easily derive spectral absorption from reflectivity measurement (Equation 3.1.4). Figure 4.6.1 shows FTIR working principle. A beam of broadband Infrared light is sent to an interferometer [103], which produces an optical signal with all IR frequencies encoded in it. On its way out of the interferometer the light beam hits the sample where it is transmitted through or reflected off the surface of the sample itself, depending on the type of analysis performed. The sample absorbs light at specific wavelengths. The signal reflected (or transmitted) by the sample is collected by a detector. The output signal is time dependent, and it is characterized by a measured power intensity versus time. Fourier Transform [104] is used to convert the intensity-vs-frequency spectrum. Like for Integrating Sphere-OSA technique, the spectral reflectivity can be estimated by comparing the light power reflected by the test sample with that reflected by a reference sample of known spectral reflectance (Equation 4.5.1).



Figure 4.6.1 Fourier Transform Infrared Spectroscopy (FTIR), working principle.

Experimental Setup

For NIR to FIR measurements (1.4-20.0 μ m) Jasco FT/IR 6300 Fourier Transform Infrared Spectrometer has been used, a calibrated aluminium film reference (uncertainty less than 2%) has been used as the reflectance reference standard.

Figure 4.6.2 shows experimental result of optical spectroscopy carried out with the Integrating sphere (blue line) and FT-IR experimental measurements (green line) (numerical simulation of the coating is also reported). The two instruments overlap in the range 1.00-1.75 μ m indicating a good agreement between the two different measurement techniques.



Figure 4.6.2 Cr₂O₃-Ti- Cr₂O₃ multi-layer on Al substrate: experimental result of optical spectroscopy carried out with the Integrating sphere (blue line), FT-IR experimental measurements (green line), numerical simulation of the multilayer (red dotted line)

4.7. Profilometry

In this work a contact type profilometer has been used to measure the thickness of the deposited films. These type of profilometers are widely used in industrial fields, research, and development. A contact profilometer is an instrument used to measure surface properties of a material like a variety of roughness parameters, waviness, step height and others. The working principle of a profilometer is shown in Figure 4.7.1. Figure 4.7.1 a) (adapted from [105]) shows the profile data acquisition by a stylus type profilometer. The stylus tip is in direct contact with the surface whose properties are to be measured. To measure the profile of the surface under investigation the probe tip is moved linearly along the surface and the changes in position z captured by the tip are transmitted to a sensor by the arm, and they are used to reconstruct the surface profile. A feedback loop ensures that the stylus is pressed by a force coil (Figure 4.7.1 b)) against the surface with the proper force setpoint. The shape and the dimensions of the tip can significantly affect the measurements. Tip radius can be of less than 1 micrometre, and it is usually made of diamond. Figure 4.7.1 b) [106] shows a classic capacitance sensor that captures the z movements of the tip. Thickness of a thin film could be easily measured using a contact profilometer if a step height is obtained as shown in Figure 4.7.1 c) [107]. The step height is usually obtained using standard photolithographic techniques [108]: a mask is applied on the substrate before the coating process, and it will be chemically removed after the thin film has been deposited, leaving behind a step between the coating and the substrate.

The profilometer used for the measures of the multilayer test samples is a KLA Tencor P-15 profilometer profilometer (KLA Tencor P-15) with scan repeatability 0.8 nm or 0.1% of step height, whichever is greater, and the reproducibility is 1.5 nm or 0.25% of step height, whichever is greater. It can measure thicknesses ranging from few nanometres to microns with an uncertainty of \pm 5nm. The step height used to calibrate the deposition rates (section 5.3.2) are typically about 300 nm and they are obtained in dedicated layers by lift-off procedure in acetone, using standard photolithographic techniques. An example of a step height measurement performed with KLA Tencor P-15 profilometer is shown in Figure 4.7.2.



Figure 4.7.1 Stylus type profilometer a) [105]. Force coil and capacitance sensor that captures the z movements of the tip [106] b). Thickness measure of a thin film through a step height measurement c) [107].



Figure 4.7.2 Step height measurement measured with KLA Tencor P-15 profilometer.

5. Multilayer for Evacuated flat plate solar collectors

As discussed in section 3.3 the emerging technology of EFPCs places itself in a new field where the high working temperatures without concentration require special attention to be given to both solar absorptance and thermal emittance in the design of the selective coatings. The two most widespread solar thermal devices (Concentrating solar power (CSP) and standard flat plate solar collectors) justify the lack of interest by both the SSA manufacturers and the researchers in fine-tuning the thermal emittance against solar absorptance. In fact, for CSP the solar absorptance is dominating over thermal emittance because of the high value of the concentration ratio, while for the flat plate collectors the greater importance of solar absorptance over thermal emittance is justified by the low temperature output [14] (details in section 3.3).

Commercial solution of solar selective coatings such as Mirotherm® and Sunselect® from Alanod [56], and several types of TiNOx® from Almeco [57] still result in excellent performances up to 150 °C, but for higher temperatures no marketed solutions neither research studies that propose a valid SSA coating optimized for EFPC technology are released. There are in fact authors that tried to optimize a coating suited for high vacuum insulated flat collectors obtaining encouraging results but still far from being optimal. For example, Thomas et al. [109] optimized a solar coating for mid-temperature unconcentrated application, obtaining a stagnation temperature of about 230 °C under vacuum, still too low for the potentiality of EFPCs. The same authors declare that the coating could be further optimized to potentially increase the stagnation temperature to about 300 °C, but they did not show experimental evidence, and not even in this case they would be able to outperform the existing commercial absorbers.

The purpose of this PhD research project is to develop a method to optimize solar selective coatings well suited for EFPCs emerging technology, focusing on a simple-to-realize, industrially feasible and robust selective coating, for both low and medium-high temperature applications.

Among the possible SSA designs, as discussed in section 3, multilayer selective absorbers appears to be the best suited for the purposes of this work, because they allow to control thermal emission still guaranteeing high solar absorption and excellent thermal stability [49]. Multilayer architecture ensures the highest performance designs built and tested to date [38], their design is really flexible because it meets the need of having coatings qualified for different operating temperature by simply changing thickness of the layers leaving the architecture unchanged, it is easy to simulate and to optimize, while being simple to be industrially realized. As discussed in 3.4, multilayer absorbers consist in a stack obtained alternating a dielectric thin layer (high absorptance in solar range, transparent in Infrared region) and a metal layer, thin enough to allow for partial transparency. An antireflective layer is often used to reduce the reflection due to the generally high refractive index of the dielectrics composing the interference stack, further enhancing the performances of the coating. Like most of the selective solar absorbers designs they also make use of a metallic IR reflector substrate. Chromium Oxide and Chromium (or Titanium) proved to be valid candidates for the dielectric layer and metal layer respectively. The choice fell on these materials because Cr₂O₃/Cr structure has been already deeply studied above all in form of ceramic-metal composite, being applied in commercial absorbers such as Mirotherm® or Sunselect® by Alanod [56]. A $Cr_2O_3/Cr/Cr_2O_3$ multilayer deposited by e-beam has also been studied, showing interesting optical properties [50] and good thermal stability [110]. Last but not least, these materials are relatively cheap and easy to be handled. A single SiO₂ layer is used as antireflective coating to improve absorptance, while aluminium and copper are used as metallic IR reflector substrate.

Once the architecture of the multilayer coating is established, the optimization problem addressed in this chapter consists in evaluating the thickness of each one of the layers composing the multilayer stack which allows for a spectral reflectivity curve of the coating that guarantees the desired spectrally averaged radiative parameters α and $\epsilon(T)$ that ensure the highest efficiency at the target operating temperature, on the basis of the considerations discussed chapter 3.

5.1. Methods

5.1.1. Evacuated flat collectors: governing equations

The solar absorptance α_s and thermal emittance $\epsilon(T)$ can be then evaluated using respectively the equations 3.1.7 and 3.1.8.

Evaluating α_s and $\epsilon(T)$ from ρ_{λ} allows to evaluate the thermal transfer efficiency for the coating under investigation (unconcentrated application) using the following equation:

$$\eta_{coat} = \frac{q_h}{H} = \alpha_s - \frac{\varepsilon(T_h)\sigma_{sB}(T_h^4 - T_{amb}^4)}{H}$$
(5.1.1)

Where q_h (Wm⁻²) is the heat flux to the thermal system, T_h (K) the absorber temperature, T_{amb} (K) the environmental temperature, H (Wm⁻²) the solar irradiation, and σ_{SB} (Wm⁻²K⁻⁴) the Stefan-Boltzmann constant.

Equation 5.1.1 allows us to evaluate the coating efficiency without taking into account boundary conditions (such as the glass optical losses, conductive losses and substrate radiative losses due to the heat exchange between the back side of the absorber and the collector vessel). In case of negligible conductive and convective losses (as in the case of an absorber suspended in a high vacuum envelope), Equation 5.1.1 can be modified in order to evaluate the overall absorber efficiency, η_{all} of a flat absorber as following:

$$\eta_{all} = \alpha_S \cdot \tau_{Glass} - \frac{\varepsilon(T_h)\sigma_{SB}(T_h^4 - T_{amb}^4)}{H} - \frac{\varepsilon_{Sub}\sigma_{SB}(T_h^4 - T_{amb}^4)}{H}$$
(5.1.2)

where τ_{Glass} is the glass transmittance, and ε_{Sub} is the equivalent thermal emittance relative to the absorber back-side and the vessel and it could be considered temperature-independent. Equation 5.1.2 could be useful not only to evaluate the effective performances of an actual solar collector with good approximation, but it can be implemented in the optimization process of the selective coating, allowing to take into account factors like a relatively high emissive substrate in the trade-off between solar absorptance and thermal emittance. Needless to say that if we exclude the optical losses due to the glass transmittance, Equation 5.1.2 will define the efficiency of the absorber η_{ass} considering the absorber in its entirety, as consisting on both the selective coating on the front side (facing the glass cover) and a substrate on the back side:

$$\eta_{ass} = \alpha_s - \frac{\varepsilon(T_h)\sigma_{SB}(T_h^4 - T_{amb}^4)}{H} - \frac{\varepsilon_{Sub}\sigma_{SB}(T_h^4 - T_{amb}^4)}{H}$$
(5.1.3)

5.1.2. Accurate optical characterization of thin films

As discussed in section 4.4, ellipsometry is an indirect technique, because the measured quantities cannot be directly converted into the optical constants of the material. After a sample is measured, a model that describes the sample is constructed and an iterative procedure is used to vary the optical properties or thickness of each layer to fit the simulated optical response to the experimental data (detailed description in section 4.4). The inherent disadvantage of this technique lies in the fact that the required optical model should define the number of constituents, the structure and morphology of each constituent and the overall structure and morphology of the sample. For the correct interpretation of the measurements in most cases it is it is not possible to make an optical model without additional information like the number of layers, their structure, surface roughness, interfaces etc. For this reason additional measurements are usually required to build a valid optical model [111]. The optical model constructed for the analysis represents merely an approximate structure and the analysis result may include artifacts or large errors even when the fitting is sufficiently good [95]. In particular, an optical model could be easily expanded adding more information (i.e. more fitness parameters), but although increased degrees of freedom could improve the overall fitting, it would also increase the uncertainty in the physical structure model applied [112]. For this reason, it is important to limit to a minimum the degrees of freedom. To solve these issues and limit the uncertainty in the evaluation of the optical constants of the investigated films, in this PhD project, a new method to analyse the samples has been perfected to perform accurate ellipsometric analysis. This new method will be called *bound deposition method* for reasons to be explained below. Figure 5.1.1 shows the flow chart of the novel deposition method proposed. Two blank substrates (Al film on glass substrate) are loaded in the vacuum chamber of the PVD system. At this point the first multilayer Dielectric-Metal-Dielectric is deposited on both the substrates, it will be called *multilayer A*. At the end of the deposition the vacuum chamber will be opened, and of the two samples one will be kept for Optic Characterization (OC) and ellipsometric analysis, while the other will be loaded in the deposition system with a blank substrate (step III, Figure 5.1.1). The last step involves depositing a second multilayer Metal-Dielectric on the loaded samples. Two new multilayer coatings will be obtained in this step. They will be called multilayer B and multilayer C. Multilayer B will define Metal-Dielectric bi-layer on the aluminium-glass substrate, whereas multilayer C will define Dielectric-Metal-Dielectric five-layer on the aluminium-glass substrate (Figure 5.1.1, left column). The procedure leads to the production of three different samples that are bound together, allowing to constrain the fitting parameters during the ellipsometric data analysis. Figure 5.1.1, right column, shows the electron beam deposited samples E052, E053 and E054, representing multilayer A, multilayer C, and multilayer B, respectively.

The multilayers can be bound both 'internally' and 'externally' correlated. We define *internal* correlation the correlations between layers of the same material within a single multilayer. Internal correlation is based upon the assumption that the percentage deviation on the final thickness with respect to nominal value is the same for each layer of a given material, this allows to bind the layers of a multilayer within a single multilayer. Figure 5.1.2 shows an example of internally correlated layers within a multilayer. Nominal thickness values are derived from the estimated deposition rate knowing the deposition time.



Figure 5.1.1 Flow chart of a new deposition method (bound deposition method) to perform accurate ellipsometric analysis. Left column, example for a Cr₂O₃-Cr based multilayer. Central column, steps of the bound model. Right column, e-beam deposited experimental samples following the bound deposition method.

Nominal thickness values (nm)								
L6 6 F 65	FCr2O3.dsp							
L5 5 F 10	F Ti.dsp	L4=L6*0.38						
L4 4 25	F Cr2O3.dsp	L3=L5*1.00						
	F Ti.dsp	L2=L6*0.23						
	F Cr2O3.dsp							
L1 7.30	Al2O3_pal.ref							
S	Al_HJY.ref							

Figure 5.1.2 Example of internal correlation between layers of the same material within a single multilayer.

We define *external* correlation the correlations between samples deposited in the same batch. External correlation is based upon the assumption that the final thickness is the same for each layer of a given material for samples that belongs to the same deposition. Figure 5.1.3 shows an example of externally correlated layers within multilayers of the same batch.



Figure 5.1.3 Example of external correlation between samples deposited in the same batch.

The internal and external correlations will be exploited for the data analysis and fitting. A simultaneous fit is performed on the models of the multilayers, binding the parameters according to the *internal* and *external* correlations. For each material one and only one dispersion formula is used to fit the experimental results.

DeltaPsi2 is an integrated software platform for thin film analysis that powers and drives the HORIBA Scientific spectroscopic ellipsometers (section 4.4). The bound multimodel is a feature of the DeltaPsi2 software. The bound multi-model is used to perform fits on many different models, binding parameters between models, which makes it the perfect instrument for the data analysis of the bound deposition samples. Other samples externally or internally correlated with the three main samples can be added to the multimodel, to increase the statistical validity of the results and reduce the uncertainty that comes with the optical models flaws discussed before. The bound multimodel will return the thickness for each layer of the fitted models and the optical constants for each material that best fit the experimental data. Figure 5.1.4 shows the result of a fit for multiple multilayer test samples performed with the bound multimodel tool. I_c (red) and I_s (blue) are functions of the quantities Ψ and Δ . Each dotted curve represents the experimental data related to one sample, while the lines show the fitting result for each sample. The multimodel fitting of Figure 5.1.4 shows a quite perfect match between experimental and calculated curves, considering that multiple models are fitted at once. Although the fitting is slightly worse than in the case of a single model, it ensures the validity of the physical structure model applied.



Figure 5.1.4 Fit of material optical properties and layer thickness for multiple multilayer test samples: experimental data (dotted curves) Vs fitting (solid curves). I_c and I_s are functions of the quantities Ψ and Δ .

Figure 5.1.5 shows a comparison between the refractive index obtained by a simple ellipsometric fitting of a single sample (orange) and the refractive index obtained performing a bound multimodel fitting (blue) on multiple bound samples. Percentage deviation between the results of the two fitting methods (dash black line) shows moderate differences in the real part of the refractive index n, while for the extinction coefficient k significant deviation between the two methods is to be highlighted.



Figure 5.1.5 Left axis) Refractive index (a) and extinction coefficient (b) of electron beam deposited chromium oxide: result of ellipsometric fitting of a single sample (orange) compared to the result of bound multi-model fitting (blue). Right axis) Percentage deviation (dash black line) between the results of the two fitting methods.

Figure 5.1.6 shows the experimentally measured spectral absorptance (lines) and numerical simulation (dash lines) of electron beam deposited samples E052, E053 and E054 (picture in Figure 5.1.7) according to the bound deposition method, and sample E046 that is outside of the bound deposition. Figure 5.1.6 shows how there is a perfect match between measurements of the fabricated coatings and their numerical counterpart. Optical simulations make use the complex refractive index obtained with the bound deposition method. Percentage deviations between experimental data and the numerical counterparts are mostly within 5% for all the sample except for sample E054, confirming the validity of the physical model used and the obtained fit results. The higher percentage deviation for multilayer E054 could be due to the fact that being it the thinnest multilayer, eventual flaws in its optical model (roughness, partial oxidation of the metal during the deposition stage, deposition conditions...) affect to more significant extent the error. Sample E046 shows a perfect match between numerical and experimental data despite being outside of the bound deposition, adding value to the validity of the fit results.



Figure 5.1.6 On the left axis: experimentally measured spectral absorptance (lines) and numerical simulation (dash lines) of the electron beam PVD samples E052, E053 and E054, deposited according to the bound deposition method, and sample E046 that is outside of the bound deposition. Right axis, dash dot lines: percentage deviation between numerical and experimental data.



Figure 5.1.7 Picture of the samples E052, E053 and E054, deposited with electron beam technique according to the bound deposition method.

As discusses before in section 4.4, after a sample is measured a model that describes the sample is constructed. In the model it should be indicated the substrate and the layers which compose the coating positioned in the right order, an expected thickness and a dispersion model which best describes the material for each layer. An example of an ellipsometric model is shown in Figure 5.1.8. In the figure titanium and oxide layers are placed in the correct order on the aluminium substrate, a nominal value for the thickness of each layer is introduced in the model. Al₂O₃ natural passivation layer of the Al substrate has been included in the model and its thickness fixed to 7 nm. Aluminium layer is to be considered optically infinite as it is the substrate. In the model the nominal thickness values of titanium and chromium layers are derived from the estimated deposition rate knowing the deposition time. Thickness and dispersion formulae parameters are both fitted for titanium and chromium oxide, while being

fixed for the Al (and Al_2O_3) substrate. No surface roughness is considered in the model thanks to the choice of depositing the coatings on aluminium film on smooth glass substrates. The material of each layer is supposed to be homogeneous, so there are not gradient in the composition.

3	F	85.71	F Cr2O3.dsp
2	F	7.30	F Ti.dsp
1		7.30	Al2O3_pal.ref
S			AI_HJY.ref

Figure 5.1.8 Ellipsometric model generated in DeltaPsi2 software. The model describes a multilayer coating composed of a titanium layer and a chromium oxide layer on aluminium smooth substrate

For both titanium and chromium metals a classical Drude's dispersion formula has been used [101]. Drude's model uses the classical theory of free electrons. It is based on the kinetic theory of electrons in a metal which assumes that the material has positive motionless ions and a noninteracting electron gas. This model describes well the optical properties of the metals, but it does not take into account the band gap energy Eg. For this reason, Drude's model cannot be applied to dielectric materials as the chromium oxide, which is a dielectric material. Khelifa et al.[50], Contoux et al. in [113] and Barshilia et al. in [114] studied the structural properties of chromium oxide grown by PVD methods. These studies all confirm the amorphous nature of this material, hence Forouhi-Bloomer dispersion equation [99,100], which is well suited to amorphous semiconductors and dielectrics is used as the dispersion formula for chromium oxide. Forouhi-Bloomer formulation is based on the quantum-mechanical theory of absorption, and it considers the optical band gap in the inter-band region. Peaks that can be seen in the optical spectrum of the material described by Forouhi-Bloomer formula correspond to transition of electrons between valence and conduction band. Forouhi-Bloomer formulation was verified to reproduce our data very well as it is confirmed by fit of the measured experimental data (Figure 4.4.4), multiple fit of the bound multi-model (Figure 5.1.4) and optical measurements (Figure 5.1.6).

5.2. Electron beam deposited Cr₂O₃/Ti coating: optimization via target curve

As discussed in section 3.2, the ideal selective solar absorber is a reference point when dealing with solar absorbers, because it is an idealized absorber that guarantees the highest possible performances. Needless to say, a way to optimize a selective solar absorber is to define the best possible solution in terms of spectral emissivity, i.e. the ideal SSA, and use it as the target curve for a fitting procedure aimed at finding the parameters of the coating (such as thickness of the layers in the case of a multilayer absorber) that result in a selectivity spectrum as close as possible to the ideal one. The curve of the ideal absorber will be built entering the operating temperature, the eventual concentration ratio, and the reference irradiation spectrum. The spectral curve built in this way will be the target for our optimization process. In this work, a new absorber coating optimized to work at mid temperature, in high vacuum, without concentration will be developed based on an ideal selective absorber suitable for mid-

temperature application (the procedure is applicable also for other temperature ranges) [115]. Figure 5.2.1 shows an ideal SSA for mid temperature applications.



Figure 5.2.1 Ideal selective solar absorber curve that will be used as a target curve in the optimization process. Cut-off wavelength is varied in function of solar concentration and operating temperature. In the optimization process the relative importance between solar absorptance and thermal emission will be considered.

5.2.1. Materials and architecture

The SSA under investigation is based on $Cr_2O_3/Ti/Cr_2O_3$ tri-layer. The Cr_2O_3/Cr structure has been already deeply studied in form of cermet and it also used in some commercial absorber such as Mirotherm®. The multilayer $Cr_2O_3/Cr/Cr_2O_3$ deposited by e-beam has also been studied: it presents quite good optical properties [50] and good thermal stability [110]. The chromium metallic layer has been replaced with titanium with the aim to improve the limited solar absorptance reported in previous works [50,110]. A single SiO₂ layer is used as antireflective coating to improve absorptance. A sketch of absorber structure is reported in Figure 5.2.2: a Titanium absorbing layer is sandwiched between two Chromium Oxide (Cr_2O_3) dielectric layers on an aluminium substrate that acts like an IR reflector. Al₂O₃ natural passivation layer of the Al substrate has been included in the numerical simulations model. The multilayer structure is completed by an antireflective coating (ARC) based on SiO₂ to further enhance solar absorption. The materials were deposited by e-beam evaporation on an aluminium film on glass substrate and their complex refractive indices, used to simulate the solar selective absorber have been experimentally estimated via ellipsometry measurements [116].



Figure 5.2.2 Schematic structure of the multilayer under investigation. From bottom to top: glass substrate, aluminium film (250 nm) and its natural oxide (Al₂O₃), Chromium oxide (Cr₂O₃), Titanium (Ti), Chromium oxide (Cr₂O₃) and silicon dioxide (SiO₂).

5.2.2. Samples preparation and deposition technique

The materials composing the multilayer solar absorber coatings were deposited on smooth glass substrates (roughness 1 nm) using e-beam evaporation physical deposition technique

(Figure 5.2.3). The glass slides (TED Pella inc. #260230 made from optical grade soda lime glass) were cut in pieces of 25 mm \times 50 m and cleaned using soapy water and ultrasonic washing in acetone and isopropanol baths. The temperature of the substrates was monitored during the deposition process, and it never exceeded 80 °C.

The evaporating materials are Al, (Cr_2O_3) and Ti pellets with a purity of 99.999%. Prior to depositions, the vacuum chamber was pumped down to a base pressure of 10^{-5} Pa and the materials were slowly outgassed to remove unwanted trapped gases (impurities).

Evaporation rates were set on 0.2 nm/s for Al and Ti layers and on 0.1 nm/s for Cr_2O_3 layer. To facilitate optical studies all coatings have been deposited an aluminium coated glass substrates that have been exposed to air in order to obtain a reproducible Al_2O_3 natural passivation layer similar to that of the commercial aluminium rolls. The final SiO₂ anti-reflective layer was deposited by RF magnetron sputtering from a four inches high purity (99.995%) SiO₂ target. The deposition was performed at 200 W in a pure argon atmosphere (Ar pressure 2.5×10^{-1} Pa) and deposition rate was 0.11 nm/s, determined using the same procedure described before.



Figure 5.2.3 Electron Beam vacuum chamber: glass substrates mounted on rotating plates (left); multiple crucible e-gun and Cr₂O₃ crucible (centre), multilayer samples deposited on glass substrate.

5.2.3. Optical Characterization

Aluminium film thickness has been chosen to be optically thick and fixed to 250 nm for all produced samples. The Cr_2O_3 layer thicknesses have been varied from 5 nm up to 200 nm to study the possible influence of layer thickness on the optical properties. The film thickness was measured using a profilometer (section 4.7) The measured step heights were then confirmed by ellipsometric analysis. The refractive indices of the coatings were investigated using a phase modulated spectroscopic ellipsometer (section 4.4). Forouhi-Bloomer dispersion formula [99] was verified to well reproduce the experimental data, while Titanium was modelled using a classical Drude dispersion model [101] (detailed discussion in section 5.1). For aluminium, Al_2O_3 and SiO_2 layers literature data have been used [117–119] since from optical analysis they proved to fit well experimental data. Figure 5.2.4 shows the refractive index obtained by the characterization procedure and used in the numerical simulation of the multilayer solar absorber coating. The use of glass substrates allows us to obtain very smooth surfaces and, as consequence, the optical response can be fitted without including any surface roughness. The refractive index data outside the explored wavelength range were extrapolated using the theoretical models.



Figure 5.2.4 (a, b) Complex refractive index for Cr_2O_3 and Ti respectively: real part n on the left axis, imaginary part k on the right axis. (c) Emissivity curve of $Cr_2O_3/Ti/Cr_2O_3$ multilayer: experimentally measured absorptance (blue dotted line) and numerical simulation (black line).

 Cr_2O_3 refractive index (Figure 5.2.4 a) shows how both the real part of the refractive index *n* and the extinction coefficient *k* decrease with the wavelength, characteristic of the dielectric behaviour. In particular, extinction coefficient *k* reaches values close to zero already in the visible region, which indicates the transparent properties of the film at longer wavelength. That is an important property for a SSA since at high wavelengths the emissivity is dominated by the low emissivity copper substrate if the chromium layer is thin enough to be transparent in the infrared region. The refractive index of the pure Cr layer (Figure 5.2.4 b), shows typical metallic characteristics, i.e. *n* and *k* indices increasing with wavelength. In particular, the value greater than zero of the extinction coefficients, in all the wavelength range, indicates that Cr layer is primarily responsible for the light absorption.

Before proceeding with the multilayer optimization, it has been verified that the measured refractive indices and the numerical simulation program provide the correct multilayer optical response. A multilayer with the following layer thicknesses: 70/10/70 nm has been first simulated and then deposited on aluminium on glass substrate by e-beam evaporation (the ARC layer was not deposited in this case). In Figure 5.2.4 c) are reported the numerical simulation and the experimental measurements showing the good agreement. The experimental optical response of the produced multilayer has been measured from 300 nm to 10 μ m. To cover the whole spectral range we used an Optical Spectrum Analyzer (OSA) (300 nm up to 1700 nm) and a Fourier-Transform InfraRed (FTIR) spectroscopy (from 1200 nm up to 10 μ m) (sections 4.5 and 4.6, respectively). The almost perfect agreement in the overlapping region confirms the measurement quality as well as the simulation and deposition accuracy.

5.2.4. Optimization

A genetic algorithm is used to adjust layer thicknesses (including the antireflective coating layer) to fit the target curve, in this case an ideal SSA. The genetic algorithm creates a starting population of P individuals (in our case P=30 individuals per generation, i.e. 30 multilayers with different layer thicknesses) and a Figure of Merit (FOM) is determined; only individuals with best FOM will be retained. FOM function is defined as follows:

$$FOM = \frac{\sum_{i=1}^{N_{mo}} w[i] \cdot |Y[i] - Y_{mo}[i]|^n}{\sum_{i=1}^{N_{mo}} w[i]}$$
(5.2.1)

where w[i] is the weighting factor for the ith point, Y[i] is the value of the function being optimized for the ith point, $Y_{mo}[i]$ is the value of the target function for the ith point. $\Delta(FOM)/FOM < \zeta$ (with $\zeta=1e^{-5}$ the convergence tolerance value) determines the convergence of the algorithm. $\Delta(FOM) = \langle FOM \rangle -FOM$ and the quantity $\langle FOM \rangle$ corresponds to the average of *FOM* over the previous *X* generations of individuals (in our case *X* is set equal to 10). The exponent *n* has been set equal to 2. Fraction of genes randomly mutated in each generation is set to 20%. The weighting factor is used to take into account the relative weight of α and ε and it is set according to considerations discussed in paragraph 3.3. The spectral emissivity curve of an ideal selective solar absorber with a temperature dependent $\lambda_{cut-off}$ defined as in [14] was used as a target function (Y_{mo}). *Y* functions, representing individuals spectral emissivity curves, are calculated by optical simulations once multi-layer materials thicknesses and the ARC layer thickness are fixed.

Numerical simulations and the genetic algorithm optimization have been performed using IMD software [120], which allows us to estimate the optical response of a multi-layer structure. The simulated spectral emissivity curves resulting from the fitting procedure will be used to evaluate the temperature dependent thermal emittance which in turn allows us to evaluate the radiative losses and the SSA efficiency. The efficiency of the new absorber will be discussed in comparison with the efficiency of commercially available absorber currently used in HVFPs.

5.2.5. Numerical results

The optimization procedure described has been repeated for four working temperatures from 200 °C up to 350 °C, corresponding to different optimal λ_{cutoff} . Table 5.2.1 sums up the values of λ_{cutoff} , layer thicknesses, solar absorptance α_S , and thermal emittance $\varepsilon(T)$ for each selective coating, as resulting from the optimization procedure. In Table 5.2.1 are also reported Mirotherm® (from Alanod [40])solar absorptance and thermal emittance.

Reported values have been obtained by measuring the emissivity curve and they are in agreement with values declared from the producer [40].

1		5		1	L	3
Sample	Α	В	С	D	Ε	Mirotherm®
Optimization Temperature (°C)	200	250	300	350	-	-
$\lambda cut-off$ (μm)	2.47	2.37	2.19	1.79	1.50	≈2.5
Top dielectric layer thickness (nm)	110	98	81	59	46	-
Metal layer thickness (nm)	16	16	15	13	12	-
Bottom dielectric layer thickness (nm)	42	38	32	25	20	-
SiO ₂ Anti-Reflective Coating (nm)	70	67	63	60	52	-
Solar absorptance α_S	0.91	0.91	0.91	0.89	0.86	0.95
Thermal Emittance ε (200 °C)	0.056	0.050	0.041	0.031	0.026	0.058
Thermal Emittance ε (250 °C)	0.067	0.060	0.048	0.035	0.029	0.067
Thermal Emittance ε (300 °C)	0.080	0.071	0.057	0.041	0.034	0.076
Thermal Emittance ε (350 °C)	0.094	0.083	0.066	0.047	0.038	0.087

Table 5.2.1 Optimization temperature, $\lambda_{cut-off}$ for the desired operating temperature, layer thickness obtained from the optimization process, solar absorptance α_s and thermal emittance $\varepsilon(T)$ at 200 °C, 250 °C, 300 °C and 350 °C, calculated from Equations 3.1.7 and 3.1.8, for 5 multilayer absorbers. Sample E was designed to have a $\lambda_{cut-off} = 1.50 \ \mu$ m. In the last column the absorptance and emittance values of Mirotherm® are reported [40].

Figure 5.2.5 a) shows the spectral emissivity curve of the four optimized multi-layer absorbers and the spectral emissivity curve resulting from the optimization process obtained for $\lambda_{cut-off}$ = 1.5 µm (sample E). The results are compared with the Mirotherm® commercial absorber (blue line with square markers in Figure 5.2.5 a)) and they show that the SSA $\lambda_{cut-off}$ can be adjusted by varying the layer thicknesses, preserving a high solar absorption and a low thermal emission. In Figure 5.2.5 b), the temperature dependent thermal emittance of multi-layers, calculated according to Equation 3.1.8, is compared with the commercial coating currently used in highvacuum solar collectors (blue line with dots). Multi-layers with lower $\lambda_{cut-off}$ can reduce the thermal emittance and its temperature dependence, resulting in more than 50% emittance reduction at all temperature values.



Figure 5.2.5 (a) Spectral emissivity of multilayer selective absorbers optimized for different temperature and consequent $\lambda_{cut-off}$ compared with the emissivity curve of the commercial coating (blue line with square markers). (b) Temperature dependent emittance for different $\lambda_{cut-off}$ calculated using equation 3.1.8.

The SSA efficiency for the simulated multilayers and the commercial absorber, calculated from Equation 5.1.1, is plotted in Figure 5.2.6. The graph shows how temperature dependent thermal emittance shapes the selective absorber performance curves. Mirotherm® commercial absorber is optimized for standard flat-plate solar collectors: it shows the highest efficiency for lower values of operating temperature because of its higher solar absorption coefficient and a relatively low thermal emittance (see Figure 5.2.5 b)). Multilayers A and B are good options for mid temperature applications: although these two coatings have a lower solar absorptance α_S with respect to the commercial absorber, the improvement in thermal emittance (Figure 5.2.5 b, Table 5.2.1) results in comparable performances for high working temperatures. Multilayer C and D offer the highest stagnation temperatures thanks to the lowest thermal emittance, but a slightly lower efficiency in low to mid temperatures range. This is due to the low cut-off that reduces the power achievable from the Sun spectrum, resulting in a lower total absorptance α_S . However, starting from 200 °C, they present a coating efficiency higher than the other absorbers, including the Mirotherm®.



Figure 5.2.6 Absorber efficiency versus operating temperature for five multilayer absorbers with different $\lambda_{cut-off}$ optimized for different temperatures, and Mirotherm[®] commercial absorber (blue line with square markers).

In Figure 5.2.6 is also reported the efficiency of sample E, whose spectral emissivity was designed to have a $\lambda_{cut-off} = 1.5 \ \mu\text{m}$. Its cut-off is outside the typically explored wavelength interval, since it corresponds to a region of zero intensity in the Sun spectrum, one of the so-called *hidden regions* [14]. Despite the relatively low absorptance of sample E (0.86 respect to 0.95 for Mirotherm®), starting from 220 °C, its coating efficiency is higher than Mirotherm® thanks to its lower thermal emittance (0.029 respect to 0.067 of Mirotherm®).

A further reduction in $\lambda_{cut-off}$ below 1.5 µm can result in a further increase in the stagnation temperature, but drastically reduces the efficiency at lower temperatures (the curves are not reported here). This is due to the specific features of the solar irradiance spectrum, which rises very fast when wavelength reduces below 1.4 µm.

Figure 5.2.7 reports the Mirotherm® overall efficiency (as from Equation 5.1.2) when placed in the MTB (blue solid line), the numerical simulation of the experimental setup (orange dashdot line) and the overall efficiency experimentally measured using Equation 5.1.2 (black dots). Equation 5.1.2 was validated by using the MTB (the custom-made experimental setup described in Section 4.3, which allows us to evaluate the overall efficiency of the absorber by performing stagnation temperature measurements in high vacuum. In Equation 5.1.2 the thermal emittance of the aluminium substrate is set to be $\varepsilon_{Sub} = 0.045$, this value provides an excellent fit to experimental data, and it is in agreement with the thermal emittance calculated by FTIR measurements, as shown in [93]. The excellent agreement among numerical simulations, measured data obtained by Equation 4.3.3, and values descending from Equation 5.1.2 confirms that, if the conductive losses are negligible and the proper ε_{Sub} is taken in to account, Equation 5.1.2 is a valid instrument to evaluate the overall absorber efficiency. Figure 5.2.7 b) shows the overall efficiency calculated from Equation 5.1.2 for the coating with different cut-off and an equivalent thermal emittance of aluminium substrate of 0.045. The equivalent substrate thermal emittance is assumed to be constant with temperature.



Figure 5.2.7 a) Overall efficiency versus Absorber temperature T_h (°C): Mini-Test-Box (MTB) simulated efficiency (orange, dash dot), Led Measured MTB efficiency (black dots), Mirotherm[®] overall efficiency calculated using Equation 5.1.2 (blue solid line). (b) Overall efficiency calculated using Equation 5.1.2 for coating having cut-off as reported in Table 5.2.1 (see legend).

When estimating the overall efficiency for all the designed samples, it should be noted that the reduction in the $\lambda_{cut-off}$ affects in a less pronounced way the performances at low temperature, being all the values around 0.8 except for 1.5 µm case. In turn, when the temperature increases, the low thermal emittance plays a major role in preserving efficiency and, at temperature higher than 300 °C, the sample E shows the best performances with respect to the others and the stagnation temperature can be higher than 350 °C.

Moreover, it should be noted that for coating with $\lambda_{cut-off} < 2 \mu m$ the coating thermal emittance is lower than the industrial aluminium substrate emissivity. Hence the adoption of a substrate with a lower thermal emittance can significantly improve the efficiency. This result is not surprising: looking at the commercial absorber it is clear that the uncoated side of the absorber has a relative high roughness (Ra = 1.65 µm) and thermal emittance increases with roughness. The commercial absorbers have been developed for standard flat panels, for which the absorber uncoated side is insulated by rock wool, while the coated side is in air or inert atmosphere, and it is not useful to provide a better surface finishing to further reduce aluminium emissivity. To validate the numerical results the multilayer E has been realized on aluminium on glass substrate.

5.2.6. Experimental results

The multilayer E has been realized on aluminium optically thick film grown on glass substrate and the experimental results are reported in Figure 5.2.8 as red lines with square markers. In Figure 5.2.8 a) are also reported the simulated spectral emissivity of the multilayer E (red line) and the experimentally measured spectral emissivity of aluminium on glass substrate (black line with diamond markers). Since the refractive indices of the materials used in the simulations were experimentally measured, an almost perfect agreement between the simulation and the measured emissivity is obtained.



Figure 5.2.8 (a) The experimentally measured (red line with square markers) and numerically simulated (red line) spectral emissivity of the multilayer E. Black line with diamond markers is the experimentally measured spectral emissivity of the aluminium on glass substrate, whereas the grey area represents the normalized solar spectrum. (b) Thermal emittance as function of the temperature (right axis). On the left axis is reported the overall efficiency of the collector as function of absorber temperature according to Equation 5.1.2: $H = 1000 \text{ Wm}^{-2}$, $\tau_{glass} = 0.91$ and $T_{amb} = 25 \text{ °C}$, with $\varepsilon_{sub} = 0.045$ for the industrial aluminium substrate used in Mirotherm®.

In Figure 5.2.8 b) is reported on the right axis the temperature dependent thermal emittance $\varepsilon(T)$ of the deposited multilayer measured via FTIR spectroscopy (red dashed lines with square dots). The multilayer has a thermal emittance slightly lower than the numerical simulation (red dashed line).

On the left axis of Figure 5.2.8 b) is also reported the overall efficiency calculated according to Equation 5.1.2 using the numerical simulation (red line) and experimental values of α_s and $\varepsilon(T)$ (red line with square markers). The efficiency calculated from experimental values is higher than the calculated from numerical simulation, particularly at high temperatures, where the thermal emittance plays a major role. The improvement in efficiency and stagnation temperature highlights the importance of thermal emittance and a well-chosen cut-off. It is possible to achieve overall efficiency higher than 50% at temperature up to 267 °C and a stagnation temperature of 395 °C. At 260 °C the overall efficiency increases from 41% of Mirotherm® to 52% with optimized coatings, resulting in 25% relative increase.

Finally, it worth remembering that these results have been obtained on an aluminium on glass substrate with the aim to address the optical properties neglecting the roughness. Before to move to industrial production, the results must be repeated on industrial substrates and ageing studies must be performed.

In conclusion the results show that a reduction in thermal emittance is essential to reach high operating and/or high stagnation temperatures in solar thermal unconcentrated applications. An efficiency of 52% can be achieved up to 260 °C with a 27% relative increase respect to the commercial absorber on aluminium. The stagnation temperature can also be increased to about 400 °C without concentration. Such performances, if confirmed on industrial substrates, will allow HVFP to contribute to the energy transition from fossil fuels to renewable energy for efficient heat production. It is worth mentioning that using the presented absorber on aluminium industrial substrate the radiation losses from coating would represent only 35% of the total radiation losses at 300 °C and contribution from the uncoated aluminium side accounts for the remaining 65%. The HVFP performances would benefit from a substrate thermal emittance reduction. Such reduction could be obtained with a better finishing of the back side

of the aluminium substrate or using a substrate with a lower thermal emittance (such as copper or silver).

5.2.7. Thin film copper on aluminium bulk substrate

As discussed, the performances of a solar absorber for high vacuum insulated flat collectors would benefit from a substrate thermal emittance reduction, that could be obtained with a better finishing of the back side of the aluminium substrate or using a substrate with a lower thermal emittance (such as copper or silver). To better understand how the thermal emittance affects the performance of a solar absorber let us recall Equation 5.1.2, which defines the overall efficiency of a selective coating. The negative terms in the equation are defined as the *radiation losses* and they are responsible for the system efficiency reduction at medium-high temperatures. By reducing the thermal emittance term $\varepsilon(T)$ of the SSA its performance will be significantly increased. For relatively high emissive substrates (section 3.5), a simple and relatively cheap way to significantly reduce the emissivity of both the selective coating side and the substrate side of a solar absorber could be a low emissive thin film coating could be used increasing the performances.

For example, Mirotherm® from Alanod [40], which currently powers TVP Solar collectors, uses aluminium as a substrate. Russo et al. [36,93] showed how $\varepsilon_{Sub} = 0.045$ is the value for the thermal emittance of the aluminium that best fits the experimental results for Mirotherm® commercial coating. A simple yet effective way to enhance the performances of this solar absorber could be to deposit a low emissivity coating such as a copper coating (thermal emittance ≈ 0.02) on the back side of the absorber, on the aluminium surface, as shown in Figure 5.2.9.



Figure 5.2.9 Solar absorber with a low emissivity coating on the back side of the aluminium substrate. A titanium bonding layer is used to guarantee the adhesion of the coating.

To test the properties of the copper coating on the aluminium a Cu coating was deposited via electron beam deposition technique on aluminium bulk substrates. The actual absorptance and thermal emittance from low temperatures up to stagnation temperature (as high as 330 °C) are measured using a calorimetric instrument well described in [36] (see also section 4.3), based on the power balance equation defined in the following equation:

$$m c_p \frac{dT_a}{dt} = \alpha A P_{in} - radiation \ losses$$
 (5.2.2)

being *m*, *cp*, T_a , and *A* the mass, specific heat, temperature, spectrally averaged absorptivity and area of the absorber, and P_{in} the incident power density. Figure 5.2.10 shows the aluminium bulk substrate before and after being copper coated. Figure 5.2.11 shows the results of the calorimetric measurements for a bulk aluminium substrate before and after the copper coating: the spectrally averaged emissivity decreases from 0.05 for aluminium bulk to 0.025 for aluminium bulk-Cu coated.



Figure 5.2.10 Aluminium bulk substrate before (a) and after (b) copper coating via e-beam PVD.



Figure 5.2.11 Spectrally averaged emissivity of aluminium bulk (grey) and copper coated aluminium bulk (black).

Figure 5.2.12 shows the overall efficiency, calculated using Equation 5.1.2 for Mirotherm® solar absorber (black) and the same absorber with copper coated back side (red). The figure shows how at 250 °C efficiency of the absorber increases from 0.44 up to 0.52, with 18% enhancement in performances, and the stagnation temperature increases of about 20 °C. It is worth to note that the advantages of the low emissive coating increase with increasing temperature.



Figure 5.2.12 Overall efficiency of Mirotherm® commercial coating with bulk aluminium substrate (black), and with copper coating applied on the aluminium substrate (red).

As discussed before (section 3.4.3), for multilayer coatings, the spectrally averaged emissivity is mainly due to the low-emissive metal substrate, so it makes sense to use a low emissive

coating for the coating side of the absorber, too. This solution would allow to use cheap materials as a substrate as aluminium, while guaranteeing excellent optical properties of the absorber, using coatings of low emissive but more expensive materials at a negligible cost (see Table 3.5.1).

At high temperatures however, interdiffusion between the low emissive thin film and the aluminium substrate may cause adhesion issues and a deterioration of the optical properties, so an interdiffusion barrier should be used to limit the diffusion phenomena. A Cr_2O_3 diffusion barrier between the substrate and coating could be used, and the test of this solution is already started, and it will be part of a future work.

5.3. Sputter deposited Cr₂O₃/Cr based coating: optimization via custom algorithm

Even if in the optimization method described in section 5.2 leads to excellent results, it does not allow to achieve the best trade-off between solar absorptance and thermal emittance, when dealing with a real selective solar absorber [115], because important factors are neglected like the non-zero slope of the reflectance spectrum as well as the non-zero thermal emissivity of a real coating [39]. So, during this PhD project efforts have been made to perfect a new optimization method, based on the efficiency of the real coating that is considered as the fitness function of the optimization algorithm. The new optimization algorithm allows to find the best trade-off between solar absorptance and thermal emittance, that is strictly linked to the to the shape of the reflectivity spectrum $\rho(\lambda)$ of the coating. This method is particularly suited for the emerging technology of the unconcentrated flat plate solar collectors under high vacuum insulation, as they are able to reach high working temperature without concentration, with thermal emittance gaining importance on the solar absorptance [115].

The drawback of multilayer selective coatings is that multilayer coating architecture working principle is strongly based on multiple reflections at the interfaces between the layers composing the stack, so the performances of such solar absorbers are strongly affected by the thickness of the various layers. Aiming at the industrial mass production of these Selective Solar Absorbers we need to consider that the control on the deposition parameters could not be perfect, introducing errors on layer thicknesses, thus affecting the performances of the coatings. So, it is interesting to add to the designing stage a new, important parameter, that is the *robustness* of the performances of the coating for unpredicted errors on the thickness of the layers. Including this new factor as a part of the optimization process of a selective coating offers the possibility to pick not the absolute maximum of the solution, i.e. the coating with the highest performances that ensures the proper robustness for given errors on layer thickness.

5.3.1. Materials and architecture

For the multilayer selective solar absorber under investigation Cr_2O_3 and Cr have been chosen (the reasons of this choice are explained in section 5.2) as the dielectric and the high absorption

metallic layer, respectively. Copper was selected as a low emissive metallic substrate, while SiO₂ thin film serves as the antireflective coating.

To exclude roughness effect on the radiative properties of the solar absorber the low emissive substrate has been deposited onto smooth glass substrates. An optically thick copper layer (250 nm) has been deposited by e-beam PVD technique and then exposed to atmospheric air.

Figure 5.3.1 shows the architecture used for the multilayer coating. As shown in the figure a five-layer structure has been used. The Chromium layer directly deposited on the copper substrate acts like a bonding layer, while being able to prevent the formation of the emissive copper oxides during reactive sputtering deposition. This layer is integrated in the optimization process too, letting it be part of the absorbing package.

	SiO ₂	Layer 1 (SiO2)
	Cr_2O_3	Layer 2 (Cr2O3 top)
	Cr	Layer 3 (Cr top)
	Cr ₂ O ₃	Layer 4 (Cr2O3 bottom)
	Cr	Layer 5 (Cr bottom)
	Cu	Optically infinite substrate
	Glass	Substrate
\square		

Figure 5.3.1 Architecture used for the multilayer coating

5.3.2. Samples preparation and deposition techniques

To deposit the thin films, a magnetron sputtering machine has been used. Cr and Cr₂O₃ thin films are deposited using a 99.99% pure Cr cathode by means of DC Magnetron Sputtering (DCMS) and DC Reactive Magnetron Sputtering (DCRMS) process respectively. Argon was used as a sputtering gas for Cr deposition and oxygen was added as a reactive gas for Cr_2O_3 deposition. For Cr deposition, argon flow was set at 3.3 sccm corresponding to a pressure of 0.2 Pa. During Cr₂O₃ deposition an oxygen flow of 1.6 sccm was chosen to obtain stable deposition condition that produces Cr₂O₃ films with the required dielectric properties [113]. Figure 5.3.2 reports the discharge voltage as function of the oxygen flow rate, having set the argon flow rate at 3.3 sccm and the discharge current at 0.5 A. It can be noted that, increasing the oxygen flow rate from zero, the total pressure (right-y axis) is unchanged up to a flow rate of 3 sccm, and also the discharge voltage is almost constant, indicating that all injected oxygen is absorbed by the Cr film and partially by the Cr target that however remains metallic. At 3 sccm the discharge voltage starts to increase due to cathode poisoning [113], the total pressure has a jump and for increasing oxygen flows the pressure starts to increase linearly with the oxygen flow indicating that the oxygen pumping speed of the Cr target and of the growing film is reduced to a negligible level [90].



Figure 5.3.2 Left axis: voltage discharge for a fixed DC sputtering current (0.5 A) and fixed Argon flow rate (3.3 sccm) as function of the oxygen flow rate (black squares for increasing flow rate, red dots for decreasing flow rate). Right axis: total pressure as function of the oxygen flow rate (blue diamonds for increasing flow rate, orange triangles for decreasing flow rate).

According to [113], we fully oxidized the cathode at higher oxygen flow rate (20 sccm) and operated the deposition in the decreasing O_2 flow region, where the discharge voltage presents a maximum. Such optimal flow rate, corresponding to the maximum discharge voltage, represents the stable condition that guarantees less oxygen impurities in the growing film and it is indicated by the circle in Figure 5.3.2. For oxygen flow rates lower than the maximum, the cathode starts to fall back in the metallic condition, whereas at higher oxygen flow rate there is an excess of oxygen in the plasma that can be included in the growing film. It is worth to note that decreasing the oxygen flow rate from a fully oxidized cathode produces a linear decrease in total pressure down to the zero-oxygen flow rate that recovers the target to the original metallic condition. This reactive sputtering process shows hysteretic behaviour as mentioned in section 4.1. Before starting the deposition on substrates, the cathode is presputtered for 15 min to condition it and to obtain stable and reproducible depositions. The multilayer Cr₂O₃/Cr/ Cr₂O₃ is completed with SiO₂ thin film used as Anti-Reflective Coating (ARC) and deposited by RF magnetron sputtering (RFMS) technique in pure argon atmosphere. The deposition conditions, for the various layers, are reported in Table 5.3.1 [121]. The parameters of the copper substrate are also reported in the table to complete the SSA structure. E-beam PVD technique has been used for the deposition of the copper film that acts like the optically thick substrate. The deposition was performed in a vacuum pressure of 4 · 10^{-5} Pa with a deposition rate of 2 Å per second. The uniformity of the deposition on the substrates is guaranteed by a rotating planetary. Prior to copper layer deposition the glass substrates have been cleaned with soapy water first, then with ultrasonic baths in both acetone and isopropyl alcohol, and finally dried with a nitrogen flux. The reported deposition rates are calculated by the ratio between the layer thickness measured with the profilometer (KLA Tencor P-15) and the recorded deposition time. The step height to calibrate the deposition rates are typically about 300 nm and they are obtained in dedicated layers by lift-off procedure in acetone, using standard photolithographic techniques.

Layer	PVD	Ar flow (sccm)	O2 flow (sccm)	Power (W)/ Current (A)	Discharge Voltage (V)	Deposition Rate (nm/s)	Pressure (Pa)
Cu	E-Beam Evaporation	/	/	/	/	0.20	4E-5
Cr ₂ O ₃	DCRMS	3.3	1.6	0.5 A	390	0.14	0.3
Cr	DCMS	3.3	0.0	0.3 A	300	0.44	0.2
SiO ₂	RFMS	4.0	0.0	200 W	/	0.11	0.3

5.3.3. Optical characterization

To evaluate the refractive indices of the material constituting the multilayer absorber we used the ellipsometric technique. Measures were performed on layers deposited in the same conditions reported in section 5.3.2. Since on the copper surface it is present a copper oxide that growths in time, to obtain reproducible and reliable results the layers to be analysed were deposited on a different substrate, consisting of an aluminium film, thick enough to be considered optically infinite, and grown on a glass support to be optically flat. Thickness and complex refractive index ñ of the film were obtained by fitting the experimental data with numerical data returned by an optical model of the sample in which material dispersions are described by the proper dispersion formula. The experimental data were fitted by using the Forouhi-Bloomer formula for the chromium oxide [99,100], while for chromium Drude-Lorentz [101] dispersion relation has been used (detailed discussion in section 5.4).

Figure 5.3.3 a) and b) show the refractive index dispersion for both chromium and chromium oxide which best fits the ellipsometric experimental data, used for the optical simulations. The results are similar to those obtained for electron beam evaporated materials (section 5.2.3, [116,121]). The refractive index of the pure Cr layer (Figure 5.3.3 a), shows the typical metallic characteristics (*n* and *k* indices increasing with wavelength), where *k* value greater than zero in all the wavelength range indicates that Cr layer is primarily responsible for the light absorption. Both the real and imaginary parts of Cr₂O₃ refractive index (Figure 5.3.3 b) decrease with the wavelength, showing a characteristic dielectric behaviour. In particular, *k* index reaches values close to zero already in the visible region, which indicates the transparent properties of the film at longer wavelength. The reported refractive indices were able to fit Cr₂O₃ film for thicknesses from 15 nm up to 100 nm and Cr layer from 5 to 30 nm and they were obtained by fitting experimental data of several samples. The use of optically smooth surfaces allowed to exclude surface roughness effects in the models.

Since the ellipsometric analysis is limited in the range between 300 nm and 1600 nm, refractive indices of both chromium and chromium oxide have been extended outside the measured wavelength range by using the respective dispersion relations. The results show good agreement with literature data [117,122,123]. Reflection measurements further confirm the effectiveness of the obtained refractive indices: Figure 5.3.3 c) shows a comparison between measured and simulated reflection of a Cr_2O_3/Cr bilayer on aluminium substrate (model and layer thickness in inset). Integrating sphere coupled with an Optical Spectrum Analyzer (OSA) was used to measure the reflectance in visible and near-infrared range (0.35-1.75 µm) and
Fourier Transform Infrared Spectroscopy (FTIR) was used to measure reflectance in range 1.00-4.00 μ m. The two instruments overlap in the range 1.00-1.75 μ m indicating a good agreement between the two different measurement techniques. The optical simulation of the sample under investigation uses the refractive indices reported in Figure 5.3.3 and literature data for Al₂O₃ and Al substrate [101,117,118]. The agreement between optical simulation and the reflectance measurements validates the studied refractive index for both chromium and chromium oxide in the whole wavelength range.



Figure 5.3.3 Refractive index and extinction coefficient obtained by fitting ellipsometric measurements for Chromium a) and Chromium Oxide b). c) The agreement between experimental data and simulation obtained using the reported refractive indices is shown: simulation (green, solid line), Optical Spectrum Analyzer (OSA) (black, dash line), Fourier Transform Infrared Spectroscopy (FTIR) (red, dash-dot line).

5.3.4. Optimization

Once the optical constants of the materials have been determined and validated [121] the reflectivity spectra $\rho(\lambda)$ of the multilayer solar absorbers are determined by developing and using a MATLAB code based on the transfer matrix approach for thin films [124].

A Genetic Algorithm (GA) has been chosen to optimize the efficiency using the MATLAB code. This search-based method is frequently used to solve constrained and unconstrained optimization problems and to find optimal solutions for applications that are not well suited to be solved with classical optimization algorithms, including problems in which the objective function is discontinuous, non-differentiable, stochastic, or highly nonlinear. GA is well suited for our application because it offers the possibility to sweep a potentially huge number of solutions (thicknesses combinations in this work case), exploring the search space in a relatively short computational time. Being a global random search algorithm GA is independent from the gradient of the fitness function and it carries less risk to be stuck in local minima of the solution. It is also independent from initial conditions, whereas it is important to define the search space.

To optimize the SSA, the algorithm calculates the reflectance $\rho(\lambda)$ of the stack at each wavelength allowing to evaluate solar absorptance α_s and thermal emittance $\epsilon(T)$ according to Equations 3.1.7 and 3.1.8. Next, these radiative parameters are used to evaluate the fitness function. Either Equation 5.1.1 or 5.1.2 could now be used as a fitness function. In the present work coating efficiency was used as the fitness function.

The robustness of the performances of the coatings related to the unpreventable errors on layer thickness during manufacturing stage is included as a binding parameter of the genetic algorithm.

5.3.5. Robustness of performances

To include the robustness parameter in the optimization of the multilayer coating we took advantage of the GA capability to deal with constrained optimization for complex problems. The constraint introduced in the GA sets the fitness function to take only values comprised within given range, for a given percentage error on the thicknesses of the layers constituting the stack. In this way solutions that are not able to respect the constraint are rejected and the algorithm returns only thickness combinations that satisfy the constrains. To take into account the robustness of the performances with error on layer thickness, the constraint introduced set the maximum loss in efficiency to be of 2 percentage points, for errors on the layer thickness being within 20% range.

5.3.6. Numerical results

Figure 5.3.4 shows the results of the optimization process carried out via the GA. Three different coatings are considered, optimized for 100 °C, 200 °C and 300 °C working temperature, respectively (OPT_100, OPT_200, OPT_300). Table 5.3.2 reports the optimal thickness combinations, the solar absorptance values and the thermal emittance for the three coatings.

Figure 5.3.4 a) shows the Spectral reflectivity of the three coatings in comparison with the normalized solar spectrum. The figure clearly shows how the cut-off wavelength $\lambda_{Cut-Off}$ shifts toward shorter wavelengths as the target working temperature increases. This shifting in $\lambda_{Cut-Off}$ is due to the blackbody emission peak shifting toward shorter wavelengths, and it is a well-known behaviour for the ideal selective solar absorber.

The introduced optimization method based on the efficiency as a fitness function allows to find the best trade-off between solar absorptance and thermal emittance, that is strictly linked to the to the shape of the reflectivity spectrum $\rho(\lambda)$ of the coating. This method is particularly suited for the emerging technology of the unconcentrated flat plate solar collectors under high vacuum insulation, as they are able to reach high working temperature without concentration, hence requiring special attention to be given to both solar absorptance and thermal emittance in the design of the selective coatings [115] (section 3.3).

Figure 5.3.4 b) shows the thermal emittance for the three simulated coatings versus the temperature of the absorber. The coating optimized for higher working temperature (300 °C) shows a reduction in the thermal emittance of about 70% with respect to the coating optimized for 100 °C. The reduction in the thermal emittance that reduce the radiative losses is obtained at the expense of 10% reduction in solar absorptance (see Table 5.3.2).

Table 5.3.2 Optimal thickness combinations, solar absorptance α s values and thermal emittance ε (T) for coatings OPT_100,
OPT_200 and OPT_300.

Sample	T opt. (°C)	Layer thick. (Layer 1 to 5) (nm)	αs	ε (100 °C)	ε (200 °C)	ε (300 °C)
OPT_100	100	76-68-10-54-41	0.971	0.054	0.069	0.090
OPT_200	200	72-55-10-27-15	0.936	0.026	0.031	0.040
OPT_300	300	65-45-8-14-10	0.889	0.017	0.020	0.025



Figure 5.3.4 Optical simulations. (a) Spectral reflectivity of three coatings optimized for a target temperature of 100 °C, 200 °C, 300 °C (black, red, green curve, respectively). Normalized solar spectrum, grey filled area. (b) Temperature dependent thermal emittance of three coatings optimized for a target temperature of 100 °C, 200 °C, 300 °C (black, red, green curve, respectively).

Figure 5.3.5 reports both the coating and the overall efficiency (Equation 5.1.1 and Equation 5.1.2) for the simulated multilayer for 1000 Wm^{-2} incident power: the optimization process guarantees the highest efficiency at the setpoint temperature in every case. From the efficiency curve is possible to notice how the reduction in the absorptance in favour of a lower thermal emittance translates in higher optical losses. This consequently leads to lower efficiency at low temperatures but allows to keep higher efficiencies at higher working temperatures.

The overall efficiency as from Equation 5.1.2 in Figure 5.3.5 right, shows the performances of the coating if mounted in an actual high vacuum insulated solar collector, for τ_{Glass} =0.915 and ϵ_{Sub} =0.02 (typical thermal emittance value of the copper substrate). In terms of the overall performances each coating still guarantees the highest efficiency at the related target temperature, with an obvious reduction in the performances with respect to the coating efficiency (Figure 5.3.5 left). What Figure 5.3.5 remarks is that these coatings can work in a range from 70 °C up to 300 °C keeping their efficiency well-above 50%, being a potential revolution in the field of industrial heat process generation.



Figure 5.3.5 Optical simulations. (a) Coating efficiency η_{coat} of three coatings optimized for a target temperature of 100 °C, 200 °C, 300 °C (OPT_100, OPT_200, OPT_300; black, red, green curve, respectively). (b) Overall efficiency η_{all} of three coatings optimized for a target temperature of 100 °C, 200 °C, 300 °C (OPT_100, OPT_200, OPT_300; black, red, green dashed curve, respectively).

5.3.7. Influence of errors on layer thickness: robustness

To check the robustness of the solution with respect to thickness variations we calculated the efficiency in different thickness combinations of the multilayer stack. Each multilayer stack is obtained by varying the thickness of each layer around its optimal value in the interval *I*, defined as follows:

$$I = (d_{i,opt} \cdot (1-e), d_{i,opt} \cdot (1+e)) = \{d_i | d_{i,opt} \cdot (1-e) < d_i < d_{i,opt} \cdot (1+e)\}$$
(5.3.1)

being $d_{i,opt}$ the optimal thickness of the *i*th layer, d_i the thickness value that the *i*th layer can assume in the interval *I* and *e* the *maximum* percentage error on the layer thickness.

Figure 5.3.6 reports for each combination (*x axis*) the thickness value of each layer in nanometres (*left y axis*), and the related overall efficiency η_{all} at the temperature for which the coating has been optimized (*right y axis*). Coatings OPT_100, OPT_200, OPT_300 are shown in panel A, B and C, respectively.

The maximum percentage error *e* on the layer thickness was set to be $\pm 20\%$ around the optimal thickness, for each layer. To simplify the representation only the values at the extremes of the interval *I*, together with the optimal thickness value are reported in the figure, so that three possible thickness values are possible for each layer. Interval *I* could be conventionally defined as a *'three points interval'* (*'n-points interval'* in the case of *n* thickness values for each layer). With three possible thickness values for each layer, and because the multilayer stack is made of five layers, a total of $3^5=243$ combinations is possible, identifying 243 possible multilayer stacks (combinations). In Figure 5.3.6 combinations are numbered sequentially starting from combination 1 up to combination 243. The same observations could be extended to the case of *n* possible thickness values at equal error *e*. Efficiency is calculated as from Equation 5.1.2 for H=1000 Wm⁻², $\tau_{Glass}=0.915$ and $\varepsilon_{Sub}=0.02$.

Now, let the efficiency variation $\Delta \eta$ be defined as follows:

$$\Delta \eta = \eta_{\text{max}} - \eta_{\text{min}} \tag{5.3.2}$$

being η_{max} the overall efficiency ($\tau_{glass}=0.915$, $\epsilon_{sub}=0.02$) related to the optimal thickness package, and η_{min} the worst efficiency value among the 243 possible configurations.

Figure 5.3.6 clearly shows how the coatings are very stable in terms of efficiency: with 20% error on layer thickness, on all the possible combinations efficiency difference $\Delta \eta$ is kept below or at most equal to 2 percentage points. This figure shows an overview on the relationship between the variation in thickness and its effect on the efficiency of the coating at the target optimization temperature.

It is clear for example, that the OPT_100 coating efficiency has a smoother variation with the combinations than the coating OPT_300. This is to be attributed to the Chromium bottom layer, that in the coating optimized for 100 °C reaches a thickness as high as 50 nm, variations of 20% of this layer have less influence on the efficiency. To show in a clearer way how the efficiency is linked to layer thicknesses, Figure 5.3.7 shows a zoom-in of the Figure 5.3.6, panel A, for a fixed thickness of SiO₂ and Cr₂O₃ layers, and 3^3 combinations of the remaining layers.



Figure 5.3.6 Coatings OPT_100, OPT_200, OPT_300 (panel A, B and C, respectively). x axis: each ith combination identifies a different stack in terms of thickness, obtained by varying the thickness of each layer around its optimal value, in the case of three possible values for each layer and $e=\pm 20\%$. Left y axis: thickness value of each layer in nanometres for the ith combination. Right y axis: overall efficiency η_{all} evaluated at the target optimization temperature related to the ith combination.



Figure 5.3.7 Overall efficiency at 100 °C (orange, y axis, right) for the coating OPT_100, for fixed thickness of SiO₂, and Cr₂O₃ top layers and all the possible combinations of thicknesses values (y axis, left) of the remaining layers, obtained by varying the thickness of each layer around its optimal value, in the case of three possible values for each layer and $e=\pm 20\%$.

Figure 5.3.8 shows the spectral emissivity 1- $\rho(\lambda)$ for the three coatings optimized at 100, 200 and 300 °C in black, red and green dash lines, respectively. The solid line curves ranging from light to dark colour represent the spectral emissivity curves for the 3⁵ combinations respectively for the same three coatings. This figure shows how variations in layer thickness identify a band around the optimal value, defining the radiative parameters of each stack which determine the efficiency trend of Figure 5.3.6. It is also possible to notice how the change in layer thickness does not results in leaps of the reflectivity curves but in a smooth transition around the optimal value inside the defined band.



Figure 5.3.8 Spectral absorptivity 1- $\rho(\lambda)$ for the coatings OPT_100, OPT_200 and OPT_300, in black, red and green. Dash curves: reflectivity of the optimal thickness stack. Solid line curves ranging from light to dark colour: absorptivity curves obtained by varying the thickness of each layer around its optimal value, in the case of three possible values for each layer and $e=\pm 20\%$.

Figure 5.3.9 shows for each combination the solar absorptance α_s (left y axis, purple) and the efficiency and thermal emittance $\epsilon(T)$ at the target optimization temperature for the three optimized coating (panel A, B, and C), descending from spectral emissivity curves 1- $\rho(\lambda)$ of Figure 5.3.8.

This figure clearly shows the relative importance in terms of performances of the solar absorptance α_S and the thermal emittance $\epsilon(T)$ depending on the working temperature of the

coating. It is interesting to note how each of the three coatings handles these parameters in a different way.



Figure 5.3.9 Axis x: each ith combination identifies a different multilayer stack in terms of thickness, obtained by varying the thickness of each layer around its optimal value, in the case of three possible values for each layer and $e=\pm 20\%$. Axis y: solar absorptance α_S (left y axis, purple), overall efficiency η_{all} (left y axis, orange) and thermal emittance $\varepsilon(T)$ (right y axis) for the ith combination at the target optimization temperature, for the coatings OPT_100, OPT_200 and OPT_300 (panel A, B, and C, respectively).

For 100 °C optimized coating (Figure 5.3.9, panel A), the variation in thermal emittance $\varepsilon(T)$ is considerably high if compared to that of coatings OPT_200 and OPT_300, and still, it is not able to affect the performances of the coating. On the contrary the variation in α_S is limited with respect to coating OPT_200 and OPT_300, but they are still able to affect the performances of the coating that at low working temperature absorptance has higher importance in terms of performances.

For the coatings optimized at 200 °C and 300 °C we observe an overall decreasing in both solar absorptance and thermal emittance, together with an increased variation in α_S and a decreased variation in ϵ (T). Higher variation in α_S does not considerably affect the efficiency of the solar absorber, while variations in thermal emittance are now limited. Analysis on coating OPT_200 and OPT_300 make clear how thermal emittance gains importance on solar absorptance value

with increasing temperature and how it is of primary importance to consider the relative importance of α_s and $\epsilon(T)$ with the working temperature.

The optimization algorithm automatically meets up the need to control α_s and $\epsilon(T)$ as a function of the target working temperature, fine-tuning the layer thickness to not only ensure the best performance but also the robustness required with errors on the thickness during the deposition stage.

To better identify the role of each layer on the overall efficiency, let η_{max} be defined as the overall efficiency ($\tau_{glass}=0.915$, $\varepsilon_{sub}=0.02$) relative to the optimal thickness package, and η'_{min} as the minimum value of the efficiency related to the thickness values of two fixed layers of the stack and all the possible combinations of the remaining layers, according to interval *I* defined as in Equation 5.3.1.

To elucidate their meaning, η_{min}' values are reported as black circles linked by black dotted lines in Figure 5.3.10 a), for fixed thickness of SiO₂ layer, in the case of five possible values for each layer and e=±30%. Figure 5.3.10 b) is a close-up of Figure 5.3.10 a): the figure shows how for SiO₂ and Cr₂O₃ thickness fixed to 76 and 58 nm respectively, η_{min}' is to be found in correspondence of the combination of thickness values of the remaining three layers that returns the minimum value of efficiency.

Similarly, the same arguments could be extended for the case of *n* possible thickness values for each layer.



Figure 5.3.10 a) Overall efficiency at 100 °C optimization temperature (orange, y axis, right), for fixed thickness of SiO₂ layer and all the possible combinations of layer thicknesses values (y axis, left) of the remaining layers obtained by varying the thickness of each layer around its optimal value, in the case of five possible values for each layer and $e=\pm 30\%$. η_{min}' values are reported in black circles linked by black dotted lines. b) Close-up of Figure 5.3.10 a).

Now, let the efficiency difference $\Delta \eta'$ be defined as follows:

$$\Delta \eta' = \eta'_{\min} - \eta_{\max} \tag{5.3.3}$$

 $\Delta \eta'$ has been calculated for coatings OPT_100, OPT_200 and OPT_300, for a maximum error on the thickness of ± 30% and *five-points interval*, i.e., five possible thickness values for each layer. In Figure 5.3.11, Figure 5.3.12 and Figure 5.3.13, contour plots show the results for coatings OPT_100, OPT_200 and OPT_300 respectively: η_{max} value of the optimized coating is reported in the figure legend. The coatings are optimized to guarantee that $|\Delta \eta'| < 0.02$ for $e=\pm 20\%$: the choice to extend the analysis up to $e=\pm 30\%$ is intended to obtain larger $\Delta \eta'$ variation to better observe the influence of each layer thickness on the coating performances.

In Figure 5.3.11 $\Delta \eta'$ values for coating OPT_100 (optimized @ 100 °C) are shown as contour plots: in each plot, on the two axes are reported the thickness variations of the layer indicated by the axis label, whereas the colour indicates $\Delta \eta'$ calculated as reported above. In particular:

- SiO₂ layer thickness variations are reported in graphs A, B, C, D: for contour plot A (SiO₂ and Cr₂O₃ top), the efficiency of the solution presents an important region coloured in red which practically means a low efficiency decay ($|\Delta\eta'| < 0.015$).
- Cr₂O₃ top layer, graphs A, E, F, G: we can identify the same influence on the performances as for SiO₂, with a maximum located around its optimal value of thickness.
- Cr top layer, graphs B, E, H, I: in principle it guarantees a more limited decay in the efficiency for values on the lower side of its optimal thickness.
- Cr₂O₃ Bottom layer, graphs C, F, H, J: similarly to Cr top layer it guarantees a more limited decay in the efficiency for values on the lower side of its optimal thickness.
- Cr bottom layer, graphs D, G, I, J: it is clear how this layer is not able to affect performances.

It is interesting to note that panel A (SiO₂ and Cr₂O₃ top thickness) is the only one that presents a large red zone for which $|\Delta\eta'| \leq 0.015$. Fixed the SiO₂ and Cr₂O₃ layer thickness, the minimum value of efficiency is chosen among the worst combination of the remaining layers. This means that the combination of SiO₂ layer and Cr₂O₃ top layer are the most important parameter to control the performances of the coating.



Figure 5.3.11 Contours plots for the coating OPT_{100} (optimized (a) 100 °C) showing $\Delta \eta'$ for a maximum error on the thickness of $\pm 30\%$ and five possible thickness values for each layer.





Figure 5.3.12 Contours plots for the coating OPT_200 (optimized @ 200 °C) showing $\Delta \eta'$ for a maximum error on the thickness of $\pm 30\%$ and five possible thickness values for each layer. Darkest blue colour: locus of points for which -0.045 $\Delta \eta'$ <-0.04.

Whereas in Figure 5.3.11, the couple SiO₂-Cr₂O₃ top (contour plot A) was the one with the minimum $|\Delta\eta'|$ variation, for the coating OPT_200 (optimized @ 200 °C) *SiO₂-Cr Top* couple presents the minimum $|\Delta\eta'|$. This time Cr top layer appears to exert the major effect on the efficiency of the coating. Examining the layer one by one:

- SiO₂ layer, graphs A, B, C, D: contour plot B presents a red-coloured area corresponding to low efficiency decay ($|\Delta\eta'| < -0.015$). For contour plots A, C and D, SiO₂ against Cr₂O₃ top, Cr₂O₃ bottom and Cr bottom graphs are reported respectively. In these graphs are not present areas for which $|\Delta\eta'| \leq -0.015$ (red coloured), leading to the conclusion that the combination of SiO₂ layer and Cr top layer is mostly affecting the performances of the coating.
- Cr₂O₃ top layer, graphs A, E, F, G: a delimited zone where the $|\Delta \eta'| < 0.02$ could be identified.
- Cr top layer, graphs B, E, H, I: delimited areas are distinguished by $|\Delta \eta'| < 0.02$. This layer strongly affects the fluctuation of the solution, see plots B and E. Differently from graph I of Figure 5.3.11, contour plot I in Figure 5.3.12 describes a different relationship

between Cr Top and Cr bottom: while in the 100 °C optimized coating no particular relationship between these two is found to exist, in the 200 °C optimized coating to keep $|\Delta \eta'| \leq 0.02$, for increasing Cr top thickness a decreasing in Cr bottom thickness is required and vice versa. This is due to the fact that in 100 °C optimized coating Cr bottom was distinguished by high thickness whose variations in the range determined by *e* were not able to affect the solution.

- Cr₂O₃ bottom layer, graphs C, F, H, J: no influence on the performances is exerted by this layer.
- Cr bottom layer, graphs D, G, I, J: the same considerations as for Cr top layer could be done. For increasing Cr top layer thickness, a decreasing in Cr bottom thickness is required and vice versa. This behaviour points out the importance of the overall Chromium amount in the coating for high operating temperature: higher the Chromium content, higher the solar absorptance and the emissivity, and lower the performances at high temperatures.



In Figure 5.3.13 the contour plots for 300 °C optimized coating are reported.

Figure 5.3.13 Contours plots for the coating OPT_300 (optimized (a) 300 °C) showing $\Delta \eta'$ for a maximum error on the thickness of $\pm 30\%$ and five possible thickness values for each layer.

Being the colour scale the same for Figure 5.3.11, Figure 5.3.12 and Figure 5.3.13, it is clear to note that minima in the solution in the case of coating OPT_300 provides for higher $|\Delta\eta'|$, i.e. higher efficiency decay. All the layers are equally important in the variations in $\Delta\eta'$. Similarly to coating OPT_200, for increasing Cr top layer thickness a decreasing in Cr bottom thickness is required and vice versa to keep low efficiency decay. By observing Figure 5.3.11, Figure 5.3.12 and Figure 5.3.13 altogether, bearing in mind that the same colour scale is adopted for $\Delta\eta'$ in all the figures, it can be inferred that even with $e=\pm 30\%$, $|\Delta\eta'| \le 0.045$ for all the coatings, whereas only the coating OPT_100 could achieve $|\Delta\eta'| \le 0.015$. In conclusion, contour plots of Figure 5.3.11, Figure 5.3.12 and Figure 5.3.13 could be particularly useful to acknowledge the limits of the coatings in terms of robustness, defining the maximum error allowed on the layer thickness. For example, in the case of coating OPT_100 (100 °C optimized) SiO₂ and Cr₂O₃ top layer are the layers that have stronger impact on the performances of the coating.

Figure 5.3.14 shows how for the coating A $|\Delta \eta'| \le 0.015$ could be achieved if the error is limited to $\pm 15\%$ on the first two layers, while being allowed $\pm 30\%$ error on the remaining three layers.



Figure 5.3.14 Contours plots for the coating OPT_100 (optimized @ 100 °C) showing $\Delta \eta'$ in the case of the error on the first two layers of SiO₂ and Cr₂O₃ top is limited to ±15% while the error on the remaining layers is set to ±30%. Darker red coloured: regions for which $|\Delta \eta'| < 0.01$.

If SiO₂ and Cr₂O₃ top thickness values are restricted in the range for which $|\Delta \eta'| \le 0.015$ (red coloured range, respectively 65 nm < SiO₂ thickness < 88 nm and 60 nm < Cr₂O₃ top thickness < 80 nm), this ensures that 30% thickness variation of the remaining layers will not affect performances of the coating, because the minimum values of efficiency among all the combinations of the three remaining layers are already reported in the graph (contour plot A, Figure 5.3.11).

In other words, for the coating A (optimized @ 100 °C) to ensure $|\Delta \eta'| \le 0.015$ for all the possible configurations, it is enough to limit to ±15% the error on the first two layers, while being allowed ±30% error on the remaining three layers.

Figure 5.3.14 confirms the predicted results. This figure shows $\Delta \eta'$ for coating OPT_100, in the above-mentioned condition for which the error on the first two layers of SiO₂ and Cr₂O₃ top is limited to ±15% while the error on the remaining layer is set to ±30%.

The colour scale is the same as for Figure 5.3.11, Figure 5.3.12 and Figure 5.3.13 and it clearly shows how $\Delta \eta'$ is well below 0.02.

5.3.8. Experimental results

To validate the numerical simulations and the optimization process the coatings OPT_100, OPT_200 and OPT_300 have been experimentally realized via sputtering depositions. Pictures of the experimental samples OPT_100, OPT_200, OPT_300 are shown in Figure 5.3.15 a). Figure 5.3.15 b) and c) show the measured reflectance spectrum and the related thermal emittance of the deposited samples in comparison with the simulated reflection spectra. The measured reflectance spectra present a step at λ =1.5 µm due to the overlap of the integrating sphere and FTIR measurement techniques.



Figure 5.3.15 a) Pictures of the experimental samples OPT_100, OPT_200, OPT_300, on copper coated glass substrates. b) Measured reflectance spectrum of the deposited samples OPT_100, OPT_200, OPT_300 (black, red, green dash lines) in comparison with the simulated reflection spectra (black, red, green solid lines). Normalized solar spectrum, grey filled area. c) Thermal emittance of the deposited samples OPT_100, OPT_200, OPT_300 (black, red, green dash lines) in comparison with the simulated thermal emittance (black, red, green solid lines).

Solar absorptance values α_S and thermal emittance at different temperatures in comparison with the numerical counterparts for the three coatings are listed in Table 5.3.3. Measured samples match almost perfectly the simulated results, except for the 100 °C optimized coating, which however shows an error with respect to the numerical counterpart as low as 2% for α and 11% for the thermal emittance at the setpoint temperature. Table 5.3.4 lists the coating efficiency (see Equation 5.1.1) at the target optimization temperature for the three proposed selective absorbers, together with the related percentage deviation and the difference $\Delta \eta_{\text{coat}}$: despite the variations in α_S and $\epsilon(T)$ it is still guaranteed $|\Delta \eta_{\text{coat}}| \leq 0.02$, in accordance with the constraints imposed in optimization process.

Table 5.3.3 Measured solar absorptance values α_s and thermal emittance $\varepsilon(T)$ at different temperatures in comparison with the numerical counterparts for the three coatings

Sample	T opt. (°C)	α _{Num} .	α Exp.	ε _{Num.} (100 °C)	ε Exp. (100 °C)	ε _{Num.} (200 °C)	ε Exp. (200 °C)	ε _{Num.} (300 °C)	ε Exp. (300 °C)
OPT_100	100	0.971	0.950	0.054	0.048	0.069	0.058	0.090	0.072
OPT_200	200	0.936	0.925	0.026	0.025	0.031	0.031	0.040	0.039
OPT_300	300	0.889	0.890	0.017	0.017	0.020	0.020	0.025	0.025

Table 5.3.4 Numerical and measured values of the coating efficiency η_{coat} at the target optimization temperature for the three proposed selective absorbers, and percentage deviation and difference $\Delta \eta_{coat}$ between the numerical and measured values and the.

Sample	T opt. (°C)	η _{coat Num} .	η _{coat Exp} .	Deviation %	$\Delta\eta_{\text{coat.}}$
OPT_100	100	0.939	0.921	1.9	0.02
OPT_200	200	0.866	0.847	2.2	0.02
OPT_300	300	0.753	0.746	1.0	0.01



Figure 5.3.16 a) Coating efficiency of the experimental samples OPT_100, OPT_200, OPT_300 (black, red, green dash lines) in comparison with the optical simulations (black, red, green solid lines). b) Overall efficiency of the experimental samples OPT_100, OPT_200, OPT_300 (black, red, green dash lines) in comparison with the optical simulations (black, red, green solid lines).

Using the optical measurements of the fabricated samples together with Equations 5.1.1 and 5.1.2, the performances of the experimental coating could be estimated. The coating and overall

efficiency calculated at 1000 Wm⁻² using the experimental emissivity curves are reported in Figure 5.3.16, and compared with the numerical results. The figure shows the remarkable match between the experimentally realized coatings and the simulated counterparts, confirming the feasibility of the coatings and their applicability in the medium-temperature range.

5.3.9. Short duration thermal stability

Thermal stability of the coatings under thermal stress condition is another aspect to be considered in the feasibility of a coating.

The fabricated coatings were exposed to high temperatures in vacuum. Figure 5.3.17 shows the spectral reflectance of the 300 °C optimized coating before and after heating at 380 °C for six hours. The reflectance spectrum of the heat-treated sample is close to the one of the 'as-deposited' sample. For the heat-treated sample the reduction in solar absorptance α_S is counterbalanced by the reduction in thermal emittance $\epsilon(T)$, which allows to limit efficiency losses at higher temperatures.

Both the reduction in absorption coefficient and thermal emittance could be attributed to the diffusion of metallic chromium in the chromium oxide layers, as well as the interdiffusion of chromium and the copper substrate at high temperatures with the result that as degradation progresses, the amount of oxide in the coating increases in a process similar to that described in [125]. Long duration thermal aging tests on a bulk copper substrate showed a good stability of the SSA working at high temperature forecasting a service lifetime (> 25 years) [68], confirming the feasibility of the SSA under investigation for HVFP applications.



Figure 5.3.17 Measured spectral reflectance of OPT_300 solar selective coating before and after heating in vacuum at 380 °C for 6 hours.

5.3.10. Cr_2O_3/Cr on bulk copper substrate

To confirm the results obtained with smooth samples for bulk industrial substrates, the multilayers for operating temperature of 200 °C (Coating A) and 300 °C (Coating B) were sputter-deposited on 0.2 mm thick bulk copper Cu-ETP, standard EN13599/2014 from KME Germany GmbH and measured in the calorimetric system up to the stagnation temperature.

To correctly measure the SSA optical properties in the Mini-Test-Box (section 4.3) [36,115], the spurious contributions to absorber temperature (such as the thermal conductance and capacitance of thermocouple, support etc.) should be negligible, hence the sample dimensions have been chosen to be the largest possible for the sputtering system used (section 4.1), i.e. 10cm x10cm, comparable to the sputtering target diameter. A metallic frame was used to avoid deposition on the back side of copper substrate. The picture of multilayers after deposition can be observed in Figure 5.3.18 a). Optical properties of multilayers deposited on bulk copper were measured at room temperature by hemispherical spectral reflectivity measurement in the range (400-1700) nm using an integrating sphere connected to an optical spectrum analyzer and by absorptance and emittance measurement in operating condition under vacuum using the calorimetric method [115] (section 4.3). Given that the dimensions of the samples are comparable to the sputtering target diameter, to check thickness uniformity, we have performed the spectral absorptivity measurements in the centre of the sample as well as along the diagonals and the midlines, as reported in Figure 5.3.18 b).



Figure 5.3.18 a) Photo of the SSA just after the deposition, b) SSA reflectivity measurement on 9 points arranged as illustrated in the inset and their average (black thick curve). Also reported is the numerical reflectivity (black dashed line).

Despite the large area reflectivity is very low and uniform over all the absorber surface for wavelengths below 1 μ m. At wavelength large than 1 μ m, the results in Figure 5.3.18 b) indicate that the absorptivity follows the sample symmetry respect to the centre: the reflectivity curve measured on the midlines (green dash-dot-dot curves) are very similar among them, and they are in between the centre (thick dot dark-red curve) and the diagonal point (blue dash dot curves). The reflectivity curve measured in the sample centre presents the lowest reflectivity curve and it is in agreement with the simulation (black dashed curve). This result is not surprising since the deposition rate was calculated on the sample centre and as consequence only in the centre the correct layer thickness is guaranteed and the maximum absorptance is

obtained. In Figure 5.3.18 b) the averaged absorptivity obtained from the average of the 9 measurements is also reported as thick black curve. The averaged absorptivity will be used to compare the results of the thermal stability test.

The samples were mounted in the Mini Test Box to measure absorptance and emittance in operating conditions. The measurement allows to estimate the overall absorber emittance $\bar{\varepsilon}_{abs} = \bar{\varepsilon}(T_{abs}) + \bar{\varepsilon}_s$ and to extrapolate the coating emittance $\bar{\varepsilon}(T_{abs})$ if $\bar{\varepsilon}_s$ is known. Results for the two samples are reported in Figure 5.3.19 a) and compared with a commercial absorber (black line). The absorber emittance is higher than expected from the optical simulations for both multilayers. A possible source of such increase could be found in the influence of the surface roughness and/or in the presence of copper oxides at the interface between the substrate and the multilayer and/or interdiffusion phenomena. More investigations are needed to determine and eliminate the origin of the increased emittance, allowing to further improve the SSA performances. However, despite an emittance higher than expected the absorber efficiency is better than commercial absorber at temperatures higher than 150 °C, as illustrated in Figure 5.3.19 b). In particular, the absorber efficiency at 250 °C, calculated according to the experimental values (see Figure 5.3.19 a), increases from 0.490 for Mirotherm® up to 0.593 for coating designed to work at 300 °C, with a 10% absolute efficiency improvement (21% relative increase). At 300 °C the efficiency improvement is even more pronounced: the sample designed for such temperature has $\eta_{abs} = 0.425$ compared with $\eta_{abs} = 0.225$ of the Mirotherm® at the same temperature, with a 20% absolute improvement corresponding to about 90% relative increase. As consequence of the low emittance, the stagnation temperature, that is the temperature at which the incident power is equal to the emitted power and efficiency is equal to zero, increases from 331 °C up to 380 °C.



Figure 5.3.19 a) Absorber emittance measured at temperature up to 400 °C for commercial coating (Mirotherm® black dash-dot line), Coating A (blue dash line) and Coating B (red line). b) Absorber efficiency calculated according to Equation 5.1.3, for Mirotherm® (Black dash-dot line), Coating A (blue dash line) and Coating B (red line).

It is worth to mention that the reported results are the average on a relatively large area substrate (10 cm x 10 cm), having a slight non-uniformity. Using larger deposition system, with industrial sputtering cathode it would improve uniformity and performances.

To test the short duration high temperature thermal stability of the fabricated absorbers, they have been kept at 400 °C for four hours under high vacuum. After the thermal cycle, absorptance and emittance were measured again at operating temperature, they values are

reported in the inset in Figure 5.3.20 and show that the difference in the results are within the experimental error. The spectral reflectivity measurements before and after the short duration high temperature thermal stability test are very similar as shown in Figure 5.3.20 a) and b). For clarity we have reported only the average reflectivity curve, obtained as in Figure 5.3.18 b), before and after the test. For coating A there are basically no changes in the reflectivity curves, while for coating B the slight reduction in absorptivity is compensated by an increased reflectivity at wavelengths above 1000 nm (which result in reduced thermal emittance). Long duration thermal stability and service life time assessment of these coatings are discussed by the authors in detail in [68], where experimental details and data about the thermal aging procedure are reported. The analysis forecast a service lifetime larger than 25 years.



Figure 5.3.20 Reflectivity measurement before (continuous line) and after (dashed line) the thermal treatment at 400 °C for four hours under high vacuum for a) coating A and b) coating B.

5.3.11. Conclusions

Spectrally selective solar absorbers ($Cr/Cr_2O_3/Cr/Cr_2O_3/SiO_2$) have been designed and fabricated especially for Evacuated Flat Plate Collectors (EFPC). An optimization algorithm is developed aiming at obtaining multilayer SSA suitable for a mass industrial production. The algorithm incorporates as a binding parameter the robustness of the coating in terms of efficiency loss when errors on layer thickness are made.

Three coatings have been designed to obtain the highest efficiency at 100 °C, 200 °C and 300 °C operating temperature while having a small sensitivity to thickness variations. Each of the three coatings exhibits the best performances at the temperature for which it has been optimized. The overall efficiency (that also considers the cover glass optical losses and the substrate radiative losses) of the proposed SSAs in a EFPC is predicted to be as high as 0.84, 0.74 and 0.56 at 100 °C, 200 °C and 300 °C, respectively. Efficiency loss is less than 2 percentage points if the layer thickness variation is less than 20%.

A visual method proved to be capable to deal with the five-variables problem represented by the five-layered architecture under investigation. Coloured contours plots allow to visually inspect at a glimpse the effect of the thickness variation of each layer on the performances of the coatings. The method is useful to identify the limits of the coating in terms of robustness, defining the maximum error allowed on the layer thickness, or to identify the layers that require special attention in terms of error on their thickness. Using this method, we have been able to obtain a coating with a loss in efficiency due to variations in layer thickness as low as 0.015 in absolute value, by just limiting to 15% the error on two of the layers constituting the stack, whereas an error up to $\pm 30\%$ can be tolerated on the remaining layers.

The optimized SSAs were fabricated via sputtering depositions on optically smooth samples and showed results in agreement to the simulation.

In order to determine whether the fabrication process can be easily transferred to industrial deposition systems, the multilayers have been deposited on industrial grade bulk substrate.

The obtained selective solar absorbers have a very low emittance preserving a large absorptance and reach stagnation temperature higher than 350 °C with superior performances with respect to commercial coatings. Absorber efficiency higher than 70% at 200 °C and higher than 40% at 300 °C have been obtained. However, the measured thermal emittances on copper bulk substrates are slightly higher than expected by simulations. The origin of such increase could be the due to factors like the surface roughness, the presence of copper oxides at the interface between substrate and multilayer, interdiffusion phenomena or others and it need to be investigated. Understanding the origin of the increased emittance would allow to further improve the SSA performances.

5.4. Roll-to-roll deposited coatings for high temperatures

As discussed in section 2.3, EFPCs need to be evacuated down to 10⁻² Pa or lower pressure, allowing to eliminate both convection losses and gas conduction losses. So, to preserve the collector performances over time it is of fundamental importance to prevent the internal pressure from raising. To efficiently maintain high vacuum EFPCs make use of Non-Evaporable Getter pumps. After the initial activation getter pumps can be regenerated in situ by exposure to solar light. To regenerate a getter pump the gettering material needs to be heated at temperatures usually higher than 200 °C. The regeneration process will be more efficacious at higher temperature. TVP Solar patented, among other things, a proprietary NEG getter pump that allows to maintain high vacuum (10^{-2} Pa to 10^{-7} Pa) throughout the entire service life of the solar collector [12]. The selective coating that is currently used for the getter pump results in excellent performances, but it is quite unique and coatings with the same characteristics are not easily found on the market. Moreover, this coating is not especially thought for high temperature operation, and at high temperatures the non-optimal selectivity of the absorber increases the thermal radiation losses limiting the stagnation temperature. A multilayer coating especially intended for high temperature operation could allow the getter pump to reach even higher stagnation temperatures beneficial to regeneration of the getter material.

Being this PhD project partially funded by TVP Solar, a period of the research project was spent at TVP Solar company based in Geneve. The objective of the work at TVP Solar was to find the optimal design of a Cr_2O_3 -Cr based multilayer coating that would have allowed for the optimal stagnation temperature of the getter pump being a valid alternative to the existing commercial solution, and to modify, set and operate a roll-to-roll machine to correctly deposit the coating using an industrial system.



Figure 5.4.1 Picture of the roll-to-roll machine held in TVP Solar laboratories, in Geneva.

A picture of the roll-to-roll machine held in Geneva lab is shown in Figure 5.4.1. This machine is a roll-to-roll sputtering machine, equipped with two DC sputtering sources positioned to deposit on both sides of a thin ribbon. The machine was meant to work with an Aluminium ribbon of maximum 50 μ m of thickness, to deposit thin film NEG. Since non evaporable getters are mainly constituted by pure metals (like Vanadium, Zirconium and others), the machine was equipped only with DC sputtering sources and a single injection line (since reactive sputtering was not needed). The substrate chosen for proper assembling and operation of the NEG pump was a 0.2 mm thick copper sheet, so the first modification to be done was to provide the roll-to-roll mechanism with all the changes, accessories, and settings to work with a substrate 4 times thicker than the one for which the machine was designed. Then, since the dielectric layers of the studied multilayer absorber are deposited via Reactive DC Magnetron Sputtering (DCRMS) the machine has been equipped with an additional injection line for the reactive gas and a proper mass flow controller.

Principle of operation of the machine is shown in Figure 5.4.2. A turbomolecular pump ('turbo' in figure) evacuates the chamber at a base pressure of $2x10^{-4}$ Pa. Two valves Vg (Gate Valve) and Vb (Bypass Valve) separate the turbopump and the vacuum chamber. The valve Vg directly links the turbopump with the vacuum chamber, while the valve Vb links the turbopump with the vacuum chamber, while the valve Vb links the turbopump with the vacuum chamber through a restriction. In normal operation, before injecting the process gases, gate valve Vg is closed, while gate valve Vb is opened. This operation allows to decrease the pumping speed, saving process gases. VV1 and VV2 are venting valves used to vent the chamber before opening.



Figure 5.4.2 Principle of operation of TVP Solar roll-to-roll sputtering machine.

5.4.2. Roll to roll sputtering process

Figure 5.4.3 shows the discharge voltage as function of the oxygen flow rate for DC Reactive sputtering process of a chromium target, having set the argon flow rate at 2.5 sccm and the power at 100 W, in normal operation condition (Vg closed, Vb open). It can be noted that, increasing the oxygen flow rate from zero, the total pressure (right-y axis) is unchanged up to a flow rate of 0.65 sccm while the discharge voltage is almost constant, indicating that all injected oxygen is absorbed by the Cr film and Cr target and the target remains metallic. Above 0.65 sccm flow of O₂ the discharge voltage starts to increase due to cathode poisoning [113], and the total pressure starts to increase almost linearly with the oxygen flow indicating that the oxygen pumping speed of Cr target and of the growing film is reduced to a negligible level. Differently from what happened for the batch sputtering apparatus described in sections 4.1 and 5.3.2, for the sputtering machine in these conditions, increasing the oxygen flow makes the cathode pass from metallic state to poisoned state (fully oxidized) in a not stable and controllable_way (Figure 5.4.3, point A). Once the cathode is poisoned the oxide layer acts like an insulator, and the deposition rate is null. At this stage even if O₂ flow is null, due to the very low sputtering rate it is difficult to remove the oxide layer from the cathode (Figure 5.4.3, point **B**).

The 'metallic state' of the target is defined as the condition in which the Oxygen pressure is low and the sputtered metal acts like a getter pump for the injected O_2 . Oxide formation will occur also on the target surface, but the rate of the formation of the oxide is lower than its sputter removal rate. On the other side, 'poisoned state' (fully oxidized target) is the condition in which the gettering action of the substrate saturates and the oxygen partial pressure increases, increasing the oxide formation on the target. The lower sputtering yield of the oxide decreases the sputtered metal flux, which lowers the getter capacity of the substrate, further increasing the oxygen partial pressure. A self-enforcing loop will lead to the complete oxidation (*poisoning*) of the target [90]. A consequence of the poisoning loop is a hysteresis of the reactive gas partial pressure, and, associated to this, an unstable operation regime which often requires additional means of stabilization in practical applications. Concluding, in these conditions it was impossible to deposit a Cr_2O_3 coating for the solar absorber.



Figure 5.4.3 Chromium oxide characterization curve: unstable operation regime. Left axis, plasma discharge voltage for increasing and decreasing oxygen flow in blue and orange, respectively. Right axis, total pressure in the vacuum chamber for increasing and decreasing oxygen flow in grey and yellow, respectively.

Traditionally, the best-known approach to decrease the width of the hysteresis region is by a sufficient increase of the pumping speed. The hysteresis effect arises due to the strong coupling between the substrate gettering capacity and the target state at low pumping speed. If the target becomes moderately more poisoned due to the limited pressure increase, the increase in pumping capacity will not only have to compensate the direct flow increase but also the reduced gettering action of the substrate. If the pumping speed is high enough, the pressure rise due to an increase in reactive gas flow will be limited. Above a critical pumping speed, the target and substrate are decoupled and the hysteresis effect vanishes [90].

To increase the pumping speed and solve hysteresis issue on the roll-to-roll machine the normal operation guidelines were bypassed: during sputtering process valve Vg instead of the by-pass Vb was opened. Because of the increased pumping speed higher flows of the process gases were needed to achieve a pressure sufficient to maintain the sputtering plasma discharge. To limit the sputtering gas deployment the *standby function* of the turbopump was used to reduce the rpm of the pump. Figure 5.4.4 shows stable operation regime for the deposition of chromium oxide via DCRMS. The discharge voltage as function of the oxygen flow rate for DCRMS of a chromium target shown in Figure 5.4.4 is obtained for an Argon flow rate of 40 sccm and the power was set at 200 W.



Figure 5.4.4 Chromium oxide characterization curve: stable operation regime. Left axis, plasma discharge voltage for increasing and decreasing oxygen flow in blue and orange, respectively. Right axis, total pressure in the vacuum chamber for increasing and decreasing oxygen flow in grey and yellow, respectively.

5.4.3. Multilayer for high temperature operation

To test different solutions the investigated coatings have been optimized for the getter assembly both for solar spectrum and LED light spectrum, using an optimization method analogous to that explained in section 5. Figure 5.4.5 shows the spectral emissivity for the coatings optimized for the solar spectrum and LED light spectrum (black and red curve, respectively), in comparison with the normalized reference spectrums (Sun spectrum, LED Spectrum, yellow and blue area). Architecture, optimal thickness of each layer and refractive index are not shown for confidentiality agreement. Simulations are intended for perfectly smooth samples. Figure 5.4.5 shows how the coatings optimized for LED spectrum can guarantee high absorptance and very low emittance at the same time: the cut-off can be placed at short wavelengths, while high absorption is still guaranteed because LED spectrum is narrow and concentrated in the visible wavelengths. On the other side, solar optimized coating shows high absorptance values both for solar and LED spectrums, at the expense of a thermal emissivity three times higher than the LED optimized coating. Solar and LED absorptance values α_{Sun} and α_{LED} , and thermal emittance $\varepsilon(400 \,^{\circ}C)$ for the simulated multilayers are summarized in Table 5.4.1.



Figure 5.4.5 Optical simulations. Spectral reflectivity for the coatings optimized for the solar spectrum and LED light spectrum (black and red curve, respectively). Normalized solar spectrum and LED spectrum (yellow, blue and red filled area, respectively).

Table 5.4.1 Optical simulations. Solar and LED absorptance values α_{Sun} and α_{LED} and thermal emittance ϵ (400 °C), for the simulated multilayers.

	άιερ	αSun	ε (400 °C)
Sun Optimized	0.91	0.82	0.03
LED Optimized	0.97	0.69	0.01

5.4.4. Experimental results

Mini Test Box apparatus was used to measure the absorptance and thermal emittance of the fabricated SSAs in operating conditions (high vacuum, high temperatures). A detailed description of the system and the measurement methods are described in section 4.3. Measures have been performed on test samples measuring 14x15 cm. The test samples are cut from the deposited copper coil, in the zone of maximum thickness uniformity. Figure 5.4.6 shows three standard samples cut out of the deposited copper sheet.



Figure 5.4.6 Three standard samples cut out of the deposited copper sheet.

Figure 5.4.7 shows a measurement cycle of one of the fabricated samples (LED optimized). The temperatures of the sample, box and glass, and the pressure, are monitored during the measurements. Their values during cool down and heating up phases are used to measure the absorptance and thermal emittance of the fabricated SSA according to power balance equation 4.3.1 (section 4.3). The calibrated LED system [91] is used to illuminate the samples for all the reported measurements. Incident power on the absorber after glass transmission is of 850 Wm⁻². LED optimized sample of Figure 5.4.7 shows how, with less than 1 kWm⁻² illumination the SSA reaches temperatures as high as 410 °C, achieving a remarkable result. Table 5.4.2 summarizes the results of the calorimetric measurements for the fabricated multilayers, absorption coefficient α_{LED} and thermal emittance ε (400 °C).



Figure 5.4.7 Mini Test Box measurements. Left, Mini Test Box illuminated by a calibrated LED system, and a sample of SSA with the fixed thermocouple. Right, measurement cycle: temperatures of the sample, box and glass, and the pressure, are monitored during the measurements.

Table 5.4.2 Calorimetric measurements. Absorption coefficient α_{LED} and thermal emittance $\epsilon(400 \text{ °C})$ for the fabricated multilayers.

	aled	ε (400 °C)
Sun Optimized	0.87	0.067
LED Optimized	0.92	0.041

The values of α_{LED} measured at the Mini Test Box were used to verify the assumptions about the refractive index made for the optical simulation of the coatings, since the absorption peaks of a multilayer coating are positioned at a wavelength that depends by the refractive index and the thickness of the layers composing the stack. Figure 5.4.8 shows the absorption peaks for different multilayers compared to a normalized LED light spectrum. According to Equation 3.1.7, the wavelength at which the absorption peak is positioned with respect to the peak of the illuminating spectrum determines the absorption coefficient of the coating. By measuring the trend in the absorption coefficient obtained from coatings with different layers thickness (absorption peaks positioned at different wavelength) we can validate the initial assumptions about the refractive index. Figure 5.4.9 shows the comparison between optical simulations (orange) and Mini Test Box measurements (blue) of α_{LED} for diverse multilayers. The almost perfect match between the numerical simulations and the experimental data strengthens the hypothesis done on the refractive index used (and thickness), confirming the validity of the simulations.



Figure 5.4.8 Optical simulations. Spectral absorptivity for three multilayers compared to normalized LED light spectrum (blue filled area).



Figure 5.4.9 LED absorptance α_{LED} for diverse multilayers: comparison between optical simulations (orange) and Mini Test Box measurements (blue).

The optimized coatings were fabricated and mounted on the getter pump assembly to be tested in operating conditions. The Mini Test Box and the LED system were used to measure the stagnation temperature reached by the getter pump. Figure 5.4.10 a) shows an image of the getter pump: a proper support structure was built to secure the complete assembly inside the Mini Test Box. The getter pump mounted in the Mini Test Box system and illuminated by calibrated LED light system is shown in Figure 5.4.10 b).



Figure 5.4.10 a) Getter pump assembly on its support frame. b) Getter pump assembly mounted in the Mini Test Box system and illuminated by calibrated LED light system.

To prove the chosen architecture to be reproducible and stable against layer thickness variations around the optimal values, samples with various thickness have been inspected. The results are shown in Figure 5.4.11.

Figure 5.4.11 shows the stagnation temperature difference between getter pumps equipped with various multilayer coatings fabricated with TVP Solar roll-to-roll sputtering machine and the standard getter pump equipped with a commercial coating. The standard coating sets the zero reference point. It is clear from Figure 5.4.11 that all the fabricated SSAs, when exposed to LED spectrum, record stagnation temperatures higher than the commercial coating used at present. It is worth to notice how the solar optimized coating and LED optimized coating define respectively the lowest and highest stagnation temperature of the pump between all the realized SSAs, when exposed to LED light illumination. As discussed before, LED optimized coating shows the highest performances, since it can guarantee both high absorptance and very low emittance, due the short cut-off wavelength justified by the fact that LED spectrum is narrow and concentrated in the visible wavelengths. Solar optimized coating on the other hand is penalized (as expected) when exposed to LED light spectrum, because a sufficient solar absorption is reached at the expense of a higher thermal emittance.



Figure 5.4.11 Stagnation temperature difference between getter pumps equipped with various multilayer coatings fabricated with TVP Solar roll-to-roll sputtering machine and the standard getter pump equipped with a commercial coating. Incident light power 850 Wm⁻².

In conclusion, the roll-to-roll sputtering machine has been successfully modified and used to deposit a Cr_2O_3/Cr based multilayer solar absorber coating on a 0.2 mm copper substrate. The SSA coatings produced with the machine itself showed high performances and proved to be a valid alternative to the currently used commercial coating for the getter pump assembly. The tested architecture used for the SSA proved to be reproducible and stable against layer thickness small variations around the optimal values. However, despite the excellent results the thermal stability of the coatings should still be verified.

5.5. Coatings for a CPC collector under high vacuum

A new frontier in high efficiency solar collection could be a high vacuum flat solar panel, thick enough to be equipped with Compound Parabolic Concentrators (CPC) (section 2.3.7). The CPC installed in a high vacuum envelope leads to various advantages: no need for mirror cleaning, no corrosion due to atmospheric agents, better insulation resulting in thermal loss reduction, possibility to deposit a IR reflective coating on the interior side of the glass to benefit from 'photon recycling' mechanism [126]. A pioneering work [127] has experimentally investigated the idea to place a CPC under vacuum to reach the high temperatures needed for methanol reforming but CPC dimensions and performances were limited by the small volume of the cylindrical vacuum chamber. To extend CPC sizes the vacuum chamber must increase too, so the surface under vacuum needs a mechanical support to sustain the glass against the atmospheric pressure and the CPC must be designed to respect mechanical constraint given by the support frame. The great improvement of the performances obtained with a CPC with low concentration factor (2.4) installed in a high vacuum insulated envelope in place of a flat absorber is discussed in [94].

5.5.1. Numerical simulations of a CPC collector

In Figure 5.5.1, a schematic rendering of the studied CPC is reported. Shape and dimensions of the adopted CPC have been properly chosen to easily fit the geometrical constraints due to the internal supporting structure. The absorber is a round copper pipe coated with a selective absorbing film and the whole concentrator is hosted in the flat envelope (from TVP Solar). The real vessel is equipped with a supporting structure ([11,12], not shown in Figure 5.5.1) that avoids the glass implosion. The presence of this structure gives design constraints to the CPC, in particular the maximum span of the concentrator cannot exceed 110 mm in horizontal size. An analysis on several 2D arrangements [31] (shape and dimensions of the absorber and of the parabolic mirrors) has been conducted to find the best compromise between space constraints, working yearly hours and Sunlight concentration ratio. The solution proposed has a cylindrical absorber of 12 mm of diameter and double parabolic mirrors [128], 90 mm wide, with a concentration ratio of 2.4 and 25° acceptance angle (applicable in high solar irradiance places) (Figure 5.5.1 b).

In Table 5.5.1, some geometrical properties of the CPC are reported.

Table 5.5.1 Geometrical properties of the studied CP	C
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parabolic mirrors aperture	90 mm
parabolic mirrors height	110 mm
pipe diameter	12 mm
solar concentration (C)	2.4
half-acceptance angle	25°

The upper parts of the mirror are almost vertical and they do not influence significantly the concentration of light, the optical losses and the overall width [129], therefore the parabolic mirrors can be truncated to reduce the panel height. In the present study we reduced the mirror height to 110 mm, however a further reduction to 90 mm would not affect the performance in a substantial way. Simulations have been carried out via COMSOL Multiphysics® software, adopting Ray Tracing technique for solar rays, whereas for IR radiative emission we used both the standard diffuse emission approach and the perfectly specular IR surface for each component of CPC.

The specular behaviour of each reflected ray is ensured by the ratio between the roughness of every wall and the radiative electromagnetic wavelength [130,131]. In particular, in the solar spectrum the parabolic mirrors are designed to perform a specular reflection and to concentrate the solar irradiation towards the absorber, where it is almost totally absorbed (0.95 of absorptivity for the commercial selective coating adopted). In the Infra-Red (IR) region the roughness of each component (parabolic mirrors, glass and pipe) is significantly lower than the electromagnetic wavelengths. In fact, the root mean square roughness of the less smooth component (the pipe) is approximately 1 μ m, while the IR emitted power wavelengths are mainly around 4 μ m. Hence, the Ray Tracing approach for the IR radiative thermal exchange seems to be more adequate.

A further complication to the simulative model is the strong wavelength dependence of the absorber emissivity. The absorber is selective, which means that its emissivity is close to 1 in the solar region of the spectrum (from 300 nm up to 2 μ m) and it is close to 0 at wavelengths above 10 μ m, with a quite sharp transition from 1 to 0 in the region 2-10 μ m.

Since it is not possible to define the spectral emissivity as an analytical function of the wavelength, to reliably reproduce the spectral dependence of the absorber emissivity, a multiband approach was used. The multi-band study approximates the radiative behaviour of each component as grey body (emittance assumed constant) for every single wavelength interval. In order to keep the computational time reasonable and the simulation accurate, the electromagnetic domain has been split into two broad ranges (Sun and IR spectrum). Furthermore, the IR domain has been divided in 40 wavelength intervals (to accurately reproduce the selectivity behaviour of the absorbing coating on the pipe). The parabolic mirror adopted for numerical simulations has 0.95 reflectivity in the sunlight spectrum and 0.98 in the IR range (it is a commercial mirror produced by ALMECO [57]). The upper glass has 0.95 of transparency in the solar spectrum (double anti-reflective coatings on the glass) and it is opaque with 0.89 of emittance in IR range. In order to reduce the radiative thermal losses, the vacuum vessel can be covered by the commercial mirror. To validate the numerical apparatus the Mini Test Box apparatus described in section 4.3 has been used. In Figure 5.5.1 are depicted the sketches of the experimental arrangement (Figure 5.5.1 a: flat absorber in the vacuum chamber (Mini Test Box)) and of the CPC under investigation (Figure 5.5.1 b: parabolic mirrors and the round tube). In Figure 5.5.2 a 3-D rendering of the proposed solar collector.



Figure 5.5.1 a) Geometrical sketch of the vacuum vessel with a flat absorber used in the simulation. b) Geometrical sketch of the simulated Compound Parabolic Concentrator (CPC) inserted in a panel under high vacuum.



Figure 5.5.2 3-D rendering of the proposed CPC solar collector.

Solar range: Ray Optics simulations

Ray Tracing technique has been employed to evaluate solar incident power distribution on the CPC walls (i.e. parabolic mirrors, pipe and glass) on the 2D model. To compare the results with flat absorber, the copper pipe was assumed to be coated with a selective solar absorber having the same optical characteristics of the flat absorber (Mirotherm® coating from Alanod [40], solar absorptance α =0.95; thermal emissivity ϵ =0.05 @ 100°C in air). In the optical simulation, rays are released from a grid placed at the CPC entry aperture, see Figure 5.5.3 a and Figure 5.5.3 b. The incident angle (with respect to the CPC symmetry axis) for the incoming rays was varied from 0° to 30° . The optical efficiency of the CPC was calculated as the ratio between the power incident on the pipe absorber and the initial total power input on the mirror aperture, without considering the glass cover. The optical efficiency, so calculated, is reported in Figure 5.5.3 c) as function of the incident angle (θ_i). It is worth to note that the optical efficiency is almost constant from $\theta_i=0^\circ$ up to acceptance angle. This is due to the balance between two opposite effects. The first effect, that would increase the optic efficiency with the incident angle, derives from the number of reflections on the parabolic mirror walls: at 0° of incident angle most rays undergo multiple reflections (Figure 5.5.3 a) whereas close to the acceptance angle a single reflection is sufficient to redirect the rays on the central pipe. The second effect, that would decrease the optic efficiency with the incident angle, leads to a reduction of the effective impinged area by cosine of θ_i (Figure 5.5.3 c). Finally, Figure 5.5.3 c shows that above 25° of incident angle the optic efficiency drastically reduces because of the geometrical design of the parabolic mirrors [128].



Figure 5.5.3 Ray tracing for solar incoming beams with an incidence angle of: a) 0 degrees, b) 20 degrees. c) Optical Efficiency as function of the incident angle.

The power fractions absorbed by each component of the CPC have been calculated in the case of normal incidence. It is worth to note that the rays reflected by the absorber and mirrors are directed to the glass cover and they are mainly transmitted to the ambient (only a small and negligible fraction is reflected back to the vessel according to Fresnel law), see (Table 5.5.2). The power fraction absorbed by the pipe can be calculated as the product of the optical efficiency and the pipe solar absorptance (0.95 in our case).

Table 5.5.2 Ray optics analysis: absorbed fraction of solar incoming power for every CPC component.

CPC part	Absorber	Parabolic Mirrors	Glass
Absorbed fraction of solar incoming power	0.813	0.096	0.091 (Transmitted fraction)

IR range: thermal radiation simulations

Generally, thermal radiation can be easily modelled according to the classical emission and reflection laws, i.e. radiant surfaces emit and reflect radiative energy uniformly in all directions (diffuse surfaces). In the case of a CPC the hypothesis of diffuse surface is not verified, since the system is composed by mirrors that specularly reflect radiation. The thermal radiation should be treated with ray optics approach (a specular approach). Figure 5.5.4 b and c show the difference between the diffuse radiation hypothesis and the specular approach. The diffuse model (Figure 5.5.4 b) assumes that the rays emitted by the pipe are hemispherically reflected by the mirror walls. In the specular approach, instead, the infrared rays, emitted by the pipe, reach the glass after one or two specular reflections on the mirror walls (Figure 5.5.4 c). It is clear that in the case of diffuse approach, the IR emission of the pipe is mainly absorbed by mirrors, whereas in case of specular reflection the pipe irradiates mainly the glass cover.

We performed numerical simulations in COMSOL Multiphysics, using both diffuse radiation and specular reflection models. Geometry of the numerical model mimics a real panel configuration with parabolic mirrors suspended inside the vessel. The flat vacuum envelope can accommodate at least 6 CPCs, but in order to reduce computational time, only one CPC mirror assembly in 2D domain has been simulated.



Figure 5.5.4 a) Sunlight rays passing through the glass, with 0° of incident angle, impinging on the parabolic mirrors and then on the tube. b) Tube infrared emitted rays impinging on the parabolic mirrors and then diffused. c) Tube infrared emitted rays that experience a specular reflection on the parabolic mirrors, reaching the glass after one or two reflections.

Boundary conditions and simulation details

The parabolic mirrors are supposed to be aluminium and their back side of emissivity 0.05 is exposed to the back side of another mirror at the same temperature (in order to simulate one of the inner CPCs of the panel). The vessel is stainless steel with surface emissivity 0.15. Natural convection is imposed on glass and vessel external surfaces. Solar incoming power is modelled as heat flux: every CPC component receives the power fraction calculated by the ray optics analysis in solar range, see Table 5.5.2. The efficiency curve is obtained by varying the power subtracted from the circulating fluid in the pipe, from 0 W/m up to the net exploitable power. In case of the flat absorber, the solar absorptivity and radiative emissivity of the absorber are the same of the pipe of the CPC. In addition, the flat absorber is in aluminium, and the uncoated side has IR emissivity of 0.045.

5.5.2. Results

The results of the numerical simulations are summarized in Figure 5.5.5. The efficiency has been calculated as the net exploitable power respect to the solar power incident over the glass (the typical solar irradiation is 1000 W/m^2). The experimental data for the flat absorber were obtained illuminating the absorber by a calibrated LED illumination system [91] and recording the corresponding absorber stagnation temperature. As discussed in section 4.3, in such configuration the power losses are equal to absorbed power:

$$\varepsilon(T_{hS}) \cdot \sigma_{SB}(T_{hS}^4 - T_{amb}^4) + \varepsilon_{sub}\sigma_{SB}(T_{hS}^4 - T_{amb}^4) = \tau_{glass}\alpha_{LED}P_{LED}(T_{hS})$$
(5.5.1)

where α_{LED} is the absorptance α evaluated as in Equation 3.1.7, where the solar spectrum is replaced by the spectrum of the LED lump used to illuminate the absorber [91], $P_{LED}(T_{hS})$ is the light power provided by the calibrated LED system and T_{hS} is the absorber stagnation temperature at the given LED power. As consequence, at $T = T_{hS}$ the efficiency can be calculated, as reported below:

$$\eta(T) = \tau_{glass} \cdot \alpha_s - \frac{\tau_{glass} \alpha_{LED} P_{LED}(T_{hS})}{H}$$
(5.5.2)

where *H* is Sun irradiated power reference, set to 1000 Wm⁻², $\tau_{glass} = 0.91$, $\alpha_S = 0.95$ in the case of Mirotherm® coating (section 2.3.8) which is actually mounted on TVP Solar high vacuum flat collectors.

The agreement between the two simulative models (diffuse and specular approach) and between such models and the experimental data is satisfactory, as can be seen Figure 5.5.5. The model of the flat absorber (section 4.3) agrees with experimental data (Black diamonds) for both specular (red circles) and diffuse (red line) models. The flat absorber case has been further simulated introducing the use of double AR coating on the glass (overall solar transmittance of the glass 0.95) combined with a low emissivity material (emissivity = 0.02) on the inner side of the vacuum vessel. The performance is improved of more than 10% at temperature higher than 200 °C (blue circles specular, blue line diffuse model). The adoption of a more transparent glass (0.95 respect to 0.91 of solar transparency) improves the thermal efficiency of 0.04 and it is highlighted at lower T-T_{amb} (T_{amb} is the ambient temperature set at 20 °C) as shown in Figure 5.5.5. At higher temperature, the improvement is also due to the low surface emissivity of the vacuum vessel (emissivity of 0.02 respect to 0.15). In this case of planar geometries, the difference between diffuse and specular models are negligible.

Figure 5.5.5 reports also the simulation results of the proposed CPC configuration for both diffuse and specular models.



Figure 5.5.5 Thermal efficiency as function of the difference between the absorber and ambient temperature: simulation results for our planar experimental set-up (diffuse surface model (red line), specular surface model(red circle)); experimental efficiency of planar absorber in a vacuum box (black diamonds); simulation results for our experimental set-up equipped with double AR coating on glass and high reflectivity mirror on the internal surface (diffuse surface model (blue line), specular surface model (blue circle)); simulation results for a CPC inserted in the high vacuum collector (diffuse surface model (orange open square)); simulation results of a CPC inserted in the high vacuum collector with all internal surfaces covered by high reflectivity mirror (diffuse surface model (black dashed line)), specular surface model (black dashed line)), specular surface model (black cross)).

Due to the increased optical losses, the use of the CPC (in place of the flat absorber) reduces the efficiency at low temperatures from 0.88 down to 0.77. However, as the temperature

increases, the reduced emitting area and the presence of a high reflective mirror surrounding the absorber tube allows to obtain efficiency higher than 0.5 at temperature of 300 °C (0.4 at 350 °C, 0.2 at 400 °C). In this configuration, the adoption of the low emitting coating (emissivity 0.02) on all internal surfaces of the stainless-steel vessel produces negligible improvements (see straight orange line and dashed black line for diffuse model): most of the power emitted by the absorber pipe impinges on the parabolic mirrors and it is directed towards the glass.

As expected for the CPC configuration, the specular and diffuse models are not equivalent. The diffuse model predicts efficiency higher than the specular one, since mirrors can return to the pipe more of its thermal emission. In order to validate the specular model, an experimental setup is needed, and it will be subject of further investigations.

5.5.3. Optimized coating

The performance of the CPC collector could be further improved if an optimized coating is used. The coating proposed is a multilayer coating, composed of a Chromium metal layer sandwiched between two Chromium oxide layers (Cr_2O_3 -Cr- Cr_2O_3), on copper substrate. An SiO_2 layer has been used as an AR coating (design of the multilayer in Figure 5.5.6). The multi-layered absorber suitable for the CPC system embedded in a high vacuum envelope is designed for concentration ratio of 2.4 and 400 °C operating temperature, taking into account the relative importance of solar absorptance and infrared emissivity of the SSA.



Figure 5.5.6 Architecture used for the multilayer coating optimized for the CPC collector.

The following equation will be used to estimate the overall thermal efficiency η_{CPC} of the investigated device:

$$\eta_{CPC} = \alpha_S \cdot \tau_{glass} \cdot \rho^N - \frac{\varepsilon(T)\sigma_{SB}(T_h^4 - T_{amb}^4)}{H \cdot C}$$
(5.5.3)

where *N* is the average number of solar rays reflections onto parabolic mirrors before reaching the absorber (in this case is N = 1.5) [94]. The glass solar transmittance (τ) is set 0.95 (double AR coated) and parabolic mirrors reflectivity (ρ) is 0.95 (electropolished aluminium foils).

The thickness combination obtained using the optimization algorithm is of 68-45-13-23 nanometres for SiO₂-Cr₂O₃-Cr-Cr₂O₃ respectively (layer 1 to layer 4).

Figure 5.5.7 shows the spectral emissivity curves of the commercial absorber (TiNOx Energy® from ALMECO [57]) and the multi-layered coating proposed. What emerges is that the multilayer has $\lambda_{\text{cut-off}}$ lower than the commercial one.



Figure 5.5.7 Left axis: Spectral emissivity of a multilayer selective absorber optimized for a CPC embedded in a high vacuum thick envelope (blue), compared to a commercial absorber commonly used in high vacuum tube technology (red); Right axis: Solar Spectrum ASTM G173-03 (yellow).

The different shapes of the spectral emissivity define different α_s and $\varepsilon(T)$ values. Table 5.5.3 summarizes the results for both types of absorbers. The multilayer coating has the spectrally averaged emissivity $\varepsilon(T)$ significantly lower than the commercial absorber. Although the multilayer coating has a lower α_s with respect to the commercial absorber (0.90 versus 0.95), there is a strong reduction in thermal emittance.

Table 5.5.3 Spectrally averaged emissivity and absorptivity of TiNOx Energy $\widehat{\mathbb{R}}$ and the proposed multilayer coating.

	α_s	ε (100 °C)	ε (200 °C)	ε (300 °C)	ε (400 °C)	ε (500 °C)
TiNOx Energy®	0.95	0.038	0.048	0.064	0.085	0.112
Multilayer coating	0.90	0.019	0.023	0.029	0.037	0.046

Figure 5.5.8 shows the calculated overall efficiencies of the previously described CPC collector in case of the proposed multilayer and commercial TiNOx Energy® absorbers, through Equation 5.5.3. The overall efficiencies are reported depending on the difference between the absorber and ambient temperature (T- T_{amb}). Below T- $T_{amb} = 200$ °C the TiNOx Energy® absorber reaches higher efficiencies than the proposed multilayer, on the contrary, above T- $T_{amb} = 200$ °C the multilayer induces a better efficiency and significantly extends the working temperature.

Such results have an interesting correspondence with the behaviour of the weighting factor w, see Figure 3.3.1. The absorber temperature of 200 °C for 2.5 kWm⁻² is a turning point for w, since w is equal to 1. At higher temperatures, w > 1 and thermal emission is more important than solar absorption. The multilayer coating has been designed to operate above 200 °C and for this reason we paid much more attention to $\varepsilon(T)$ than α values, resulting in a lower cut-off wavelength than the commercial absorber.



Figure 5.5.8 Overall efficiency of the investigated CPC solar collector as a function of T - T_{amb} in case of the proposed multilayer absorbing coating and a commercial absorber (TiNOx Energy® from ALMECO).

A properly designed absorber can strongly impact on the performances of the investigated device. For example, when the TiNOx Energy[®] is applied, the stagnation condition is reached at $T - T_{amb} = 470$ °C, whereas at the same temperature the optimized multilayer still works with 0.50 of efficiency.

In conclusion, according to numerical simulations, it turns out that a Compound Parabolic Concentrator (CPC), with a low concentration factor 2.4, encapsulated within a high vacuum vessel can easily operate in the range 200 °C- 400 °C. The adoption of a commercial selective absorbing coating (TiNO_x Energy®, already used for concentrating systems) is not the best choice, instead if the absorber is properly designed high thermal conversion efficiency (up to 0.50 at 450 °C) could be reached. Despite the solar absorption of the proposed solar coating being lower than that of the commercial coating, the strong reduction in emissivity at infrared wavelengths guarantees better performances at mid-high temperatures opening the route to several applications.
6. Conclusions

For Evacuated Flat Plate Collectors (EFPC), the high working temperatures reached without concentration require special attention to be given to the radiative parameters of the selective coating. In the present work multilayer selective coatings have been optimized for EFPC technology, because even if there are some commercial solutions of solar selective coatings, they are not optimized for high vacuum insulated flat collectors, and the literature still lacks articles that propose valid selective coatings optimized for EFPC technology.

The multilayer selective coatings studied in this work are based on Chromium Oxide, Chromium or Titanium. Thin films of the material under investigation have been fabricated via Electron Beam and Sputtering Physical Vapour Depositions (PVD) to characterize the optical properties of the selected materials. A new ellipsometric analysis method is introduced. This new method allowed to perform accurate and reproducible analysis to evaluate the refractive index of the dielectric and metal films that compose the multilayer selective stack. The analysis method has been validated by comparing the experimentally measured spectral absorptance of the PVD deposited samples and the numerical simulations of the samples, performed using the extrapolated complex refractive index. A perfect match is shown between measurements of the fabricated coatings and their numerical counterpart. Percentage deviations between experimental data and the numerical counterparts are mostly within 5% confirming the validity of the physical model used and the obtained fit results.

The measured complex refractive index is used for the numerical simulations of the coatings and their optimization. Throughout the work different selective solar coating are studied. Diverse designs, deposition technologies, methods for the optimization, operating temperatures and application fields are investigated.

A $Cr_2O_3/Ti/Cr_2O_3/SiO_2$ tri-layer on aluminium substrate has been optimized using a fitting procedure aimed at finding the parameters of the coating that result in a selectivity spectrum as close as possible to the ideal one. The curve of the ideal absorber is built entering the operating temperature, the eventual concentration ratio, and the reference solar spectrum. The tri-layer under investigation is suited for mid-temperature applications, high vacuum insulation and no concentration. The results of the optimization process, which have been experimentally validated, show that a reduction in thermal emittance is essential to reach high operating and/or high stagnation temperatures in solar thermal unconcentrated applications. An efficiency of 52% can be achieved up to 260 °C with a 27% relative increase respect to one of the best commercial solutions. The stagnation temperature can also be increased to about 400 °C without concentration. It is worth mentioning that using the presented absorber on aluminium industrial substrate the radiation losses from coating would represent only 35% of the total radiation losses at 300 °C and contribution from the uncoated aluminium side accounts for the remaining 65%.

The HVFP performances would benefit from a substrate thermal emittance reduction. Such reduction could be obtained with a better finishing of the back side of the aluminium substrate or using a substrate with a lower thermal emittance (such as copper or silver). A simple yet effective way to enhance the performances of this solar absorber could be to deposit a copper coating (thermal emittance ≈ 0.02) on the back side of the absorber, on the aluminium surface. To test the properties of the copper coating on the aluminium a Cu coating was deposited via electron beam deposition technique on aluminium bulk substrates. The overall efficiency calculated for a commercial absorber equipped with the copper coating shows that at 250 °C

the efficiency of the absorber increases from 0.44 up to 0.52, with 18% enhancement in performances, and the stagnation temperature increases of about 20 °C, and the advantages of the low emissive coating increase with increasing temperature.

The second design of multilayer selective solar absorber presented in the thesis is a five-layer structure on copper substrate based on sputter deposited chromium oxide and chromium metal $(Cr/Cr_2O_3/Cr/Cr_2O_3/SiO_2)$. For this coating the optimization algorithm is developed aiming at obtaining multilayer SSA suitable for a mass industrial production. To guarantee the best result the method of ideal SSA fitness function has been abandoned in favour of a custom developed algorithm that considers the efficiency of the real coating as the fitness function of the optimization algorithm. The algorithm incorporates as a binding parameter the robustness of the coating in terms of efficiency loss when errors on layer thickness are made. Three coatings are designed to obtain the highest efficiency at 100 °C, 200 °C and 300 °C operating temperature while having a small sensitivity to thickness variations. Results of the optimization procedure predict an overall efficiency of the proposed SSAs in a EFPC as high as 0.84, 0.74 and 0.56 at 100 °C, 200 °C and 300 °C, respectively. Efficiency loss is less than 2 percentage points if the layer thickness variation is less than 20%. With the help of contour plots designed to efficiently deal with a five variables problem (as the five-layer structure used) enabled to identify a coating with a loss in efficiency due to variations in layer thickness as low as 0.015 in absolute value, by just limiting to 15% the error on two of the layers constituting the stack, whereas an error up to $\pm 30\%$ can be tolerated on the remaining layers. The optimized SSAs were fabricated via sputtering depositions both on optically smooth samples and bulk copper substrates. Smooth samples have been characterized via optical analysis, showing excellent results, in agreement to the simulation. Multilayers on bulk copper substrates have been characterized by both thermal and optical analysis. The measured thermal emittances on copper bulk substrates are slightly higher than expected from the simulations. The origin of such increase could be due to factors like the surface roughness or the presence of copper oxides at the interface between substrate and multilayer and it need to be investigated. Understanding the origin of the increased emittance would allow to further improve the SSA performances. However, the coatings on bulk copper substrate have a very low emittance preserving a large absorptance and reaching stagnation temperature beyond 350 °C with superior performances with respect to commercial coatings. Absorber efficiency higher than 70% at 200 °C and higher than 40% at 300 °C have been obtained. The outstanding results obtained for the samples deposited on bulk substrate fabricated via sputtering deposition technique confirm that the fabrication process can be easily transferred to industrial deposition systems. Short duration high temperature thermal stability tests of the fabricated absorbers delivered encouraging results on the resistance of the coating to high operating temperatures.

A valuable option to further increase solar-to-thermal conversion efficiencies is represented by the Compound Parabolic Concentrators (CPC), which offer possibility to reach high temperatures thanks to moderate concentration, at high efficiency without incurring in the expenses of complicated tracking systems and high maintenance costs. In this work a CPC with low concentration factor (2.4) embedded in a high vacuum vessel in place of a flat absorber has been simulated. The selective coating used in the numerical models is a commercial coating. Due to the increased optical losses, the use of the CPC (in place of the flat absorber) reduces the efficiency at low temperatures. However, as the temperature increases, the reduced emitting area and the presence of a high reflective mirror surrounding the absorber tube allows to obtain efficiency higher than 50% at temperature of 300 $^{\circ}$ C (0.4 at 350 $^{\circ}$ C, 0.2 at 400 $^{\circ}$ C).

Thermal simulations showed how the adoption of a low emitting coating (emissivity 0.02) on all internal surfaces of the stainless-steel vessel produces negligible improvements since most of the power emitted by the absorber pipe impinges on the parabolic mirrors and it is directed towards the glass. The CPC architecture has been simulated with both diffuse and specular approach: as expected for the CPC configuration, the two approaches are not equivalent. The diffuse model predicts efficiency higher than the specular one, since mirrors can return to the pipe more of its thermal emission. However, to validate the specular model, an experimental setup is needed, and it will be subject of further investigations.

The performance of the CPC collector could be further improved if an optimized coating is used. The design proposed for the CPC high temperature application is a tri-layer coating, based on Chromium and Chromium oxide layers (Cr_2O_3 -Cr- Cr_2O_3). An SiO_2 layer has been used as an AR coating. The multi-layered absorber suitable for the investigated CPC system is designed for concentration ratio of 2.4 and 400 °C operating temperature. The results show how proper design of the solar absorber allows to reach high thermal conversion efficiency, up to 0.50 at 450 °C, outperforming a non-optimal coating whose stagnation temperature is not above 470 °C.

Lastly, a Cr_2O_3 -Cr based coating has been optimized for high stagnation temperature applications for the purpose of guaranteeing the high operating temperatures needed for the regeneration of the getter pumps that keep high vacuum inside the collector vessel. The multilayer has been optimized via the developed custom algorithm aiming at high operating temperatures. The selective coatings have been deposited via roll-to-roll industrial sputtering machine on a 0.2 mm copper substrate. The SSA coatings fabricated with the machine showed high performances, reaching stagnation temperatures as high 410 °C with less than 1 kWm⁻² incident power. The architecture used for the SSA proved to be reproducible and stable against layer thickness small variations around the optimal values. Experimental results show that when mounted on the getter pump assembly the coatings allow to the getter to reach stagnation temperatures higher than the commercial coating used at present (for LED light spectrum).

The excellent results obtained with the roll-to-roll sputtering machine on an industrial grade substrate confirm the industrial feasibility of the investigated coatings.

The results obtained, if confirmed on industrial large-scale production, indicate that properly optimized solar coatings, together with high vacuum technology could revolutionize the solar energy market, promising unparalleled performances for flat plate collectors. In this way the solar energy could supply heat at medium temperature at high efficiency, providing a cost competitive alternative to fossil fuels, being more attracting to the industrial sector and thus being more integrated in industrial plants.

7. Future developments

Experimental measurements of the investigated selective coatings show that thermal emittance of the multilayers deposited on bulk substrate is higher than expected from simulations (simulation are for smooth samples). A possible source of such increase could be due to factors like the influence of the surface roughness or in the presence of copper oxides at the interface between the substrate and the multilayer. So, in future works the origin of the increased emittance should be investigated, allowing to further improve the SSA performances.

Thermal stability is a rather important parameter for selective solar absorbers because a stable absorber guarantees its performances all along its service lifetime: even if literature and preliminary experimental tests showed encouraging results in terms of thermal stability for the selective coatings developed in this work, a detailed and accurate study of the ageing mechanisms which are characteristic of the fabricated selective absorbers should be provided. In future studies accelerated thermal ageing tests should be tailor-made for high vacuum insulated flat plate collectors, since the standard tests are developed for low temperature application in air. A proper test rig for experimental measurements should confirm the thermal stability of the coatings, as well.

Solid state diffusion mechanisms between the different phases of the coating and between the coating and the substrate involve alteration of the optical properties and a deterioration of the performances of the coatings. Testing a diffusion barrier to avoid diffusion mechanisms should be object of future studies.

Simulations of a CPC with low concentration factor (2.4) embedded in a high vacuum vessel and equipped with a properly optimized coating promise excellent performances, an increase solar-to-thermal conversion efficiencies at mid to high temperatures end an extended temperature range. It is suggested for future studies to design and build a prototype of such collector to perform experimental measurements and validate the simulation results.

8. References

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