La borsa di dottorato è stata cofinanziata con risorse del Programma Operativo Nazionale Ricerca e Innovazione 2014-2020 (CCI 2014IT16M2OP005), Fondo Sociale Europeo, Azione I.1 "Dottorati Innovativi con caratterizzazione Industriale"



UNIONE EUROPEA Fondo Sociale Europeo







UNIVERSITÀ DEGLI STUDI DI NAPOLI Federico II

DOTTORATO DI RICERCA IN FISICA

Ciclo: XXXIV

Coordinatore: Prof. Salvatore Capozziello

Selective coatings for efficient solar energy conversion in flat panels

Settore Scientifico Disciplinare: FIS/01

Tutor Prof. Emiliano Di Gennaro Dr. Roberto Russo **Candidato** Daniela De Luca

Anno Accademico 2018/2021

Contents

Abbreviations and subscripts 1								
Sy	Symbols3Introduction5							
In								
1	Sola	r thermal systems and working principles	11					
	1.1	Basic principles of optics and radiations	11					
		1.1.1 Optical properties of materials	11					
		1.1.2 Heat transfer and blackbody emission	14					
		1.1.3 The solar spectrum	14					
	1.0	1.1.4 Radiative properties of surfaces	15					
	1.2	Solar thermal systems	17					
	1.3	The HVFP by TVP Solar	20					
	1.4	Strategies for increasing the solar conversion efficiency	21					
		1.4.1 The selective solar absorber	22					
		1.4.2 IR mirror	25					
2	Performance analysis of an HVPF equipped with an IR mirror 27							
	2.1	State of the art: IR mirror for concentrating systems	27					
	2.2	Modeling of HVFP and IR mirror	28					
	2.3	Efficiency and power loss in systems with ideal mirrors	29					
	2.4	Efficiency and power loss in systems with realistic mirrors	33					
	2.5	Monthly and annual energy conversion	34					
3	Exp	erimental setup	37					
	3.1	Thin films deposition: magnetron sputtering	37					
	3.2	Thin films characterization	40					
		3.2.1 Profilometry	40					
		3.2.2 Reflectance/transmittance measurements	40					
		3.2.3 Ellipsometry	42					
	3.3	Optical simulations: S4 and Open Filters	44					
		3.3.1 Stanford Stratified Structure Solver: S4	44					
		3.3.2 Open Filters	46					
		3.3.3 Comparison between S4 and OF	48					
	3.4	Optimization techniques	48					
		3.4.1 Matching layers and apodization functions	49					
		3.4.2 Optimization in Open Filters: thickness refinement, needles						
		and steps	49					

4	Methodology for the design and fabrication of an IR mirror				
	4.1	IR mirror: state of the art	51		
	4.2	DBR and rugate design	52		
	4.3	The choice of materials	54		
	4.4	Rugate design based on silicon nitrides	55		
		4.4.1 Deposition and characterization of single silicon nitride films .	55		
		4.4.2 The SiN _{x} -based IR mirror	60		
	4.5	Rugate design based on silicon and titanium dioxides	61		
		4.5.1 Deposition and characterization of single films of SiO ₂ and TiO ₂	62		
		4.5.2 The SiO ₂ - and TiO ₂ -based IR mirror \ldots \ldots \ldots \ldots	64		
	4.6	Final considerations on the IR mirror	66		
5	Control of thermal emissions via selective multilaver		71		
	5.1	PV cell operation	71		
	5.2	The interest in TPV technologies	74		
	5.3	Selective emitters: state of the art	76		
	5.4	Design of multilayer-based selective emitters	78		
		5.4.1 The choice of materials	78		
		5.4.2 HfC: study of the refractive index	78		
		5.4.3 Scheme of selective emitters	80		
Summary					
Co	Conclusions and perspectives				
A	A Further investigation on SiN _x samples				
B	B Details on the selective emitters design				
Bi	Bibliography				

Abbreviations and subscripts

AR	Antireflective
AM	Air Mass
ASTM	American Society for Testing and Materials
BB	Blackbody
С	Solar concentration
CPC	Compound Parabolic Concentrator
CSP	Concentrating Solar Power
FWHM	Full Width at Half Maximum
HVFP	High Vacuum insulated Flat solar thermal Panels
Ι	Solar irradiance, Wm^{-2}
IR	Infrared
IRM	Infrared mirror
MT-SSA	Mid-Temperature Selective Solar Absorber
NEG	Non-Evaporable Getter
NREL	National Renewable Energy Laboratory
PV	PhotoVoltaics
SE	Selective Emitter
SSA	Selective Solar Absorber
Т	Temperature, °C or K
TEG	Thermoelectric Generator
TPV	Thermo-PhotoVoltaics
TSC	Transpired Solar Collector
UV	UltraViolet
VIS	Visible
abs	Absorber
all	Overall
с	Collector
cut	Cut-off
q	Power loss, Wm^{-2}
sub	Substrate

thres Threshold vess Vessel

Symbols

σ_{SB}	Stefan–Boltzmann constant, $Wm^{-2}K^{-4}$
α	Absorptance
а	Absorption (or attenuation) coeffiecient
С	Vacuum propagation speed
Δ	Bandwidth, μ m
ε	Emittance
η	Efficiency
λ	Wavelength, μ m or nm
τ	Transmittance
ρ	Reflectance
ν	Frequency, Hz
υ	Propagation speed
h	Planck's constant, $J \cdot s$
k_B	Boltzmann's constant, J/K
п	Refractive index
k	Extinction coefficient

Introduction

Global warming is a relevant issue that currently engage the entire world: since the pre-industrial era ('900) the human activities, the fossil fuels burning, and the industrialization increased the heat-trapping greenhouse gas levels in Earth's atmosphere, causing an increasing of the average global surface temperature and a climate change: scientists have observed that rain has increased by 15% and the sea level has risen by 10.5 cm during the last century [1], while the Intergovernmental Panel on Climate Change predicts a temperature rise of 1 to 5 °C over the next century.

Renewable energies, including hydropower, biomass, geothermal, waves, tides, wind, solar, etc., could be a solution to this problem through the *mitigation* of the greenhouse gases in the atmosphere. The schematic of Figure 1 compares the annual energy consumption of the world to the known reserves of the finite fossil and nuclear resources and to the yearly potential of the renewable alternatives [2]. The volume of each sphere represents the total amount of energy recoverable from the finite reserves and the energy recoverable per year from renewable sources. It shows that the renewable sources are not all equivalent by far: the solar resource is orders of magnitude larger than all the others combined.



FIGURE 1: Finite and renewable planetary energy reserves (Terawatt-years). Total recoverable reserves are shown for the finite resources. Yearly potential is shown for the renewables. [2]

Various studies confirm that, despite about half of the solar radiation is either absorbed or reflected by the clouds and the atmosphere, the Earth's surface still receive enough power to meet the demands of the whole world [3, 4]. It is an abundant, free, clean and CO_2 -free source of energy with a great potentiality in reducing

global warming and supplying for fossil fuels [5–7]. And, last but not least, it is inexhaustible and limitless. According to the National Renewable Energy Laboratory (NREL) [8], "solar energy is a powerful source of energy that can be used to heat, cool, and light homes and businesses", and "more energy from the sun falls on the earth in one hour than is used by everyone in the world in one year". Therefore, as long as we develop and improve systems that are capable to capture and to harness the solar resource and convert it into useful energy, a "free" source of energy could be available to everyone. Furthermore, the environmental impact of solar power is significantly smaller than other power generation methods, in fact the impact is mainly related to the production and supply of the special materials and metals that are required to produce the devices to harness such energy.

In the last decades, more and more systems collecting solar energy have been installed in our homes and also industries have chosen to install solar panels for a cheaper source of energy. The most popular device is the photovoltaic (PV), based on the photovoltaic effect (from which it takes its name), which converts sunlight directly into electricity to power homes or businesses. There are also thermoelectric generators (TEG), also called Seebeck generators, which are solid state devices that convert heat flux directly into electrical energy through Seebeck effect. On the other side there are technologies like concentrating and non-concentrating devices which instead produce thermal energy, of great interest for both domestic and industrial use. Finally, in addition to PV and solar thermal devices there are thermophotovoltaic systems, which are currently at an earlier stage of development but represent a promising technology for the simultaneous heat recovery and electricity generation.

Why generate heat? Unlike what is commonly thought, heating accounts for a significant portion of the world's total energy demand: in Europe, for example, the energy demand for heating and cooling is of 49%, while those for electricity and transport are 20% and 31%, respectively. In the world, the building sector alone consumes 35.3%, of which more than 50% is for space heating and domestic water heating (Fig. 2).



FIGURE 2: Household energy demand. (Source: IEA Electricity/Heat in World in 2009)

Besides buildings, there is substantial heat consumption for industrial processes (food industries, textile industries, etc.) and heat-intensive services [3]. In particular, the Solar Payback (2017) showed that heat represents three quarters of industrial energy demand worldwide (Fig. 3). Of this, only the 9% is supplied by renewable sources, and half of it is required as medium and low-temperatures heat. Therefore, solar collectors could play a key role in the energy transition.



FIGURE 3: Worldwide industrial energy demand (Source: Solar Payback, 2017).

The technologies most used to produce heat are concentrating solar power (CSP) systems and flat plates. The CSP is mainly used for power plants since its structure is quite complex: it uses mirrors to reflect and concentrate sunlight into a receiver collector, that collects the solar energy. Such systems are suitable for high temperature heat (up to 500 °C), but they can be very expensive and bulky. On the other hand flat plates can be used to drive a heat engine connected to an electrical power generator, or for processing heating and cooling. They are preferred in both industrial and residential applications thanks to their minor cost, easier maintenance, and less bulky structure. Unfortunately, at temperatures above 100 °C their efficiency is quite low.

Recently, more versatile systems that convert the solar energy into heat are catching on: the High Vacuum insulated Flat solar thermal Panels (HVFP), which supply mid-temperature output with high efficiency. In fact, the high vacuum insulation reduces the conductive and convective losses due to the gas, increasing the operating temperature from the old 80-100 °C up to 200 °C. Unfortunately, the radiative losses due to the hot absorber still survive and rises rapidly with temperature, particularly in the absence of concentration [9]. This limits the use of flat panel devices at temperatures around 180 °C, since they experience a fast drop off in the radiative efficiency of the absorber [10].

Therefore, it is then clear the main limitation of solar power is linked to our ability to turn it into electricity or heating in an efficient and cost-effective way. In fact, the fraction of the produced renewable energy is still very low compared to the total demand, which makes even more interesting and indispensable the research in more efficient energy usage, generation, and conversion systems.

To provide solutions to these problems, this thesis focuses on the description and development of new optical elements useful for improving the performance of solar devices, showing that controlling and tailoring the optical properties of such elements is crucial. In fact, this Ph.D. program is born as a part of the FSE-FESR National Operational Program "Ricerca e Innovazione 2014-2020" of the Italian *Ministero dell'Istruzione, dell'Università e della Ricerca*, and intends to support the promotion and strengthening of fostering collaboration between academic world and private industry in the field of scientific research. Therefore, in this context, I have been involved in the development and optimization of new products in collaboration with the company TVP Solar [11].

The first part of this Ph.D. program has been focused on the increase of the energy conversion efficiency in high-vacuum flat solar thermal panels through the development of a novel filter, the *IR mirror*, to be applied on the glass envelope of the HVFPs developed by the company TVP Solar. In this context, such mirror is useful for triggering the cold-side external photon mechanism in evacuated collectors, allowing for the recovery of the infrared radiation emitted by the hot absorber. However, even if it has been developed for a high-vacuum flat solar thermal panel, the approach is general enough that it could potentially be extended to any emissive solar thermal device.

The second part of the Ph.D. program is focused on the development of *selective emitters* to be used in thermo-photovoltaic (TPV) technologies. In fact, the development and use of selective emitters could play a key role in increasing the efficiency of these devices and in reducing heat losses: they would act as a "filter" that lets only photons with energy above the bandgap of the photovoltaic cell pass through. The idea is to design easy-to-fabricate selective emitters based on multilayers, as the ones currently available involve mainly metamaterials, metasurfaces, plasmonics structures or nanofabrications, which could be difficult to scale at an industrial level.

One of the main drawbacks in the development of both IR mirrors and selective emitters is the need for simple and cost-effective solutions, which must be easily reproducible on a large scale production and used on a daily basis in industrial applications. This brought with it many constraints, such as the use of deposition techniques that can be easily applied on an industrial level, the design of structures which avoid complex techniques (such as nanostructuring of surfaces, nanoparticles or ion implantation), the choice of materials inexpensive and easy to handle, etc. In fact, this work represents the first step towards the broader, industrial development of these elements, where all the aforementioned characteristics are fundamental.

The thesis is structured as follows: Chapter 1 focuses on the general framework and the basic physical principles useful for this study, i.e. the fundamentals of optics and thermal radiation. The state of the art of solar thermal systems is also summarized, with a focus on the HVFP developed by TVP Solar. The introduction to the main routes that enable the increase of efficiency in HVFPs concludes the chapter. Then, in Chapter 2, follows the description of a thermal model based on the properties of the currently existing HVFP and on the calculation methods. The model has been built to gain a complete understanding of the effectiveness of an IR mirror applied to HVFPs, regardless of the specific properties of the mirror but taking into account the general limitations that these devices present. Therefore, Chapter 2 compares the performance of evacuated panels equipped with an IR mirror, alternatively with ideal or realistic properties, with the same panel without any mirror. Chapter 3 describes the experimental setup used in the course of the IR mirror development, ranging from the thin film deposition tool to the various instruments utilized for the characterization of the deposited films. The two optical simulators software used are also presented, in addition to the description of the technique used for the optimization of multilayer filters. Chapter 4 illustrates the complete methodology for the design and fabrication of an IR mirror, starting from the choice of the design and of the materials and ending with the proposal of two different IR mirror solutions that meet the industrial requirements. Chapter 5 is instead based on the simulation of the spectral emissivity of different easy-to-fabricate selective emitters design, consisting of various high-melting point materials and structures. An overview of the TPV technology and of the working principle of the PV cell is also given. Finally, the

conclusions reported at the end of this document summarize the study and gives a critical evaluation and prospects for possible future works.

The work presented in this thesis has been carried out in collaboration with: University of Naples "Federico II" in Naples (Italy); Istituto di Scienze Applicate e Sistemi Intelligenti "Eduardo Caianiello" (ISASI - CNR) of Naples (Italy); TVP Solar [11] in Avellino (Italy); Purdue University, in West Lafayette (Indiana, USA).

Chapter 1

Solar thermal systems and working principles

This introductory chapter intends to provide a general overview on solar thermal systems. First, we introduce some useful principles and basic notions (section 1.1), then we introduce solar thermal systems (section 1.2), with a particular focus on the evacuated flat solar thermal panels produced by the company TVP Solar (section 1.3). Hence, we illustrate two different approach useful to improve the performance of evacuated flat thermal solar panels (section 1.4).

1.1 Basic principles of optics and radiations

This section introduces the main concepts for a complete understanding of the optical and radiative properties of the materials, the heat transfer mechanisms and briefly describe the blackbody emission and the solar spectrum.

1.1.1 Optical properties of materials

An electromagnetic wave is a transverse wave consisting of an electric field vector, **E**, and a magnetic field vector, **B**, function of position and time, mutually perpendicular and perpendicular to the direction of propagation (Fig. 1.1).



FIGURE 1.1: Linearly polarized electromagnetic wave. Adapted from [12].

The propagation speed, *v*, is defined as follows:

$$v = \lambda \nu \tag{1.1}$$

where λ is the wavelength, i.e. the distance over which the wave's shape repeats, and ν is the frequency, i.e. number of cycles per unit of time. The speed defined in Eq. 1.1 can be also related to the dielectric constant (or permittivity) ε and the magnetic permeability μ of the medium in which the wave propagates, as predicted by Maxwell's equations:

$$v = \frac{1}{\sqrt{\varepsilon\mu}}.$$
(1.2)

Note that ε depends on the properties of the medium considered through the relative permittivity ε_r : $\varepsilon = \varepsilon_r \cdot \varepsilon_0$. The same applies to the magnetic permeability: $\mu = \mu_r \cdot \mu_0$. When light propagates in vacuum it assumes its maximum value, in fact $\varepsilon_r = \mu_r = 1$ and

$$v = c = \frac{1}{\sqrt{\varepsilon_0 \mu_0}} \tag{1.3}$$

The value of *c* is well known: $c = 2.99792 \cdot 10^8$ m/s.

The electromagnetic spectrum represents the range of frequencies of electromagnetic radiation and their respective wavelengths and photon energies. It is illustrated in Fig. 1.2, where it is evident the partition in separate bands: radio waves, microwaves, infrared, visible light, ultraviolet, X-rays, and gamma rays at the highfrequency (short wavelength) end.



FIGURE 1.2: The electromagnetic spectrum showing the boundaries between different regions and the type of atomic or molecular transition responsible for the change in energy. The colored inset shows the visible spectrum [13].

While the electromagnetic radiation propagates through a medium and hits the surface of an object, the following phenomena can affect the incident light beam [14], as schematized in Fig. 1.3:

- **Reflection**: reduction of the light velocity and bending of the rays;
- Absorption: attenuation of the beam as it progresses;
- **Transmission**: non-absorbed light passes through the medium. If the light goes through the object and bends at an angle, we talk about **refraction**.



FIGURE 1.3: Reflection, absorption, and transmission of a light beam incident on a medium.

These phenomena can be described by the coefficient of reflection (ρ_{λ}), absorption (α_{λ}), and transmission (τ_{λ}), which corresponds to the reflected, absorbed, and transmitted fraction of the total incoming irradiation, *G*. Note that the defined coefficients are wavelength-dependent; to indicate the total values (α, ρ, τ) we need to calculate their spectral average. Therefore, recalling the conservation of energy, we can state that the sum of the fraction of light transmitted, absorbed, and reflected must return the intensity of the incident beam, at each wavelength λ . In other words:

$$\rho G + \alpha G + \tau G = G. \tag{1.4}$$

The *absorption* (or *attenuation*) *coefficient*, *a*, is defined through the Beer-Lambert law as the rate at which the light is absorbed when traveling through the material:

$$I(z) = I_0 e^{-at}, (1.5)$$

where t is the object thickness, and I the beam intensity. *a* is also related to quantity named *extinction coefficient*, k:

$$a = \frac{4\pi k}{\lambda}.$$
 (1.6)

The extinction coefficient, k, describes how the intensity decreases as the light passes through the material. It is part of the complex refractive index, \tilde{n} , which describes the propagation of an electromagnetic wave through a medium. It is defined by the following equation:

$$\tilde{n} = n + ik \tag{1.7}$$

where n is refractive index, defined as the ratio between the speed of light in vacuum and in the material, n = c/v, while k measures how fast light vanished in a material. Both n and k, are functions of the wavelength.

It is possible to relate the refractive index of a medium to its dielectric constat, ε_r :

$$n = \sqrt{\varepsilon_r}.\tag{1.8}$$

Being $\varepsilon_r = \varepsilon_1 + i\varepsilon_2$, results:

$$\varepsilon_1 = n^2 - k^2,$$

$$\varepsilon_2 = 2nk.$$
(1.9)

Assuming a plane wave that is partially reflected and transmitted when arrives at the object surface, its electric field vector can be decomposed in E_s and E_p , components normal and parallel to plane of incidence, respectively. The reflection of the

components is described by the *Fresnel coefficients* of reflection:

$$r_p = \frac{E'_p}{E'_p} = |r_p|e^{i\delta_p}, \qquad r_s = \frac{E'_s}{E'_s} = |r_s|e^{i\delta_s}.$$
 (1.10)

The modules of r_p and r_s give the change in amplitude of the electric field components, while their phases describe the shift due to reflection.

1.1.2 Heat transfer and blackbody emission

From thermodynamics, we have learned that energy can be transferred by interaction of a system and the surrounding environment. There exist three different processes of thermal energy (heat) transfer, also known as *modes* [15]. The first mode is named *conduction*, and refers to the heat transfer that occur across the medium; the second mode is the *convection*, which represents the heat transfer that occur between a surface and a moving fluid at different temperatures; the third and last mode is the *thermal radiation*: all surfaces at a certain temperature emit energy in form of electromagnetic waves. While conduction and convection modes require the presence of a material medium to allow the energy transfer, radiation does not. In fact, radiation transfer occurs most efficiently in vacuum.

The intensity of the emission depends mainly on the object's temperature, according to the Planck's law of blackbody radiation, described by equation 1.11. Note that the blackbody radiation is defined as the thermal radiation emitted by an ideal body, the *blackbody* (BB), that is both a perfect absorber and a perfect emitter. In fact, it always absorbs and emits more energy than any other object at the same temperature.

$$B_{\lambda}(T) = \frac{2\pi hc^2}{\lambda^5} \cdot \frac{1}{e^{(\frac{hc}{\lambda k_B T})} - 1}.$$
(1.11)

In Eq. 1.11 *h* is the Planck's constant, $h = 6.62 \cdot 10^{-34} J \cdot s$, *c* the speed of light, λ the wavelength, $k_B = 1.38 \cdot 10^{-23} J/K$ is the Boltzmann's constant, and T the temperature in Kelvin degrees. As temperature increases, the maximum intensity of black body radiation is shifted to shorter wavelengths, according to the Wien's displacement law, $\lambda_{max} = b/T$, b=2898 $\mu m \cdot K$. This is illustrated in Fig. 1.4.

The maximum limit to the *emitted power*, the rate at which energy is released per unit of are (W/m^2) , is given by the Stephan-Boltzmann law:

$$E_{BB} = \varepsilon \sigma_{SB} T^4 \tag{1.12}$$

where T is the absolute temperature (K), $\sigma_{SB} = 5.67 \cdot 10^{-8} \text{ W/m}^2 \cdot \text{K}^4$ is the Stephan-Boltzmann constant, and ε is the surface emissivity, $0 \le \varepsilon \le 1$ ($\varepsilon = 1$ for blackbodies).

1.1.3 The solar spectrum

The Sun's surface behaves like a blackbody at a temperature of about 5800 K, with some near-zero intensity regions due to the light absorption in the atmosphere. The portion of electromagnetic spectrum emitted by the Sun is well known as *solar radiation*. Because it varies according to the location and time of the year, Fig. 1.5 shows the standard solar irradiance at the Earth's surface, as defined by the American Society for Testing and Materials (ASTM) G173-03, for an Air Mass (AM) of 1.5 [16]. The AM coefficient quantifies the reduction in the power of light as it passes through the atmosphere and is absorbed by air and dust. It is defined as the length of the path



FIGURE 1.4: Blackbody radiation spectrum at different temperatures: 273 K (black line), 473 K (red line), and 673 K (blue line). Inset (logarithmic scale): the position of the wavelength for the maximum intensity of the BB radiation at different temperatures are highlighted.

that light travels through the atmosphere normalized to the shortest possible path length (i.e. when the sun is vertically upwards).

As evident from the figure 1.5, the solar radiation exists in the UV, VIS, and near-IR regions, such as between 0.3 and 2.5 μm . The reader should note that a BB in thermal equilibrium at the temperature of 673 K or below emits in a wavelengths range that negligibly overlaps with the solar spectrum [17].

1.1.4 Radiative properties of surfaces

As the blackbody emits the maximum radiant energy at each considered temperature, we can define the *spectral emittance*, ε_{λ} , of a material as the fraction of energy radiated by the material with respect the one emitted by a blackbody at the same temperature and in the same range of wavelengths:

$$\varepsilon_{\lambda}(T) = \frac{E_{\lambda}(T)}{B_{\lambda}(T)}.$$
(1.13)

The *total emittance* or *thermal emittance*, ε , is defined by integration of ε_{λ} over the whole range of wavelengths:

$$\varepsilon(T) = \frac{\int_0^\infty \varepsilon_\lambda(T) B_\lambda(T) d\lambda}{\int_0^\infty B_\lambda(T) d\lambda}.$$
(1.14)

As already mentioned in Section 1.1.1, when the radiative energy hits the surface of an object it is partially reflected, transmitted, and eventually absorbed. Of course, the principle of energy conservation must be satisfied (Eq. 1.4), and in case of opaque surfaces it becomes:

$$\alpha_{\lambda} = 1 - \rho_{\lambda}. \tag{1.15}$$



FIGURE 1.5: Solar spectral irradiance at AM 1.5 as defined by ASTM-G173-03. The seven pure spectral colors are highlighted. Note that the ranges indicated in the illustration are an approximation, as the real spectrum is continuous. Two BB emissions at 573 K and 673 K are included: olive green and grey dashed lines, respectively.

According to the Kirchhoff's law of thermal radiation, when the examined surface is in thermal equilibrium radiates a quantity of power which is equal to the power absorbed. In other words, if the transmission through the designed structure is negligible, the emissivity of an object is equal to its absorptivity.

$$\alpha_{\lambda}(T) = \varepsilon_{\lambda}(T) \tag{1.16}$$

By combination of Eqs. 1.15 and 1.16 we obtain a direct link between α_{λ} , ε_{λ} , and ρ_{λ} . Therefore, the spectrally averaged solar absorptance and the thermal emittance can be defined as follows:

$$\alpha(T) = \frac{\int_0^\infty (1 - \rho_\lambda) \cdot S_\lambda(T) d\lambda}{\int_0^\infty S_\lambda(T) d\lambda},$$

$$\varepsilon(T) = \frac{\int_0^\infty (1 - \rho_\lambda) \cdot B_\lambda(T) d\lambda}{\int_0^\infty B_\lambda(T) d\lambda},$$
(1.17)

where $S_{\lambda}(T)$ indicates the solar spectral irradiance (Wm^{-3}).

From the measurement of the optical reflectivity and the determination of the previous we can evaluate the thermal efficiency of a device.

In solar thermal systems the *thermal transfer efficiency* η represents the fraction of solar irradiation that is actually converted into thermal energy. It depends on the temperature and on the solar concentration ratio, *C*, which represents the ratio of observed intensity to the solar intensity *I* (generally considered to be 1000 Wm^{-2} under standard testing conditions [16]) [18]:

$$\eta = \alpha(T) - \frac{\varepsilon(T)\sigma T^4}{C \cdot I}.$$
(1.18)

1.2 Solar thermal systems

Solar thermal systems are devices used to collect the solar radiation and convert it into thermal energy through a *transport medium*. They are usually classified in terms of the working temperature as:

- **low-temperature technologies**, involving working temperatures below 70°C requested by applications like space or water heating, etc.;
- **medium-temperature technologies**, with temperatures between 70°C and 200°C of interest for solar cooling, solar distillation, etc.;
- **high-temperature technologies**, with temperatures above 200°C useful in solar thermal power generation systems.

In the following we introduce the main types of solar collectors used for solar water heating systems: unglazed collectors, flat plate collectors, evacuated tubes, parabolic troughs (Fig. 1.6).



FIGURE 1.6: Different types of solar thermal collectors. Adapted from [19].

Typically, **unglazed collectors** consist of a dark metallic or black plastic absorber plate without a cover. The absence of glazing allows them to absorb a larger portion of the solar energy, but because they are not insulated a large portion of the heat absorbed is lost, particularly when it is windy. In fact, they are mostly involved in low temperature applications, below 30 °C, such as for heating swimming pools. The most common type of unglazed collector on the market is the *transpired solar collector* (TSC), widely used in Canada and USA. They use solar energy to heat the absorber surface (usually steel or aluminium), which transmits thermal energy to the ambient air. The contact surface between the absorber and air is increased by drawing air through the multiple small perforations into the cavity between the skin and building facade. The schematic of a TSC is illustrated in Fig. 1.7.

Parabolic trough collectors are more appealing for the industrial purposes, as they can reach high operating temperatures (200-500 °C) with relatively high efficiency. To sustain the high temperatures, the solar absorber is made of stainless steel pipes and a selective coating, and the transfer fluid used could be either synthetic oil or molten salt. However, their structure is quite complex, as they consist of a concave reflective mirror that concentrates the solar light into its focus, where the receiver pipe is located. As they mostly collects the direct solar irradiation, and the



FIGURE 1.7: Schematic of a transpired solar collector [20].

diffuse portion of the radiation only if it falls within a specific acceptance cone angle, such systems require a tracking infrastructure that allows to tilt the whole device to ensure that the solar radiation is parallel to the mirror axis. This, of course, adds to the expense and complication of the device itself, to the high maintenance costs and installation problems, which overall limit its use.

Another trough-type technology that concentrates solar energy onto a tube receiver is the **Compound Parabolic Concentrator (CPC)**. Two symmetric parabolic segments with different focal lengths are combined together to enable the collection of any solar radiation entering the collector aperture within an acceptance angle onto the tube receiver by means of multiple internal reflections. This allows CPCs to operate without continuous tracking. They have been found to provide the best optics for systems with a low solar radiation concentration and can be designed with low concentrating ratios (<5). They are well-suited for medium- to high-temperature applications [21].

On the other hand, conventional flat-plate collectors can collect both the direct and the diffuse component of radiation. Their basic structure is relatively simple: a metallic chamber is equipped with a transparent glass cover on the top that let the solar radiation hit a solar absorber which, thanks to its adequate characteristics (on which we will focus on later), absorb the solar radiation. A transport medium, which is often a fluid like oil or water, flows into the conducting pipes. Both for the better price-to-performance ratio and for the easier mounting options (on the roof, standalone, etc.), flat systems are spreading a lot. Unfortunately, their demand is currently limited only to the more common low temperature applications (e.g. in residential sites, to heat or cool water and environments). In fact, their temperature output is too low ($\simeq 150$ °C) to meet the industrial requirements of mediumand high-temperature heat (above 250 °C). This is due to the fact that there are various source of loss in these devices: reflection losses, due to the glass cover and the absorber; conduction and convection losses, caused by the various connection elements within the panel and by the gas trapped into the chamber; radiative losses, mainly generated from the absorber, but a small part comes from all the components at high temperature.

As flat-plate collectors have the potential of reaching performance higher than that of compact parabolic concentrating collectors [22], it is essential to improve their

performance and work to extend the applicability of these systems. Fortunately, all the above causes of loss can be reduced with a proper design of the collector and with the use of new or improved elements.

A first step towards the improvement of the performance of these devices could be done with a partial evacuation of the panel, in fact at pressures lower than 10⁴ Pa the conduction losses almost vanish [23] (continuum regime of gas heat conduction being independent of pressure [24]). Gases like argon, xenon, krypton or sulfur hexafluoride could be introduced into the chamber: [24] demonstrated that they allow for lower conductivity compared to air, as shown in Fig. 1.8.



FIGURE 1.8: Conduction losses from the hot absorber to the metallic case in a flat plate collector, at different gas pressures and different filling gases.

Further improvements can be done with evacuated tubes, that can reach temperatures above 200 ° C with high efficiencies [25]. Their main innovation consists in the evacuation of the space between the absorber and the external box: taking the pressure down to 10^{-2} Pa greatly reduces the level of convective and conductive heat losses. In evacuated tubes the absorber can be either metallic or be concentrically attached to the inner and outer surface of the glass tube. There could be different types of devices: glass-metal or glass-glass evacuated tubes. The glass-metal tubes are made of curved absorber sheets placed inside a single glass tube, in vacuum, and an AR layer helps increasing the transparency. The glass to metal seal is subject to thermal stress and degradation because of the usually different thermal expansion coefficients [26]. Then, the vacuum seal can be at risk. The glass-glass tubes are made of two glass tubes fused together, and the absorber is placed at atmospheric pressure in the inner tube. This on one side solves the previous issue, while on the other side determines a reduction in absorption because of the double layer of glass. Both types of evacuated tubes suffer of a further issue: because of their structure, the regions between individual tubes and the gaps between each tube and its absorber do not contribute to absorption. Therefore, as according to the ISO 9806 standard [27] the efficiency has to be measured in terms of the area occupied by the device (gross area), flat plates appear as the most favourable systems.

To combine the advantages of evacuated tube collectors and flat plate collectors, a new type of collector is also gaining interest in the past years: the **evacuated flat**

plate collector. Similarly to the partial evacuated panel, their novelty is based on the lowering of the pressure, which in these systems is brought down to 10^{-2} Pa.

As already mentioned in the case of evacuated tubes, realizing evacuated flat collectors is not an easy task either: they need a glass-metal seal to join the glass cover and the metallic evacuated envelope, and a support against the atmospheric pressure. The company *TVP Solar* [11], based in Geneva (CH) and Avellino (IT), overcame the technical issues and is currently one of the leaders on the market in the production of evacuated flat plate collectors: it designs, develops, and manufactures high-performance High Vacuum insulated Flat Plate solar thermal Panel (HVFP) based on a proprietary technology for cooling and heating applications. The details on these devices are described in the next section.

1.3 The HVFP by TVP Solar

The solar thermal collectors produced by TVP Solar is showed in Fig. 1.9: it consists of two return and supply copper pipes, a support glass, and an absorber coated on a copper substrate and enclosed between a highly transparent glass cover and a stainless steel vessel. The glass support structure has pins capable to sustain the pressure exerted on the external glass, to realize a more solid structure, while the font glass is welded to the rest of the system by an adhesive paste. Therefore, the absorber has holes that have to include the pins. To guarantee the proper vacuum seal, the panel is tested by using a leaks detector and helium as a tracer gas. Finally, the system is baked in a proper oven at high temperature. The working principle of the HVFP could therefore be summarized as follows: as the absorber gets hotter, heat is transferred through the copper pipes to the transfer fluid, which raises its temperature. Of course, part of the heat emitted by the absorber is also transferred to the surrounding space: to minimize losses from the bottom and lateral sides, the collector has been insulated with aluminum.



FIGURE 1.9: Schematic of the HVFP produced by TVP Solar and of the getter pump (inset).

The technology is based on two innovative and patented ideas [28]:

• a flexible glass-metal seal made from inorganic material provides an efficient barrier to prevent air gas entering the vacuum envelop, thus reaching and maintaining a high vacuum (from 10^{-2} to 10^{-7} Pa, depending on the operating temperature);



FIGURE 1.10: Comparison between conversion efficiency (%) of (a) a traditional fiberglass insulated flat plate and (b) a HVPF.

 a proprietary Non-Evaporable Getter (NEG) holder allow getter activation during the panel evacuation and it is used to maintain the high vacuum throughout the service life of the collector by absorbing gas molecules outgassed from the inner surface of the collector. Then, it can be regenerated *in situ* by exposure to solar light.

The system is highly reliable (the estimated lifespan is of 25 years), 100% recyclable and designed as ideal thermal energy source for large-scale applications between 80 °C and 180 °C such as: air conditioning, desalination, and process heat [11]. In fact, the high vacuum insulation and the careful choice of the materials to use in the fabrication allow those systems to achieve a high efficiency up to operating temperature of 200 °C, as shown in Fig. 1.10: at 150 °C, the panel efficiency is of 50% and it reaches the stagnation point with 0% efficiency at about 300 °C. In particular, to avoid degassing (that in turn raise the internal pressure), low vapor pressure materials are used.

Nevertheless, Fig. 1.10 shows that, even though vacuum encapsulation brings many advantages, both the optical and the radiative contributions to the global losses remain. The latter, in particular, increases with the fourth power of the temperature (as stated by the Stephan-Boltzmann law in Eq. 1.12), limiting the efficiency of the devices. Therefore, in the next section we will discuss various strategies useful to overcome/reduce this problem.

1.4 Strategies for increasing the solar conversion efficiency

As mentioned in the previous section, the conversion efficiency in evacuated flat solar thermal devices drops quite fast when working at high operating temperatures, meaning that these panels cannot be used to extract solar heat at or above 180°C. It is evident from the Fig. 1.10 that the main contribution to the efficiency drop is due

to the radiation mechanism, which mainly comes from the hot absorber. Then, we must consider that if on one hand the hot absorber emits infrared radiation towards the glass cover, on the other hand, the glass cover absorbs it and loses it. Therefore, to reduce these losses and increase the current operating temperature of 180 °C to higher values, the first approach is to work on two different areas of the HVFP, the absorber and the glass cover, of which we will talk about in sections 1.4.1 and 1.4.2, respectively.

Another approach aimed at the increasing of the solar conversion efficiency is instead focused on the use of the high vacuum insulation in more complex systems, as for example in thermo-photovoltaic (TPV) or hybrid systems, i.e. systems made of the combination of two (or more) power generation technologies to make best use of their operating characteristics and to obtain efficiencies higher than that obtained from a single power source [29]. We will present this strategy in the chapter 5, by introducing TPV systems and selective thermal emitters.

1.4.1 The selective solar absorber

The absorber is the most important component of solar thermal devices, as it has to absorb as much solar radiation as possible for maximizing efficiency. Its performance is determined by solar absorptance (α) and thermal emittance (ε). To reduce the radiative loss, increase the panel efficiency and satisfy the needs for mid- and high-temperature heat (i.e. from 200 to 400 °C), the commercial absorber must be replaced by a spectrally-Selective Solar Absorber (SSA) [30, 31].



FIGURE 1.11: a) Normalized solar spectral irradiance (orange line) and normalized BB emission spectra at different temperatures: 473 K (solid black line), 673 K (solid red line), and 873 K (solid blue line). Ideal absorptivity curves for solar selective absorbers with different cut-off wavelength λ_{cut} , depending on the operating temperature (dashed-dotted lines). b) The cut-off wavelength, λ_{cut} , for the ideal SSA at different working temperatures.

Ideally, its behavior would be well described by the dash-dotted lines in Fig. 1.11 a), exhibiting an absorptivity curve described by:

$$\alpha_{\lambda} = \begin{cases} 1 & if & \lambda < \lambda_{cut}(T) \\ 0 & if & \lambda > \lambda_{cut}(T) \end{cases}$$
(1.19)

where $\lambda_{cut}(T)$ is the cut-off wavelength, defined as the transition wavelength from high-to-low absorptivity that maximizes the efficiency at a certain working temperature. Generally, this transition occurs at the wavelength where the blackbody

emission exceeds the incident solar radiation [32], and decreases with increasing the operating temperature, as highlighted in Fig. 1.11 a). Therefore, at temperatures higher than 200 °C, a significant part of the solar radiation is lost because of thermal emissions. Fig. 1.11 b) provides the optimal values of $\lambda_{cut}(T)$ as a function of temperature, calculated at C=1. The optimal values of $\lambda_{cut}(T)$ are obtained from an optimization procedure that maximizes the thermal efficiency, allowing for $\alpha \simeq 1$ in almost all the solar region. Note that the zero intensity regions in the solar spectrum at the Earth surface is responsible for the stepped behaviour of λ_{cut} [32].



FIGURE 1.12: Schematic of the various design of selective solar absorbers: (a) intrinsic absorbers, (b) semiconductor-metal tandems, (c) multilayer absorbers, (d) cermets (metal-dielectric composites), (e) surface texturing, and (f) PhC-based designs. [9]

Research on selective absorbers has been going on for several years and currently there are six different types of designs [10], shown in Fig. 1.12 and listed below:

- **intrinsic absorbers** [33]. They are made of materials with intrinsic selectivity (transition metals, semiconductors), induced by dielectric dispersion as a function of wavelength. Unfortunately, no natural materials have a perfect ideal selectivity;
- **semiconductor-metal tandems** [34, 35]. The semiconductor (most likely Si, Ge, and PbS), which efficiently absorbs the visible light, is deposited over a metal reflector, which reflects the long-wavelength radiation;
- **multilayer absorbers** [36, 37]. They consists of alternating layers of dielectric and metal and the working principle is based on the multiple reflections at the layers interfaces, which enhance the absorption of the incoming light;
- ceramic-metal composites (cermets)) [32, 38]. They consist of nanoscale metal
 particles embedded in a ceramic matrix, and are made of an AR layer, one or
 more cermet layer(s) that act as the primary absorber, and a reflective substrate
 to help minimizing the absorption of undesired IR wavelengths. They show a
 good selectivity at high temperatures;
- **textured surfaces** [39, 40]. In this case dendrite or porous microstructures are used to generate multiple internal reflections, to trap the incident light in the visible spectrum while rejecting the longer wavelengths (IR range);
- **photonic crystals** [41, 42]. They are made of periodic arrangements of materials with high and low dielectric constants. It generates a photonic bandgap in

which certain wavelengths are fully reflected for all incident angles and polarizations.

Realizing a selective solar absorber with ideal properties can be truly challenging: maintaining an ultra-low emissivity even at high temperatures is complicated, especially within a single structure subject to large temperature variations. In addition, the possibility that the emissivity curve has a finite slope in the transition from high absorptance to low emittance must be taken into consideration. The SSA currently installed in the HVFPs by TVP Solar is the commercial Mirotherm 1300 produced by *Alanod* [43], based upon an aluminum strip and an innovative threelayer absorber. Fig. 1.13 shows its emissivity spectrum and the BB emissions at three different temperature. It is evident that the absorber is optimized for low-



FIGURE 1.13: Left-hand axis: Solar spectral irradiance (orange line), BB (continuous lines) and SSA (dash-dotted lines) irradiance at different temperatures: a) 100 °C (blue line), c) 200 °C (red line), and d) 300 °C (green line). Right-hand axis: emissivity of a commercial absorber (Mirotherm, black line). b) Enlarged view of Fig. a) showing the low emittance of the commercial SSA working at 100 °C.

temperatures operation: it results in good performance at 100 °C, while shows rising thermal losses at 200 °C and above: at such temperatures the thermal emittance curves in Fig. 1.13 c) and d) cross the commercial absorber emissivity in a region where it is still high. In fact, one should remember that the heat losses increase with the operating temperature, according to Planck's law (Eq. 1.11). Thus, when working at temperature higher than 250 °C, the λ_{cut} moves towards shorter wavelengths, increasing the percentage of heat loss.

A remarkable improvement has been reached in the past years with an easy-tofabricate SSA based on a sputter-deposited $Cr_2O_3/Ti/Cr_2O_3$ tri-layer design [44]: it can reach an efficiency more than double than that of the Mirotherm at temperatures up to 300°C (48% Vs 20%). However, despite its stronger selectivity with respect the commercial absorber, the SSA optimized for 250 °C has a non-negligible emissivity at longer wavelengths ($\varepsilon \neq 0$ in the IR) and a non-zero slope, as proved by red line in Fig. 1.14. Therefore, the thermal radiation remains a source of loss and limits the energy conversion efficiency. Indeed, as the absorber exchanges radiation with the glass cover, the radiated infrared power is absorbed by the glass and is completely lost.



FIGURE 1.14: Left-hand axis: Solar spectral emission at the Earth surface (orange line) compared with the BB and the optimized SSA emissions at 250°C (green lines). Right-hand axis: emissivity of the ideal SSA (grey dashed line), the commercial SSA installed in the HVFPs (black solid line), and a SSA optimized for an operating temperature of 250°C (red line). Reflectivity of an ideal IR mirror (orange area).

1.4.2 IR mirror

To further reduce the radiative losses coming from the components of the HVFP at high temperatures, including the SSA, it is crucial to recycle the power lost as thermal radiation. The best way to do that is by exploiting the *cold-side external photon recycling*. In this mechanism, an optimized infrared mirror reflects and thus recaptures infrared emission in the desired mid-infrared region back at the receiver, to suppress heat loss. Such a mirror, placed on the inner side of the cover glass, would operate at room temperature and hence would cause a very low emission. The working principle is schematically showed in Fig. 1.15.

Prior experimental work [45] has demonstrated that surrounding an incandescent filament of a light source with properly designed interference structures triples its overall efficiency. The design allows visible light to be transmitted and IR light to be recycled, for a wide range of emission angles. Therefore, in [45] the authors managed to reject light at unwanted wavelengths and, on the other hand, they enabled its reabsoption by the emitter, allowing for resistive heating.

In the case of a HVFP, the ideal mirror must be perfectly transparent ($\tau = 1$) in the visible/near-IR region up to a temperature-dependent threshold wavelength, $\lambda_{thres}(T)$, to avoid the reduction of the incident power on the absorber, and yet perfectly reflective ($\rho = 1$) in the mid-IR, as showed in Fig. 1.14 (orange area). The $\lambda_{thres}(T)$ value can be evaluated by maximizing the efficiency of a collector equipped with an SSA having the chosen λ_{cut} and the ideal IR mirror facing the absorber (eq.



FIGURE 1.15: Schematic of a HVFP showing that the addition of an infrared mirror coating to the inner part of the glass covering the panel (green layer on the right-hand side) helps reducing the radiative losses. In fact, the IR mirror reflects all or a fraction of the emitted radiation back to the absorber (orange arrows).

2.1, with $\rho_{IRM}(\lambda) = 1$ for each $\lambda > \lambda_{thres}(T)$). It has been verified that, at each temperature, $\lambda_{thres}(T)$ coincides with $\lambda_{cut}(T)$, showing that $\lambda_{thres}(T)$ does not depend on the optical properties of the absorber. The reason is that for $\lambda < \lambda_{thres}$, the absorber spectral emissivity calculated at the specific working temperature affects solar absorption and radiative emission in the same way, whereas for $\lambda > \lambda_{thres}$ the ideal absorber also behaves as an ideal IR mirror. Therefore, from now on we will consider $\lambda_{thres}(T)=\lambda_{cut}(T)$.

Chapter 2

Performance analysis of an HVPF equipped with an IR mirror

Since the IR mirror has to be reproduced industrially, before starting the experiment, it is important to evaluate the characteristics that it must have in order to allow an effective improvement of the performance of a HVFP. In fact, in the absence of substantial improvements, one must estimate whether it makes sense to design such a mirror, as its use already brings an additional cost to the current total cost of the panel.

Therefore, in this chapter, after highlighting the limitations of the previous models developed to describe the properties and the benefits of mirrors in concentrating systems (section 2.1), the details of the HVFP and IR mirror used in this study are illustrated (section 2.2). Results on the increasing of efficiency and on the reduction of the power loss for different operating temperatures of the panel, as well as for different values of the mirror reflection bandwidth, reflectivity and transparency are showed (sections 2.3 and 2.4). Finally, the monthly and annual energy gain associated with HVFP equipped with an IR mirror are analyzed (section 2.5).

The results presented in this chapter have been published in Applied Energy [46].

2.1 State of the art: IR mirror for concentrating systems

Reducing thermal losses in solar thermal devices is fundamental for enhancing conversion efficiencies, particularly at high operating temperatures. Prior works have already highlighted the benefits achievable with the addition of IR mirrors to concentrating systems: it could bring a gain in efficiency over a year comparable to the one obtained with an AR treatment [47]. A prior work [48] proposes the use of a hot mirror on the glass cover instead of a selective coating on the absorber pipe to reduce IR losses, demonstrating that the glass cover temperature remains much cooler than the absorber pipe, thus experiencing less thermal expansion-driven mechanical stress. A later work [49] has proposed the idea of using the hot mirror coating in a hybrid system, by taking advantage of the selective coating on the absorber pipe on the lower temperature section of the receiver, and of the hot mirror coating in the high temperature sections, where the selective coating would disintegrate.

However, these studies are based on numerical models which consider both solar transmissivity and IR reflectivity as constant functions, neglecting the wavelength dispersive character of both properties. This represents an important limitation: transmissivity is a crucial parameter in HVFPs as, if low, it significantly alters the absorber performance. For a deeper and more accurate analysis, we introduce a thermal model (described in the next section) that includes both the spectral analysis and the potential non-idealities associated with experimentally manufacturing a real



FIGURE 2.1: Schematic cross view (not to scale) of the system. The glass cover a) is naked or b) could be coated on the inner side by an IR mirror.

IR mirror, which may include limited reflection bandwidths, wavelength-dependent reflectivity values, etc. Therefore, this study is crucial to evaluate the effectiveness of the IR mirror regardless of its specific properties, but taking into account the general limitations that these devices present.

2.2 Modeling of HVFP and IR mirror

28

The HVFP under study consists of an SSA developed to work at medium temperatures (MT-SSA)¹ coated on a copper substrate and enclosed between a highly transparent glass cover and a stainless steel vessel, as schematically represented in Fig. 2.1 a). As in the evacuated flat collector the distance between the glass and the absorber is two orders of magnitude lower than the absorber size, the system can be schematized as made up of three effectively infinite and parallel layers. Hence, the thermal exchanges between them can be described by the equation of radiative exchange between flat parallel plates in a one-dimensional thermal model that neglects thermal gradient and boundary effects, as experimentally demonstrated in a prior work [50].

In the following, we compare two different cases: one in which the absorber loses thermal power only through irradiation ($\varepsilon_{sub} = 0$, $\varepsilon_{vess} = 0$, and $\tau_{glass}=1$), and one in which the substrate emissivity, the radiative exchange with the stainless-steel vessel, and the non-ideal glass transparency are included ($\varepsilon_{sub} = 0.02$, $\varepsilon_{vess} = 0.15$, and $\tau_{glass}=0.95$, respectively. The analysis is carried out up to temperatures of 500 ° C, to consider all possible applications involving low, medium or high temperatures; the comparison between the performance of a HVFP equipped with an IR mirror (Fig. 2.1 a)) is described.

We must also consider that from an experimental point of view realizing an ideal IR mirror is not an easy task: while one can readily obtain a near-ideal mirror for a relatively small bandwidth [51, 52], transmissivity and reflectivity may deviate considerably from the ideal ones as the bandwidth is increased substantially. Therefore, since an infinitely wide reflection window and high transparency in the solar region could be difficult to be simultaneously realized in experiment, the range of reflected wavelengths must be bounded. For this reason we introduced a new parameter, Δ_{IRM} , which represents the high-reflection window width (*stopband*). In this way, we assume that the *ideal IR mirror* has ideal behavior only in a finite region: that region has a fixed starting point, corresponding to $\lambda_{cut}(T)$, but a variable ending point, $\lambda_{cut} + \Delta_{IRM}$, depending on the SSA emission. Below λ_{cut} the ideal IR mirror coating is supposed to be perfectly transparent, showing the cover glass with the typical emissivity $\varepsilon_{glass} = 0.89$. This concept is schematized in Fig. 2.2.

However, to reach a configuration that can actually be experimentally produced by using a realistic set of materials, we also introduce the *real IR mirror*. It is defined

¹Mid-Temperatures Selective Solar Absorber



FIGURE 2.2: Schematic of the IR mirror with a finite stopband Δ_{IRM} .

by a solar transparency τ_{IRM} less than 1 for each $\lambda < \lambda_{cut}$, while an IR reflectivity ρ_{IRM} less than 1 over the range $[\lambda_{cut}, \lambda_{cut} + \Delta_{IRM}]$. In this way we consider and evaluate how the presence of some non-idealities of the mirror, which can easily come out following realization, affects the overall collector efficiency. Note that once the mirror is no longer ideal, to obtain the overall solar transparency value one should multiply the mirror transparency, τ_{IRM} , by the one of the glass, τ_{glass} , i.e. $\tau_{all} = \tau_{glass} \times \tau_{IRM}$.

Therefore, we separate the cases of an IR mirror with ideal properties (section 2.3) from the one with realistic properties (section 2.5).

2.3 Efficiency and power loss in systems with ideal mirrors

As mentioned in the previous section, the ideal mirror is characterized by $\tau = 1$ in the visible/near-IR region up to a temperature-dependent threshold wavelength, $\lambda_{cut}(T)$, and $\rho_{IRM}(\lambda) = 1$ in Δ_{IRM} . Such an ideal mirror, coated on the inner side of the cover glass, gives a negligible contribution to the spectral emission, as it operates at room temperature. Conversely, the absorber operating at a chosen temperature of 250 °C has a non-negligible emission in the IR region between 1 and 12 μ m, as showed in Fig. 2.2 by the grey line.

Therefore, the radiative efficiency of such an ideal system can be defined in terms of absorbed, emitted, and incident power, as follows:

$$\eta_{abs} = \frac{P_{absorbed} - P_{emitted}}{P_{incident}} = \frac{\int_{\lambda_1}^{\lambda_2} \varepsilon_{abs}(\lambda) I(\lambda) d\lambda - \int_0^\infty \varepsilon_{abs-glass}(\lambda) [E_{BB}(\lambda, T_{abs}) - E_{BB}(\lambda, T_{amb})] d\lambda}{\int_{\lambda_1}^{\lambda_2} I(\lambda) d\lambda},$$
(2.1)

where T_{abs} is the absorber temperature, $I(\lambda)$ is the solar spectral irradiance, $E_{BB}(\lambda, T_{abs})$ is the blackbody spectral emission calculated at the absorber temperature value. $\lambda_1 = 0.25 \,\mu\text{m}$ and $\lambda_2 = 2.5 \,\mu\text{m}$ represent the lower and the higher limits of the solar region, respectively, $\varepsilon_{abs}(\lambda)$ is the spectral emissivity of the absorber. $\varepsilon_{abs-glass}(\lambda)$ is the equivalent emissivity of the absorber facing the glass, calculated as a reduced equation of the radiative heat transfer [53]:

$$\varepsilon_{abs-glass}(\lambda) = \frac{1}{\frac{1}{1 - \rho_{IRM}(\lambda)} + \frac{1}{\varepsilon_{abs}(\lambda)} - 1}.$$
(2.2)

Note that

$$\varepsilon_{abs-glass}(\lambda) = \begin{cases} \varepsilon_{abs}(\lambda) & if \quad \rho_{IRM}(\lambda) = 0\\ 0 & if \quad \rho_{IRM}(\lambda) = 1 \end{cases}$$
(2.3)

meaning that the ideal mirror reflects back to the absorber all the photons thermally emitted.

In such a system the power loss can be evaluated as

$$q_L = \bar{\varepsilon}_{abs-glass}(T)\sigma(T_{abs}^4 - T_{amb}^4), \qquad (2.4)$$

where $\bar{\epsilon}_{abs-glass}(T)$ is the spectral averaged emissivity of the system. Therefore, according to Eq. (2.2), when $(1 - \rho_{IRM}(\lambda)) \leq \epsilon_{abs}(\lambda)$ the quantity $\bar{\epsilon}_{abs-glass}(T)$ reduces and, consequently, the power loss reduces.

Results for systems equipped with ideal mirrors

On the basis of the previous considerations, we evaluated both the efficiency and the power loss for the two cases mentioned in section 2.2 in case of systems equipped with ideal IR mirrors characterized by finite reflection bandwidth Δ_{IRM} . This study has been performed at different operating temperatures of the absorber and variable Δ_{IRM} , in 0-10 μm . The case Δ_{IRM} =0 corresponds to calculations made in absence of the IR mirror.



FIGURE 2.3: Effect of an ideal IR mirror on the power loss of a) an MT-SSA absorber and b) an HVFP collector equipped with an MT-SSA, as a function of the working temperature and of Δ_{IRM} .

The analysis concerning the power loss, calculated according to Eq. 2.4, suggests that the ideal IR mirror keeps the power losses low even for absorber temperatures higher than 250°C: for example, when an ideal IR mirror with $\Delta_{IRM} = 2 \,\mu$ m is added to the system only approximately 200 Wm^{-2} are lost at a temperature of 325°C. Of course, if the radiative losses from both the substrate and the vessel are taken into account, the power loss increases and reaches approximately 350 Wm^{-2} at the same

temperature. This also leads to a reduction of the absorber stagnation temperature, which pass from 450°C to 405°C at $I = 1000 \text{ W} \cdot \text{m}^{-2}$.

In general, the analysis showed that, at a fixed temperature, the losses decrease as the window broaden. The results of this study are depicted in Fig. 2.3. In particular, Fig. 2.3 a) shows results of the power loss for the absorber-glass system ($\varepsilon_{sub} = 0$, $\varepsilon_{vess} = 0$, and $\tau_{glass}=1$), while Fig. 2.3 b) that of the whole collector ($\varepsilon_{sub} = 0.02$, $\varepsilon_{vess} = 0.15$, and $\tau_{glass}= 0.95$). The patterned area in the latter figure represents the region where the power loss is higher than the absorbed power.

Furthermore, an additional small contribution to the power loss is due to the substrate emissivity towards the vessel. This could also be recovered if an additional coating is applied to the stainless steel vessel. In this case there would be no need for transparency, so the coating could be easily made of a thin layer of silver, which has a $\rho = 0.99$ in the IR region [54].



FIGURE 2.4: Efficiency change trend as a function of working temperature and Δ_{IRM} for a) the MT-SSA alone and b) the HVFP collector equipped with an MT-SSA

The reduced power losses due to the presence of the ideal IR mirror directly increase the efficiency: as expected, the results showed that the broader the IR window the bigger the *efficiency change* ($\Delta\eta$), calculated as the difference between the efficiency with and without the IR mirror at $I = 1000 \text{ W} \cdot \text{m}^{-2}$ and $T_{amb} = 20^{\circ}\text{C}$. However, a reflection bandwidth of 2 μ m is already enough to produce an appreciable improvement in the system efficiency at 325°C, but more substantial improvements in terms of efficiency are expected as the absorber temperature increases. The results of this study have been represented in Fig. 2.4. As for the power loss, also in this case the analysis has been carried out both for the absorber alone (η_{abs} , Fig. 2.4 a)), and for the whole collector (η_c , Fig. 2.4 b)). As expected, the latter figure shows a patterned area starting at 405 °C (stagnation temperature) and representing the physical limit beyond which $\Delta\eta$ cannot be calculated.

To highlight the effect of the cold-side external photon recycling on the panel performance, we can compare the *available power*, i.e the power converted into heat by the absorber in presence of the IR mirror and defined as $\eta \times I(\lambda)$, to the *recovered power*, defined as $\Delta \eta \times I(\lambda)$ at different absorber working temperatures. Results are shown in Fig. 2.5 a) for the system absorber-glass and b) for the whole collector. By comparing the two cases, it is evident that the presence of the substrate and vessel only changes the available power, since the power losses due to the substrate are not recovered in the present configuration. Moreover, as expected, the increase of Δ_{IRM} contributes to the increase in efficiency: in fact, the recovered power increases and sums up to the power converted by the absorber alone, leading to values of available



FIGURE 2.5: Recovered (continuous lines) and available power (dashed lines) at different temperatures for (a) an MT-SSA absorber and (b) an HVFP collector with MT-SSA and an ideal mirror with different Δ_{IRM} .

power almost equal to the ideal ones ($\bar{\alpha} \times \tau_{glass} \times \tau_{IRM} \times I$).

However, for large Δ_{IRM} the amount of recovered power saturates, in fact the MT-SSA emissivity becomes almost negligible at longer wavelength (see Fig. 1.14), implying that there is less power available to be recovered per unit of wavelength. This also suggests that the IR mirror is more effective when working at high operating temperatures, as the black-body emitted power peaks towards shorter wavelengths (Fig. 1.11).



FIGURE 2.6: Efficiency of an absorber with an ideal IR mirror designed at 300°C and different Δ_{IRM} . Results refer to $I = 1000 \text{ W/m}^2$ and $T_{amb} = 20^{\circ}C$, calculated for the absorber only (dashed lines) and the whole collector (continuous lines).

The recovered power also extends the temperature range achievable by the MT-SSA, as shown in Fig. 2.6, where the efficiency is calculated for both scenarios ($\varepsilon_{sub} = 0$, $\varepsilon_{vess} = 0$, $\tau_{glass}=1$, or $\varepsilon_{sub} = 0.02$, $\varepsilon_{vess} = 0.15$, $\tau_{glass}=0.95$), considering an ideal IR mirror with $\lambda_{cut} = 2.2 \,\mu m$, an incident power of $1000 \,\text{W/m}^2$, variable Δ_{IRM} , and $T_{amb} = 20^{\circ}\text{C}$. When $\lambda_{cut} = 2.2 \,\mu m$, the mirror starts to recover a noticeable fraction of power at temperatures higher than 150°C and the absorber stagnation temperature
increases significantly and reaches values above 400 °C. As expected, the collector efficiency improves with increasing Δ_{IRM} , and a $\Delta_{IRM} = 2\mu$ m is already sufficient to increase η_c from 50% to 58% at 350°C, from 30% to 46% at 350°C, and from 0 to 30% at 400°C.

2.4 Efficiency and power loss in systems with realistic mirrors

To calculate the overall efficiency of an evacuated flat collectors also the glass transparency and the substrate and vessel emissivities have to be taken into account. The finite bandwidth, Δ_{IRM} , and the reflectivity values $\rho_{IRM} < 1$ over the range [λ_{cut} , $\lambda_{cut} + \Delta_{IRM}$] can be easily taken into account in Eq. 2.1 and 2.2 by assuming the proper values for $\rho_{IRM}(\lambda)$. Therefore, the analytical formula for the collector efficiency calculation, η_c , based on the described thermal model, becomes:

$$\eta_{c} = \frac{\int_{\lambda_{1}}^{\lambda_{2}} \tau_{glass} \tau_{IRM}(\lambda) \varepsilon_{abs}(\lambda) I(\lambda) d\lambda - \int_{0}^{\infty} \varepsilon_{all}(\lambda) [E_{BB}(\lambda, T_{abs}) - E_{BB}(\lambda, T_{amb})] d\lambda}{\int_{\lambda_{1}}^{\lambda_{2}} I(\lambda) d\lambda}$$
(2.5)

where

$$\varepsilon_{all} = \varepsilon_{abs-glass} + \varepsilon_{sub-vess} \tag{2.6}$$

and

$$\varepsilon_{sub-vess}(\lambda) = \frac{1}{\frac{1}{\varepsilon_{sub}(\lambda)} + \frac{1}{\varepsilon_{vess}(\lambda)} - 1},$$
(2.7)

which describes the thermal loss due to the substrate of the absorber that faces the interior side of the vessel. The emissivity values of the stainless steel vessel and the copper substrate are subsequently assumed to be 0.15 and 0.02, respectively. In the previous formula we assumed that both glass and vessel remain at room temperature. This is not a risky assumption, in fact it has been experimentally observed that, when in operation, both the glass and the vessel of an HVFP do not exceed T_{amb} by more than 10°C. The mathematical model describing the collector efficiency (Eq. 2.5) has been already validated in absence of the IR mirror in a prior work [55], thanks to numerical simulations performed using COMSOL Multiphyics [56] and an experimental system [44].

Results for systems equipped with realistic mirrors

Since it has already been shown that an optimized HVFP can be more efficient than concentrators up to 250°C [57], we will focus our attention on the effect of a real IR mirror at temperatures equal or higher than 250°C to extend the HVFP operational temperature range. To investigate this point in detail, we study the power loss of the couple absorber-glass in absence ($\Delta_{IRM} = 0 \mu m$) or in presence of an IR mirror ($\Delta_{IRM} = 1, 2, 3, 4 \mu m$) at different operating temperatures and for different reflectivity values ranging from 0.80 to 1. The study confirms that the power loss of the absorber through the glass can significantly be reduced by the presence of the IR mirror, in particular at T_{abs} above 350°C, and that the higher the ρ_{IRM} the greater the benefits in terms of recycled power. The results related to the power loss are represented as colormaps in Fig. 2.7.

The power loss is a fundamental parameter to evaluate, but it is independent from the IR mirror transparency. We therefore studied the influence of Δ_{IRM} , ρ_{IRM}



FIGURE 2.7: Power loss of an HVFP collector equipped with a MT-SSA and an ideal IR mirror having different bandwidths: $\Delta_{IRM}=0 \,\mu$ m (a), $1 \,\mu$ m (b), $2 \,\mu$ m (c), $3 \,\mu$ m (d) $4 \,\mu$ m (e).

and τ_{IRM} on the collector efficiency to determine their relative weight on the overall performance. In this analysis both transparency and reflectivity of the mirror have been varied in the range of 0.80 to 1.00 and it has been observed that the higher the τ_{IRM} and ρ_{IRM} values the higher the efficiency change (for any Δ_{IRM}). Conversely, increasing the Δ_{IRM} reduces the requirements on the transparency at the same temperature: at temperatures of 250°C and 300°C the efficiency change is higher than zero for each of $\rho_{IRM} > 0.80$ and for each value of τ_{IRM} close to 1. On the contrary, reflectivity values close to 1 still need a high transparency. Therefore this analysis suggests that in designing an IR mirror for mid-temperature applications (at I=1000 W/m²) the priority has to be given to the mirror transparency and Δ_{IRM} more than reflectivity.

All these results are presented in Fig. 2.8, where colormaps of efficiency change with respect to these factors are shown: each row refers to different T_{abs} , whereas columns to different IR mirror bandwidth values. The white areas in the Fig. 2.8 are regions of non-positive efficiency change.

The collector efficiency values, η_c , reported in the legends of Fig. 2.8 are the ones calculated from eq. 2.5 in absence of the IR mirror on the glass ($\rho_{IRM} = 0$). Therefore, to obtain the collector efficiency in presence of an IR mirror, one should also add the correspondent efficiency change value to η_c .

2.5 Monthly and annual energy conversion

All the efficiency change values reported in Fig. 2.8 are peak efficiencies at $I = 1000 \text{ W/m}^2$, i.e. efficiencies calculated for normal incidence of solar radiation [58], whereas the power irradiated by the Sun on the Earth varies according to the seasons, the time of day, and the weather conditions. Therefore, when the available power is lower than the nominal solar power, the efficiency change can be recalculated according to the formula:

$$\Delta \eta_x = \bar{\alpha} \tau_{glass} \left(1 - \tau_{IRM} \right) \left(\frac{I}{I_x} - 1 \right) + \Delta \eta_{1000} \frac{I}{I_x}, \tag{2.8}$$

where $\Delta \eta_x$ is the efficiency change at Sun irradiance, $I_x = xW/m^2$ and $\Delta \eta_{1000}$ is the efficiency change calculated at 1000 W/m².

When Eq. (2.8) is applied to Typical Meteorological Year Data (TMY) [59], we observe improvements in efficiency higher than those seen at the peak efficiency.



FIGURE 2.8: Efficiency change of a collector equipped with an MT-SSA and possible realistic mirrors with Δ_{IRM} from 1 (top row) to 4 μ m (bottom row) at different temperatures, from 250°C (left column) to 400°C (right column), as function of mirror reflectivity and transmissivity. $I = 1000 \text{ W/m}^2$, $T_{amb} = 20^{\circ}\text{C}$ and radiative losses from the envelope have been assumed in the calculation.

The study has been performed on two European cities as Naples² in Italy and Copenhagen³ in Denmark, and on an American city, Phoenix⁴ in Arizona. It shows a more pronounced relative increase in the monthly distribution of the converted energy at $T_{abs} = 250$ °C during winter, particularly at higher latitude: in Copenhagen the use of the IR mirror allows to extend the useful hours during the days at high temperatures. However, at such high latitudes during autumn and winter the Sun is too low on the horizon for too few hours and the system does not reach the working temperature of 250°C. Still, other applications at lower temperatures (such as district heating) could use the heat generated by the HVFP during winter. The representation of these results in terms of a monthly distribution of the converted energy at $T_{abs} = 250$ °C is shown in Fig. 2.9 (a,b,c) for Copenhagen, Naples, and Phoenix, respectively.

When integrating over the entire year, the presence of an IR ideal mirror with $\Delta_{IRM} = 2 \,\mu m$ (and $\tau_{IRM} = 1$, $\rho_{IRM} = 1$) allows reaching a peak efficiency change of 3.9% at a working temperature of 250°C. This results in an increase of the 14.7% of produced annual energy in Naples (from 3044 MJ/m² to 3493 MJ/m², see Fig. 2.9 (d)). The same peak efficiency changes produce a relative annual energy increase of 21.4% in Copenhagen, bringing the available energy from 1452 MJ/m² to 1762 MJ/m²; and of 10.6% in Phoenix (available energy from 4555 MJ/m² to 5038 MJ/m²),

²Lat.: $40^{\circ}51'N$ Long.: $14^{\circ}15'E$

³Lat.: 55°41′*N* Long.: 12°35′*E*

⁴Lat.: 33°27′N Long.: 112°04′W



FIGURE 2.9: Upper row: Monthly converted energy for a HVFP working at 250°C in the caso of no IR mirror, realistic IR mirror ($\Delta_{IRM} = 2 \,\mu m$, $\tau_{IRM} = 0.99$, and $\rho_{IRM} = 0.97$) and ideal IR mirror with $\Delta_{IRM} = 2 \,\mu m$ (left-hand axis), and monthly percentage of the energy enhancement obtained with the real IR mirror (right-hand axis). Lower row: Converted annual energy at different operating temperature: 250°C (d), 300°C (e) and 350°C (f). The analysis has been performed for three cities: (a) Copenhagen (DK), (b) Naples (IT) and (c) Phoenix (AZ).

with an annual efficiency that increases from 0.517 up to 0.572. At higher temperature the radiative losses increase and the same ideal mirror can recover even more energy (see Fig. 2.9 (e,f)), extending the operating temperature range of the panel. However the losses can became so important that the bandwidth should be extended to produce a significant amount of annual energy. Indeed, at 300°C an ideal mirror with $\Delta_{IRM} = 3 \,\mu$ m would bring the annual energy from 3063 MJ/m² to 4363 MJ/m² in Phoenix, with a relative improvement of 42% and an annual efficiency of 49.5%, and from 1731 MJ/m² to 2871 MJ/m² in Naples, with a relative increase of 65.9% and an annual efficiency of 41.8%. Instead, if we consider a realistic mirror with $\Delta_{IRM} = 3 \,\mu$ m, $\tau_{IRM} = 0.99$, and $\rho_{IRM} = 0.97$, at the same working temperature of 300°C, the annual efficiency varies from 25.2% to 36.1% in Naples, from 34.8% to 44.3% in Phoenix, and from 13.7% to 23.8% in Copenhagen.

Note that data from Ref. [59] are hourly-mean value for each month, which averages any combination of sunny and cloudy days and leads to an underestimation of the monthly output. Indeed, if one could shut down the system during the days when the light is not enough, one might increase the available energy, which be an appropriate optimization problem for future studies.

We will resume the results of this thermal analysis later in Chapter 4.

Chapter 3

Experimental setup

This chapter provides an overview of the experimental setup and simulation software used to design and develop the IR mirror briefly introduced in section 1.4.2.

Section 3.1 describes the deposition technique used for the thin films deposition; section 3.2 illustrates the various instruments used to perform the optical characterization of the deposited films. Finally, section 3.3 describes the two software used to perform optical simulations.

3.1 Thin films deposition: magnetron sputtering

The deposition of thin films is the key for designing simple and complex structures. The thin film depositions consist in creating and depositing thin layers of a material onto a substrate, commonly c-Si or glass. There exist different deposition techniques, which could be briefly divided into Physical Vapor Deposition (PVD) and Chemical Vapor Deposition (CVD), illustrated in Fig. 3.1. PVD techniques consist in



FIGURE 3.1: Schematic of PVD and CVD processes, adapted from [60].

vaporizing and then depositing a solid material in a vacuum chamber; CVD involve chemical volatile precursors, which react and decompose, depositing on the substrate surface. Despite the ability to coat complex topographies when using CVD, coatings created by PVD appear highly durable and resistant to scratching and corrosion, which is highly recommended when involved in solar cells or solar thermal devices. Also, it allows off-thermal equilibrium film growth, as well as the use of heated and heat-sensitive substrates. Finally, it is a well-established technology to coat materials with tailored properties [61].

PVD includes evaporation (electron beam, ion assisted deposition, and thermal evaporation), ion beam sputtering, pulsed laser deposition, and magnetron sputtering. The latter is the technique chosen to realize the IR mirror, as it is widely used both in research and in industry to grow films for various applications.

Magnetron sputtering is a coating process that takes place in a vacuum chamber filled with an inert gas (usually argon) and allows to coat films with thickness of a few Angstroms to several micrometers. Positively charged and highly energetic ions created from a magnetically confined plasma nearby the surface of the *target material* (i.e. the material to be deposited) collide with the negatively charged target. The result is that the atoms from the target (cathode) are sputtered, i.e. ejected, and driven to the substrate (anode), where they deposit creating a film. The schematic of the process is showed in Fig. 3.2.



FIGURE 3.2: Schematic of the sputtering process. Adapted from [62].

An important parameter in this process is the sputtering yield (SY), defined as the mean number of atoms removed from the target surface per incident ion. The efficiency of the process mainly depends on: target material, nature of the process gas, trajectory and energy of ions. The SY could be enhanced if an oblique incidence of the ions with respect to the target surface is chosen, in fact with a non-perpendicular incidence it is easier for collisions to give the atoms a direct velocity component towards the outside of the target. A higher yield is also obtained when the incident ions have a mass comparable to that of the atoms of the target material, in fact in this case there will be a more efficient exchange of energy, according to the theory of elastic collisions. Of course, it is also possible that an ion is reflected by the target without creating any sputtering, and the energy of this reflected particle (E_R) is strongly dependent on the atomic masses of the gas and the material constituting the target:

$$E_R = E_0 \left[\frac{M_t - M_g}{M_t + M_g} \right]^n \tag{3.1}$$

where E_0 represents the energy of the ions that hit the target, M_t and M_g are the atomic masses of the target material and of the gas, respectively. n is typically equal to 1.5.

In the sputtering process there are various parameters that can be controlled and affect the quality of the process itself and the characteristics of the film to be deposited: power (voltage and current) applied to the electrodes for gas ionization, substrate temperature, process gas pressure, target-substrate distance and their reciprocal dimensions. For example, an increase in the discharge power supply involves an increase in mobility of the atoms, as a consequence of the greater flow of ions and their greater kinetics energy. This translates into increased sputtering efficiency, higher crystallinity of the film, increased deposition rate, higher target and substrate temperature, reduction of the film resistivity. Also the pressure of the ionized gas has a main effect on the ions mobility: high pressures cause the reduction of the particles free path in the plasma, in fact more collisions will occur in the path between target and substrate. This also leads to a decrease in the deposition rate, greater amorphous structure of the film, increase of the film resistivity. Finally, even reduced distances between source and substrate favor a higher rate of deposition, while an area of the substrate smaller than that of the target leads to a better uniformity of the deposit, since the target is not evenly eroded by moving from the center to the periphery.

The sputtering technique allows different kind of depositions, according to the type of power supplied to the target material. It includes Direct Current (DC) sputtering, Radio-Frequency (RF) sputtering, and DC or RF magnetron sputtering. The DC sputtering is the simplest system, as it is made of two electrodes, the cathode and the anode, where the substrate is placed. The power supplied between cathode and anode is continuous and ionizes the gas present in the chamber allowing the formation of the *glow discharge*. The process is highly influenced by the working pressure, in fact too low pressures there is an insufficient ionization rate, while too high pressures cause an excessive mobility of the particles of the plasma which hinder the path of the atoms directed to the substrate. DC depositions are only suitable when using electrical conducting targets, in fact electrical insulators would not be able to sustain the glow discharge as the positive ions will accumulate on the target surface. Then, for insulating materials the RF technique is more suitable, as the alternated electric potential between the two electrodes does not allow the accumulation of charges.

The magnetron sputtering system is essentially a variant of the previously described systems that includes permanent magnets placed under the cathode. The purpose is to increase the ionization rate: thanks to the presence of a magnetic field nearby the cathode, the electrons in the plasma are affected by a *magnetic trap* that causes a greater number of ions in the process gas hitting the target and therefore a greater erosion of the target. The secondary electrons emitted from the target increase the number of collision with the gas molecules, which allows the possibility to work at pressure and voltage lower than the standard case. DC and RF technique can both be reactive or non-reactive, depending on whether a reactive gas is injected in the chamber or not (in addition to the process gas). Usually reactive sputtering processes are subject to hysteretic behaviours that affect the deposition, requiring a deeper analysis of the deposition parameters to control the quality of the film.

3.2 Thin films characterization

The complete characterization of the deposited thin films is a key element in the validation of simulations and the optimization of the desired properties of the IR mirror. It has been carried out in different steps, all described in the following paragraphs.

3.2.1 Profilometry

A profilometer is an instrument used for measurements of surface properties, i.e. roughness, step height, etc. Its working principle is shown in Fig. 3.3: a probe tip, in direct contact with the surface to measure, moves linearly along it record the vertical change (z-direction), which is useful to reconstruct the surface profile. Measurements of step height are usually obtained using standard photolithography,



FIGURE 3.3: Working principle of a stylus type profilometer [63].

i.e. by applying a mask on the substrate before deposition and chemically removing it after deposition of the thin film, and are useful to estimate the deposition rate. An example of this kind of measurement is shown in Fig. 3.4.

3.2.2 Reflectance/transmittance measurements

Optical transmittance/reflectance spectra were recorded using two different instruments to cover the ultra-broad spectral range.

In the short wavelengths region, from 350 to 1750 nm, an *integrating sphere coupled with an Optical Spectrum Analyzer* (OSA), showed in Fig. 3.5, was used to perform hemispherical reflectance measurements. The inner part of the integrating sphere is coated with a diffusive material which provides a high reflective surface and allows to obtain a homogeneous distribution of radiation thanks to the multiple Lambertian reflections on the inside of the sphere. A light source illuminates the sample and the fraction of light reflected by the sample under analysis is read by the spectrometer, which measures the spectral power (Wnm^{-1}) over the range of investigated wavelengths. Then, the reflected power can be estimated from the comparison with a



FIGURE 3.4: Thin film height measured with KLA Tencor P-15 profilometer.



FIGURE 3.5: Working principle (a) and design (b) of the integrating sphere.

measurement made on a reference sample, which has a known reflectivity (ρ_{ref}):

$$\rho = \frac{R_{sample}}{P_i} = \frac{R_{sample} \cdot R_{ref}}{P_i \cdot R_{ref}} = \frac{R_{sample}}{R_{ref}} \cdot \rho_{ref},$$
(3.2)

where P_i is the power intensity incident on the sample, R_{sample} and R_{ref} the spectral power reflected by the sample and by the reference sample, respectively. The reference sample used in this work is the Spectralon WS-1-SL diffuse reflectance standard from Labsphere, with a 99% reflectivity in the range of 400 to 1500 nm, while > 96% reflectivity in the range of 250 to 2000 nm.

Alternatively, optical transmittance spectra in the range of 200 nm to 2500 nm can be recorded using a spectrophotometer. The working principle is shown in Fig. 3.6: a lamp provides the source of light; the beam of light strikes the diffraction grating, which works like a prism and separates the light into its component wavelengths. The grating is rotated so that only a specific wavelength of light reaches the exit slit; at this point the light interacts with the sample and the detector measures the transmittance of the sample, i.e. the amount of light that passes completely through the sample and strikes the detector.

The Fourier-transform Infrared Spectrometer (FTIR) has been used for reflectance



FIGURE 3.6: Working principle of a common spectrophotometer.

measurement in the range of 1.5 μm to 30 μm . The working principle of this instrument is shown in Fig. 3.7: a broadband infrared light beam is sent to an interferometer which produces an optical signal with all the IR frequencies encoded into it. Then, the light beam hits the sample, which absorb a fraction of light at certain wavelengths and the signal is decoded by applying a Fourier Transform (FT). The FT convert the intensity-time spectrum into intensity-frequency, and the spectral reflectance is estimated from the comparison with a reference sample.

3.2.3 Ellipsometry

Ellipsometer is by far the most important and complex instrument in our study, as it allows to characterize the film thickness and optical constants. Its layout and working principle are shown in Fig. 3.8: by means of an optical fiber, the light ejected from a source reaches the polarizer, where the state of polarization of the light is defined. Then, the light strikes the sample and the reflected component is modulated and sent to the analyzer and monochromator, that separates the light into its various components before it reaches the detector.

Ellipsometric measurements are based on the measurement of the change in polarization of the light incident on the sample of interest, and depends on the optical properties and thickness of the individual materials included in the sample.

The change in polarization is quantified by the amplitude ratio and phase difference:

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

$$tan(\psi) = \frac{|r_p|}{|r_s|} \in [0, 90^\circ],$$

$$\Delta = \delta_p - \delta_s \in [0, 360^\circ].$$
(3.3)

The quantities r_p and r_s are the Fresnel reflection coefficient for s- and p-polarization (Eq. 1.10), respectively, while ψ and Δ are the *ellipsometric angles*: from them it is possible to obtain the optical properties of the sample. Unfortunately, they cannot be directly converted into the optical constants of the material, but are used to validate a material structure model that allows to predict the material optical properties, i.e. the complex refractive index, by means of mathematical relations, *dispersion formulae*. There are several degree of freedom in this analysis: incident angle, as well as thickness, roughness and refractive index of each layer included in the sample. Any



FIGURE 3.7: FTIR spectrometer with source, interferometer, and detector [64].

of these properties is varied to improve the match between experiment and calculation. Therefore, it is important to carefully choose the model and control the χ^2 value returned by the fit, which defines its quality.

Figure 3.9 shows an example of the measured quantities I_c and I_s , which are functions of ψ and Δ according to

$$I_{s} = \sin(2\psi) \cdot \sin(\Delta),$$

$$I_{c} = \sin(2\psi) \cdot \cos(\Delta),$$
(3.4)

and the relative fit lines, which are in agreement with the measurement. In our analysis, the model used to fit the ellipsometric data faithfully reproduces the experimental samples: a thin film of the deposited materials lies on a silicon/glass substrate. Also, two additional thin layers were included to simulate the roughness at the interface between the substrate and the film and on the film surface, as shown in Fig. 3.10.

Measurements must be conducted at the *Brewster angle* (θ_B) of the substrate, where the highest sensitivity is observed. In fact, it corresponds to an angle of incidence at which the p-polarized light is perfectly transmitted through a transparent dielectric surface, with no reflection. It can be calculated from the indices of the two media:

$$tan(\theta_B) = \frac{n_1}{n_0}.$$
(3.5)



FIGURE 3.8: a) Layout and b) working principle of a classical ellipsometer.

Results of the characterization of silicon nitride films and that of SiO₂, TiO₂, and $[SiO_2]_x[TiO_2]_{1-x}$ films are presented in Chapter 4.

3.3 Optical simulations: S4 and Open Filters

Before starting the sample fabrication it is crucial to perform simulations to forecast the sample response, especially when the structures are very complex and consist of many layers. The optical simulation presented in this work have been carried out using two different software: *Stanford Stratified Structure Solver* (S4) [65] and *Open Filters* (OF) [66].

3.3.1 Stanford Stratified Structure Solver: S4

Stanford Stratified Structure Solver, briefly *S4*, is a frequency domain code to solve layered periodic structures. It is based on the Rigorous Coupled Wave Analysis (RCWA), also called the Fourier Modal Method (FMM) [67] for computing modal expansions within layers, combined with the scattering matrix (S-matrix) algorithm



FIGURE 3.9: Example of a good fit ($\chi^2 < 1$): the ellipsometric measured quantities I_c and I_s (blue and red dots, respectively) and the fitted quantities (I_c as a blue line, and I_s as a red line) are compared.



FIGURE 3.10: Diagram of samples (not to scale), including roughness-equivalent layers.

[68, 69] to join together layers for solving electromagnetic fields throughout a threedimensional structure. The the S-matrix method is used to solve transfer matrix problems for all grating models with upward- or downward-propagating and decaying waves (Fig. 3.11). The basic idea behind the FMM is to expand the electromagnetic fields within each layer into eigenmodes, which are represented using a Fourier basis in the plane of periodicity. The modal expansion coefficients are then related at layer interfaces to satisfy field continuity conditions in the Fourier basis.

For an arbitrary layer p, $0 \le p \le n$, the following equation is satisfied:

$$\begin{bmatrix} u^{(p+1)} \\ d^{(0)} \end{bmatrix} = S^{(p)} \begin{bmatrix} u^{(0)} \\ d^{(p+1)} \end{bmatrix},$$
(3.6)

where $S^{(n)}$ is a stack S-matrix, u and d represent a set of wave amplitudes as column vectors for upward- and downward-propagation waves in each layer, respectively. In this way the waves in layer (p+1) is linked with medium (0). Eq. 3.6 can also be written in the following form:

$$\begin{bmatrix} u^{(p+1)} \\ d^{(0)} \end{bmatrix} = \begin{bmatrix} T^{(p)}_{uu} & R^{(p)}_{ud} \\ R^{(p)}_{du} & T^{(p)}_{dd} \end{bmatrix} \begin{bmatrix} u^{(0)} \\ d^{(p+1)} \end{bmatrix},$$
(3.7)



FIGURE 3.11: Layered grating structure (adapted from Ref. [69]).

where T and R are the transmission and reflection matrices, respectively. As only decreasing exponential functions appear in the matrices (unlike in the transfer-matrix method), the S-matrix approach is unlikely to encounter numerical instabilities.

For each structure solved by S4, $u^{(0)} = 0$ and $d^{(n)}$, which is the incident wave, is given. Therefore, $u^{(n)}$ and $d^{(0)}$, total reflection and total transmission, can be computed as:

$$u^{(n)} = R_{ud}^{(n-1)} d^{(n)},$$

$$d^{(0)} = T_{dd}^{(n-1)} d^{(n)},$$
(3.8)

and, of course, the total absorption can be calculated by subtracting reflection and transmission from the total incident wave amplitude.

The S4 tool has two types of input: *graphical interface* and *input deck*. The latter can be used by writing the control file in the Lua scripting language and allows to define more complex structures.

3.3.2 Open Filters

Open Filters calculates the multilayer properties using the characteristic matrix approach [70], where the *i*-th layer is represented by

$$\begin{bmatrix} \cos\varphi_i & (i/\eta_i)\sin\varphi_i\\ i\eta_i\sin\varphi_i & \cos\varphi_i \end{bmatrix}$$
(3.9)

where

$$\eta_{i} = \begin{cases} \sqrt{N_{i}^{2} - \alpha^{2}} & s - polarization\\ N_{i}^{2} / \sqrt{N_{i}^{2} - \alpha^{2}} & p - polarization \end{cases}$$
(3.10)

is the pseudoindex of the layer and

$$\varphi_i = \frac{2\pi}{\lambda} \sqrt{N_i^2 - \alpha^2} d_i \tag{3.11}$$

is the phase shift of the wave inside the layer, $\alpha = N_i \sin \theta_i$, d_i the thickness of the *i*-th layer, and λ the wavelength of light in vacuum.

The characteristic matrix describing the multilayer is

$$M = \begin{bmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{bmatrix} = \prod_{i=q}^{1} M_{i},$$
(3.12)

where *q* is the number of layers, and the product is taken in reverse order since the matrices of upper layers must be multiplied on the left. The amplitude reflection and transmission coefficients of the multilayer are

$$r = \frac{\eta_{inc}m_{11} - \eta_{ex}m_{22} + \eta_{inc}\eta_{ex}m_{12} - m_{21}}{\eta_{inc}m_{11} + \eta_{ex}m_{22} + \eta_{inc}\eta_{ex}m_{12} + m_{21}},$$

$$t = \frac{2\eta_{inc}}{\eta_{inc}m_{11} + \eta_{ex}m_{22} + \eta_{inc}\eta_{ex}m_{12} + m_{21}},$$
(3.13)

where η_{inc} and η_{ex} are the pseudoindices of the incidence and exit media, respectively. Therefore, reflectance, transmittance, and absorptance are calculated as

$$R = rr^* = |r|^2,$$

$$T = \frac{ReN_{ex}}{ReN_{inc}}|t|^2,$$

$$A = 1 - R - T.$$
(3.14)

To account for the effect of the substrate backside, one can simply add multiple reflections and transmissions occurring in the substrates (see Fig. 3.12). Therefore,



 $T_{\mathrm{F}}T_{\mathrm{B}}\exp 2\beta_{\mathrm{i}} = T_{\mathrm{F}}R_{\mathrm{B}}R_{\mathrm{FR}}T_{\mathrm{B}}\exp 6\beta_{\mathrm{i}}$

FIGURE 3.12: Optical filter with backside [66].

the old Eq. 3.14 becomes

$$R = R_{F} + \frac{T_{F}T_{FR}R_{B}e^{4\beta_{i}}}{1 - R_{B}R_{FR}e^{4\beta_{i}}},$$

$$T = \frac{T_{F}T_{B}e^{2\beta_{i}}}{1 - R_{B}R_{FR}e^{4\beta_{i}}},$$
(3.15)

where R_F and T_F are the reflectance and transmittance of the front side, R_B and T_B the

ones of the backside, while $R_F R$ and $T_F R$ that of the front side in reverse direction. The quantity

$$\beta_i = Im(\frac{2\pi}{\lambda})\sqrt{n_{sub}^2 - \alpha^2} d_{sub}$$
(3.16)

is related to the absorption in the substrate, and n_{sub} is the refractive index of the substrate.

3.3.3 Comparison between S4 and OF

Given the high reliability of both software, we compared the results of the simulations performed with S4 and OF to verify their agreement. The example shown in Fig. 3.13 shows that the agreement is perfect in the whole range of wavelengths investigated. Therefore, even if both software have been used in the modeling of the IR



FIGURE 3.13: Comparison between the spectra resulting from S4 and OF simulation of the same optical structure.

mirror, in the next sections only the results of the OF simulations will be taken into account, as it is less time consuming and easier to use, especially when it comes to optimization processes. In fact, in OF there are three optimization methods already developed and ready to use (see the next section for further details).

3.4 Optimization techniques

Designing a filter which respects the exact desired specifications it's manually hard: strongly undesired peaks can appear in some regions, disrupting the achievement of a specific goal. Generally, the strength of these sidelobes is a function of the mismatch of the equivalent index of the structure and the index of the surrounding media. Therefore, to improve the properties of a filter, especially if it is based on a multilayer structure, we can add single or multiple *matching layers* at its interfaces (Section 3.4.1). Of course, the last step in the optimization process would be the refinement of the thicknesses or the addition of new layers in specific positions of the design (Section 3.4.2).

3.4.1 Matching layers and apodization functions

To improve the properties of the designed filter, we can consider adding single or multiple layers at its interfaces to reduce the mismatch with the refractive index of the surrounding media by smoothing the discontinuity at the edges.

The simplest example of a matching layer is a single dielectric film with thickness equal to one quarter of the wavelength of the incident light (quarter-wavelength layer) and refractive index equal to the geometric mean of the refractive indices of the the surrounding media [71]:

$$n_{ARcoating} = \sqrt{n_{air} \cdot n_{substrate}} \tag{3.17}$$

When the single matching layer is not enough, the spectrum can be further improved by considering an *apodization function*, as suggested by W. H. Southwell in [72]. There exists different apodization functions, such as: quintic polynomial [73], Bartlett [74], Gaussian [75], etc. An example of the change in the index profile after application of a fifth-order polynomial function is shown in Fig. 3.14. However, we must consider that the removal of the sidelobe ripple can be obtained at the price of decreased reflectance in the stopband [72].



FIGURE 3.14: Index profile for a period structure in absence (left) or in presence (right) of matching with a fifth-order polynomial function [72].

3.4.2 Optimization in Open Filters: thickness refinement, needles and steps

The main advantage of *Open Filters* is that it allows to optimize the filter properties towards three different methods, listed below.

1. Refinement method

This method, based on prior literature [76], consists in the adjustment of the thickness and/or refractive index of each layer of the starting design to reach a final configuration where the filter properties are sufficiently close to the target curve specifications. To check the quality of the design, OF allows to define and minimize a Merit Function (MF):

$$\chi^{2} = \sum_{i=1}^{m} (\frac{B_{i} - \bar{B}_{i}}{\Delta B_{i}})^{2}$$
(3.18)

where m is the number of targets, B_i is a property of interest, \overline{B}_i is the target value for that property, and ΔB_i is the tolerance for that property.



FIGURE 3.15: Schematic representation of (a) the needle and (b) the step methods [66].

The optimization algorithm used by OF is the Levenberg–Marquardt (LM) algorithm [77]. The properties of a filter that are optimized are represented by a vector \mathbf{a} =[a_1 , a_2 , ...]. The LM algorithm calculates the first derivatives of the MF with regard to every parameter a_k and determines the point where the MF is the lowest in a trust region centered around the present value of \mathbf{a} . Repeated improvements of the MF allow the Levenberg–Marquardt algorithm to find a local minimum.

2. Needle method

The needle method was first described by Tikhonravov [78]. It consists of adding thin layers at optimal positions in the filter and then adjusting their thickness by refinement. Needles are added until a satisfactory solution is found or the addition of more needles does not improve the filter. The optimal position to add needles is determined by calculating the derivative of the MF with regard to the thickness of an infinitesimally thin layer as a function of the position where it is added. Where the derivative is negative, it is favorable to add a needle (Fig. 3.15 (a)).

3. Step method

Similar to the needle method, the step method adds layers at optimal positions in the filter, determined by the derivative of the MF, and then adjusts their thickness by refinement. Conversely, this time infinitesimal steps in the index profile are considered instead of needles (Fig. 3.15 (b)).

Both the needle and step method are useful when solving complex design problems, but their use lead to possible additional thin layers.

Chapter 4

Methodology for the design and fabrication of an IR mirror

Designing the IR mirror introduced in section 1.4.2 is a multi-step task: first, a collection of materials with appropriate properties have to be selected; then, a suitable design has to be chosen to avoid spurious and undesired reflections in some regions of the spectrum. In addition, further constraints such as the use of low-cost materials, low-cost and easy manufacturing, etc. must be taken into account: keeping the production process easy would make the mirror suitable for industrial production.

In the following sections all the necessary steps for a complete design of an IR mirror are covered in details: we start with a brief introduction to the designs commonly used to make IR mirrors, highlighting the flaws that make them not useful for our study (section 4.1). Thus, the one used in this work, the rugate structure, is deeply described in section 4.2. The design process of an IR mirror continues with the selection of the materials that composes each layer of the rugate filter (section 4.3). Follows their deposition as thin films by using the Physical Vapor Deposition (PVD) technique, their optical characterization, and their final fabrication of the IR mirror (sections 4.4 and 4.5). We conclude the chapter with some fundamental considerations on the IR mirror and on the technique used to optimize its properties (section 4.6). The various steps mentioned, useful to manufacture the IR mirror, are schematically shown in Fig. 4.1.

The results presented in this chapter have been published in various manuscript [52], [79], [80], [81].





4.1 IR mirror: state of the art

The idea of developing IR mirrors to be applied in solar thermal devices is not new: the first works on selective filters that take into account the need for solar light to pass and for IR emission to be reflected have been developed in 1981 [82, 83]. The IR mirrors developed so far can be classified into three categories [47]:

- thin metal layers like silver, gold, copper or aluminum deposited on glass substrates. They suffer from low selectivity (particularly in the case of Al [84]), and low solar transmissivity: 9 nm of silver determines a poor solar transmissivity, of approximately 40%;
- doped semiconductors like indium tin oxide (ITO) or In₂O3:Sn which despite the good selectivity [82, 85] have usually a low reflectivity (< 85%) [86];
- composite layers consists in structures made by alternating layers of metals and dielectrics: TiO₂/Ag/TiO₂ [87] or ZnO/Ag/ZnO [88], etc. The dielectric act as an antireflective layer and increases the solar transmissivity above 70%. But still, the metallic layer causes the above problems.

In summary, both metal-based and doped semiconductor structures exhibit low transmittance or reflectance, making the hot mirror useless for use in HVFPs. The idea of composite layers appears more appropriate, even though the metallic layer still limits solar transmittance and IR reflectance. Therefore, in the next section we will focus on structures entirely based on the use of dielectric materials.

4.2 DBR and rugate design

The first design we took into account is the Distributed Bragg Reflector (DBR), or Bragg mirror, which consists of a multiple layers structure composed of two materials with different refractive indices (high- and low-refractive index materials) and has extremely low losses at optical and IR frequencies compared to ordinary metallic mirrors. Typically, the first and last layers are chosen to have high refractive index. The optical thickness of each layer, *t*, is calculated such that $n \cdot t = \lambda_0/4$, being λ_0 the design wavelength: when the wavelength is close to 4*t*, the constructive interference makes the whole structure a high-quality reflector. The range of wavelengths where reflections occurs, namely *stopband* (Δ), is strictly related to the materials chosen, as highlighted by the following formula:

$$\Delta = \frac{4\lambda_0}{\pi} asin(\frac{n_H - n_L}{n_H + n_L}).$$
(4.1)

Therefore, the higher n_H/n_L the larger the stopband. However, after the first 10 periods, the quarter-wave stack no longer offers improved efficiency as additional layers are added. Another well-known issue with a quarter-wave stack design is the presence of odd-order reflection bands at $\lambda_0/3$, $\lambda_0/5$, and so on, as demonstrated in Fig. 4.2. This phenomenon limits the breadth of the passband as well as the transmission in the near- and mid-IR (the ideal properties of the IR mirror have been better described in section 1.4.2), making it unsuitable for our goal.

To obtain near-ideal performance, more complex structure have thus been examined as alternative candidates. In particular, a coating design that allows one to effectively reduce all higher-order reflection bands, leaving only the band at λ_0 , is the *rugate filter*. Idealized rugate filters are characterized by a continuous, sinusoidal variation of the refractive index as a function of optical thickness in the direction perpendicular to the film plane [89]. Such structures present several advantages in terms of suppression of high order harmonics. Furthermore, [90] demonstrated that, thanks to the smooth modulation of the layers, the rugate filter is subject to less residual stress than that of filters made from discrete quarter-wave layers with alternate high and low indices.



FIGURE 4.2: Simulated reflectance spectrum of a DBR made by alternating layers of TiO_2 and SiO_2 on a glass substrate. Odd-order reflection bands are pointed out.

Any continuous and sinusoidal profile can be used to describe a rugate structure, but the most exhaustive suppression of higher order harmonics is achieved when the logarithm of the refractive index is a sinusoidal function of n_L and n_H [91], which represent the refractive indices of the layers with the lowest and highest refractive index values, respectively:

$$\ln[n(t)] = a \cdot \cos(k_0 t) + b, \qquad (4.2)$$

where *n* is the refractive index, *t* is the optical thickness, and $k_0=4\pi/\lambda_0$. The coefficients *a* and *b* are chosen to give the correct higher and lower limits to the refractive index profile, and are given by:

$$a = \frac{1}{2} \ln(\frac{n_L}{n_H}),$$

$$b = \frac{1}{2} \ln(n_L \cdot n_H),$$
(4.3)

where n_L and n_H are the refractive indices of the layers with the lowest and higher refractive index values, respectively.

While a rugate filter might seem like the ideal candidate, its major drawback is its fabrication: the refractive index must be constantly varied, requiring *in situ* growth monitoring and complex algorithms to adjust fabrication parameters. Fortunately, previous work [92, 93] demonstrated that it is still possible to achieve appreciable improvements if the sinusoidal curve describing the refractive index variation is discretized. This means that the standard rugate filter made of infinite layers can be approximated by a discrete number of layers with steps in the refractive indices, creating a *Stepped Index Rugate* (SIR) filter. A pictographic representation of the sinusoidal variation of the refractive index with increasing film thickness is shown in Fig. 4.3 (a), while Fig. 4.3 b) shows the case of the SIR filter.

In a SIR filter the layers are stacked according to a [ABC..X..CBA] scheme, repeated periodically. The proposed SIR filter uses multiple different layers, each having a



FIGURE 4.3: Refractive index profile of a) a standard rugate filter and b) an SIR filter.

certain refractive index, to approximate the sinusoidal variation of a standard rugate filter. Its main goals are: i) easier fabrication and ii) similar performance when compared to a standard rugate filter. Despite rugate structures having already been used in various applications involving thermo-photovoltaic (TPV) systems [94] or hypersonic structures [95], they have not been experimentally applied in the case of solar thermal systems.

4.3 The choice of materials

54

Once the suitable design has been found, the process continues with the selection of materials to be involved in the design: the best candidates are dielectric materials, as most likely they are characterized by low or near-zero extinction coefficients (k \simeq 0).

Several dielectric materials have been initially taken into account, such as SiO, SiO₂, TiO₂, Si₃N₄, Ta₂O₅, ZnS, ZnO, Al₂O₃, etc. Their complex refractive index is showed in Fig. 4.4.



FIGURE 4.4: a) Refractive index and b) extinction coefficient trends of various dielectric materials useful in the IR mirror design.

In the choice of the materials we must remember that, according to equation 4.1, they must have the highest possible refractive index contrast to ensure a wide stopband [96]. However, even though the best discretization to a continuous function can be obtained by using a large number of materials with closely-spaced refractive indices, lowering the number of materials involved reduces the challenge of fabrication. In fact, most sputtering deposition tools are limited to one material at a time, with a limited number of targets available. This implies that if different materials are involved in the design of the IR mirror, different and frequently target substitution must be performed to deposit each period of the IR mirror. This, therefore, would considerably slow down the fabrication process and, on the other hand, would lead to greater expenses for the realization, even at an industrial level. Therefore, two techniques were taken in consideration for fabrication of the different index layers: i) mix different percentages of two materials, and ii) vary the composition of a single material. Both approaches are more likely to be beneficial when compared with the deposition of films from different target materials. In fact:

- varying the composition of a material by changing the parameters of deposition (i.e. gases flow rate, pressure, power, etc.) allows to obtain different refractive indices from a single target;
- mixing a low- and a high-index material through co-sputtering in principle could allow one to create composite materials with different properties, which leads to a huge flexibility in achieving any refractive index value between those of the starting materials.

On one side, co-sputtering of a high and low index materials such as titanium dioxide and silicon dioxide was chosen for its simplicity and versatility. Both materials are easy to handle and well-known in the literature [97]. In addition, the high refractive index contrast $n_H/n_L \ge 1.5$ make their choice even more interesting as the wavelength range in which reflection occurs is strictly related to this value [96].

On the other side, prior studies conducted on silicon nitride demonstrates that it is a very versatile material and its physical properties can be strongly influenced by the environmental condition during deposition. For example, [98, 99] studied the influence of the Ar and N₂ gas concentrations on the refractive index and deposition rate of silicon nitride films and reported that an increase in nitrogen flux leads to higher refractive indices and lower deposition rates; other works demonstrated that the physical properties of silicon nitride films are strongly influenced by the substrate temperature [100] and N₂ partial pressure [101]. Therefore, it is well suited to being the ideal candidate for obtaining different compositions, i.e. different refractive indices.

We therefore focused on two different design of IR mirror: one entirely made of silicon nitride composites (SiN_x) , and one based on layers of silicon dioxide (SiO_2) and titanium dioxide (TiO_2) .

4.4 Rugate design based on silicon nitrides

This section presents a rugate filter made of different layers obtained from a single cathode of Si, exploiting the idea of varying the refractive index by varying the deposition conditions. This structure was developed at the *Institute of Applied Sciences and Intelligent Systems* (ISASI) in Naples (Italy).

4.4.1 Deposition and characterization of single silicon nitride films

Deposition

Thin silicon nitride films were produced in Naples (CNR-ISASI) by reactive sputtering deposition using a magnetron source operated by an RF power supply (Advanced Energy, HiLight 613). The cylindrical vacuum chamber is equipped with four targets (10 cm in diameter) placed at 90° from each other, and a rotating plate



FIGURE 4.5: a) Sputtering deposition system at CNR-ISASI (Naples). b) Rotating plate with four sample holders.

with four Cu sample holders (10.7 cm in diameter) connected to ground (Fig. 4.5). A rotating shutter placed close to the target helped to control the deposition time and film thickness. A water-cooled silicon target (4-in diameter) with a purity of 99.99% is placed 10 cm from the sample holder. Smooth, alkali-free boro-aluminosilicate glasses (Corning: 1737F, 2.5 cm x 2.5 cm) are used as substrates, after appropriate cleaning in ultrasonic acetone and isopropanol baths. To facilitate optical studies, lightly doped n-type $(1.0 - 1.5 \times 10^{-3} \Omega \cdot cm)$ single-side polished silicon (100) wafers (2.5 cm x 2.5 cm) were also used as substrates.

Using a 1500 L/s turbo molecular pump, the vacuum chamber is pumped down overnight to a base pressure below 2×10^{-5} Pa before starting the experiment. A throttle valve is activated to reduce the pumping speed and obtain a pressure suitable for sputtering without wasting too much gas. The throttle activation did not increase the base pressure above 2×10^{-5} Pa. Indeed, the high vacuum is necessary to avoid oxidation of the source and have clean surfaces, and allows vapor particles to travel directly to the substrate, where they condense.

High-purity Ar and N_2 gases were introduced into the chamber and monitored using separate mass flow controllers (MKS, Series 946), with a constant Ar: N_2 ratio (36:3) corresponding to a total pressure of 0.54 Pa, measured by a capacitance gauge (Pfeiffer CMR 364). The choice of an argon flow significantly greater than nitrogen flow is based on evidence from previous studies [102, 103], where it was demonstrated that increasing the total flux of the processing gas could reduce the hysteresis that characterizes most reactive sputtering processes.

Before starting deposition, the Si target is cleaned from surface impurities by presputtering in an Ar atmosphere for 15 min. Nitrogen is injected and the RF power supplied to the Si target is slowly increased to the desired level and maintained for 20 minutes to ensure an equilibrium condition and guarantee homogeneous film growth. This conditioning is performed with the shutter plate open over an empty sample holder to reproduce the same deposition conditions of an actual experiment. The silicon target was supplied with variable power from 100-400 W; the automatic matching line maintained the reflected RF power component at a negligible level for all power values. No external heating or cooling was provided during deposition: temperature measurements showed that the sample holder never exceeded 100°C, as shown in Fig. 4.6.



FIGURE 4.6: Sample holder temperature during deposition at different RF powers. The circled points on each curve indicate the deposition time required to obtain a film thick 140 nm.

Characterization

The thicknesses of the silicon nitride films were measured using a profilometer (KLA Tencor, P-15) and their values were compared and confirmed by ellipsometric analysis, which yielded similar results, within 3% (Table 4.1). The deposition time was varied to maintain thicknesses of approximately 140 nm at each power, whilst at 300 W different deposition times were chosen to study the influence of the film thickness on the optical properties.

TABLE 4.1: Deposition rates of thin SiN_x films at different RF sputtering powers estimated from profilometric measurements, film thicknesses measured by profilometer and obtained from the model based on ellipsometric measurements, and percentage discrepancy between the two sets of thickness values. The numbers in brackets indicate different samples deposited in the same conditions.

RF Power	Dep. Rate	Thickness (nm)		Thickness	
(W)	(Å/s)	Profilometer	Ellipsometer	discrepancy (%)	
100	0.48	138.0	141.1	2.2	
125 (1)	0.63	117.8	120.0	1.9	
125 (2)	0.66	131.2	132.6	1.1	
150	0.78	126.1	126.7	0.5	
200 (1)	1.11	145.7	149.9	2.9	
200 (2)	1.65	135.0	138.4	2.5	
200 (3)	1.43	179.4	180.2	0.4	
250	2.08	125.3	128.3	2.4	
300 (1)	2.55	235.6	237.3	0.7	
300 (2)	2.52	131.2	133.6	1.8	
300 (3)	2.56	148.4	151.2	1.9	
300 (4)	2.50	137.5	140.2	2.0	
350	3.55	157.0	159.2	1.4	
400 (1)	4.15	141.3	143.7	1.7	
400 (2)	4.05	136.7	136.9	0.1	



FIGURE 4.7: Deposition rate of SiN_x at various RF sputtering powers (red triangles). Black empty triangles (at 125 W, 300 W, and 400 W), the cyan empty square and blue circle (at 300 W) represent additional samples produced in different runs to check the rates reproducibility. The red half empty triangles highlight the lack of reproducibility at 200 W. The two lines highlight the different slope (m) in the linear relation between deposition rate and power.

During the reactive sputtering, the gases react with the target material, creating a compound that is deposited on the substrate. The speed of this process and the properties of the compound are process-dependent. The evaluation of the deposition rates showed its increase with the sputtering power at fixed Ar and N₂ pressures (Fig. 4.7), as already observed in prior studies conducted in a narrower range of powers [104, 105].

It is also evident from the Fig. 4.7 that the region around 200 W separates two different linear regimes: when the power is less than 200 W, the deposition rate increases linearly with a slope $m_1 = 0.006$ (green line in Fig. 4.7). Above 200 W the deposition rate-power relation is still linear, but has a slope $m_2 = 0.014$ (blue line in Fig. 4.7). The different behaviors can be attributed to different sputtering modes: total target coverage by nitride atoms is expected at low power (*compound sputtering mode*) while limited coverage is expected at high power (*elemental sputtering mode*) [103]. In replicating the sample series, we observed a lack of reproducibility in the deposition rate in the region around 200 W, where it varied from 1.1-1.65 Å/s (Table 4.1).

The refractive index of each film was investigated using a spectroscopic ellipsometer (Horiba Jobin-Yvon, UVISEL) equipped with a xenon lamp and a detector system for analysis of the optical response of the sample from 280-1600 nm. Measurements were conducted at an incident angle of 70°. The complex refractive index of the silicon nitride film was well-fitted by the Tauc-Lorentz dispersion formula [106, 107]. Each fit returned negligible thicknesses for the two roughness-equivalent layers (≤ 5 nm) and the χ^2 was always ≤ 3 for each sample, proving the goodness of fit.

Figure 4.8 shows the refractive index and extinction coefficient trends of the samples deposited at different RF powers. As with the deposition rate, the refractive index increases sharply with the RF power. Indeed, the plasma confined near the target determines the release of silicon particles proportionally to the RF power: an



FIGURE 4.8: (a) Refractive index and (b) extinction coefficient trends for samples produced at different sputtering powers. The inset shows the extinction coefficient in semilogarithmic scale. The overlapping curves at 125 W, 300 W, and 400 W were obtained from different samples, and indicate the reliability of the experiment.

increase in the RF power results in consumption of nitrogen particles and formation of silicon-rich SiN_x films. Thus, it is observed that samples deposited at powers greater than 300 W have a refractive index greater than that of the stoichiometric Si₃N₄ [108] (black squares in Fig. 4.8 (a)), which is almost perfectly consistent with the films deposited at 300 W (olive green squares, magenta circles, empty purple squares, and cyan rhombuses in Fig. 4.8 (a)). Films deposited at powers less than 300 W have refractive indices less than that of Si₃N₄: with low atomic ratio (Si/N) values, the ionized nitrogen is easily back-scattered from the cathode and trapped in the growing film, introducing lattice defects and distancing the SiN_x films from the stoichiometric one. This qualitative analysis was confirmed by the EDS measurements (see Appendix A).

The extinction coefficient in Fig. 4.8 (b) has values less than 0.05 for powers up to 300 W, decreasing rapidly to zero before reaching a wavelength of 600 nm. For sputtering powers greater than 300 W, the extinction coefficient is no longer negligible, and decreases to zero when $\lambda > 600$ nm. Thus, we can conclude that most of the samples were completely transparent in the near-IR region, and nearly transparent in the visible region.

The complex refractive index does not depend on the thickness of the sample at the same power, as indicated by the magenta circles and the cyan rhombuses in Fig. 4.8), representing films deposited at 300 W with thicknesses of 131 nm and 235 nm, respectively. The overlapping curves at 125 W (light blue pentagon and empty red rhombuses), 300 W (magenta circles, olive green squares, empty purple squares, and cyan rhombuses), and 400 W (orange stars and empty black circles) in Fig. 4.8 show that the reproducibility of the deposition rate shown in Fig. 4.7 corresponds to the reproducibility of the refractive index curves, with a variation of less than 1%. Likewise, the missing reproducibility at 200 W of the deposition rate also occurs in the refractive index analysis, as showed in Fig. 4.9, which compares the refractive index dispersion curves of SiN_x films deposited at 300 W and 200 W: a significantly different behavior is observed in the refractive index of samples deposited at 200 W; contrasting the four almost perfectly overlapping curves for samples deposited at 300 W. Thus, the region around 200 W will be no longer taken into account.

Reflectivity measurements of each sample were performed by the integrating sphere (Ocean Optics ISP-REF) in the spectral range of 350-1750 nm, and the Jasco FT/IR 6300 spectrometer above $1.4 \,\mu m$. Both measurements were compared with



FIGURE 4.9: Refractive index of silicon nitride films deposited at 200 W and 300 W. Samples deposited at 300 W and samples deposited at 200 W exhibit different reproducibility.

the simulation results from *Open Filters*: the good agreement between the two sets of data over the entire range of investigated wavelengths confirms the effectiveness of the refractive indices obtained from ellipsometric measurements and the measured thicknesses. It also represents the first step in appropriately simulating more complex multilayer optical structures. As an example, in Fig. 4.10 the optical characterization of three different samples deposited at three different sputtering power is shown.



FIGURE 4.10: Reflectance measurements (green and blue lines) and simulations performed with Open Filters software (red line) on three samples at different sputtering powers: (a) 150 W; (b) 300 W; (c) 400 W.

4.4.2 The SiN_x-based IR mirror

To build the IR mirror the single layers of SiN_x have been arranged according to the scheme [ABCDCBA]¹, where each capital letter (A, B, C, and D) indicates a material, starting from the one with the lowest index (A) to the one with the highest index (D). The variation in the refractive index was obtained by changing the RF power during deposition, as mentioned in section 4.4.1, from 100 W (layer A) to 350 W (layer D). The intermediate layers, B and C, were obtained by depositions made at 125 W and

¹Note that from the second period onwards, the first layer (A) must not be considered, as it is already present in the previous period. Therefore, the total number of layers in the first period is 7 (ABCDCBA), while it decreases to 6 (BCDCBA) for all the others.

250 W, respectively. The silicon nitride films presented here are named according to the RF power used, namely SiN-high, SiN-med, SiN-med:low, SiN-low, which correspond to 350 W, 250 W, 125 W and 100 W, respectively.

The first period of the SiN-based SIR filter has been deposited by reactive sputtering and analyzed through the integrating sphere and the optical spectrum analyzer. The measured spectrum has been compared with the one simulated, showing a very good agreement between the two sets of data (Fig. 4.11 a)).



FIGURE 4.11: a) Spectral reflectance of a simulated (red line) and measured (black line) 1-period rugate structure. b) Simulated layer number-dependent evolution of spectral reflectance: 43 layers (7 periods, blue line), 61 layers (10 periods, green line), 73 layers (12 periods, black line).

Naturally, a single period is not enough to reach a configuration where the main reflectance peak is prominent in the spectrum. Indeed, more periods and more layers are needed: in fact, Fig. 4.11 b) presents the layer-dependent evolution of the reflectance and demonstrates that the more layers involved in the design the higher the reflectance peak.

Unfortunately, although the single layers involved in the design are characterized by a relatively low extinction coefficient, the overall structure presents a nonnegligible absorption (Fig. 4.12). This may be addressed to the layer D (SiN_x deposited at 350 W) which, when used repeatedly within the periodic structure, increases its absorption. Due both to some difficulties related to the malfunctioning of the deposition tool, and to the phenomenon of absorption (that contrasts the passage of solar radiation through the mirror, thus preventing it from reaching the absorber), we decided to follow another path, presented in the next section.

4.5 Rugate design based on silicon and titanium dioxides

Having established the limitations of the previous design, we focus on a new IR mirror structure based on the use of two cathodes, SiO₂ and TiO₂, to make distinct materials through the co-sputtering technique. This structure was developed during the period spent at Purdue University (IN, USA).



FIGURE 4.12: Normalized solar spectral irradiance (orange line) and absorption of the IR mirror made of SiN_x (black line).

4.5.1 Deposition and characterization of single films of SiO₂ and TiO₂

Deposition

Silicon and titanium dioxides, as well as intermediate-index materials, were produced at Purdue University.

The vacuum chamber (PVD SD-400) is equipped with four targets and one sample holder, in addition to a rotating shutter placed between the targets and the sample holder (Fig. 4.13 a)). The turbo molecular pump (Pfeiffer Vacuum HiPace 700, 685 liters/second) and roughing pump (Edwards XDS10i) lead to a pressure of 10^{-4} Pa before starting the experiment. A probe arm and a load lock gate valve (in Fig. 4.13 b)) allow to insert and remove the sample without breaking the vacuum.



FIGURE 4.13: a) Sputtering deposition system at Purdue University and b) loadlock chamber that provide a fast and clean method of introducing samples into high-vacuum systems.

RF balanced magnetron sputtering of 2-inch SiO₂ and TiO₂ cathodes (purities of 99.99% and 99.995%, respectively) in Argon or Argon/Oxygen atmospheres were used to create five different materials: to avoid involving multiple targets all the additional intermediate-index materials were obtained from co-sputtered depositions by mixing SiO₂ and TiO₂ in different ratios to form $[SiO_2]_x[TiO_2]_{1-x}$ (ST) [109, 110].

The targets are warmed up at 5 W/min until desired power is reached. After appropriate cleaning in acetone, toluene, isopropyl alcohol, soda lime glass slides were used as substrates, to perform the deposition on the same glass used in real high vacuum flat panels. The detailed parameters of the growth process are listed in Table 4.2. As for silicon nitrides, no external heating or cooling was provided during each deposition.

Film Name	Dep. Pressure	Oxygen Flow	Argon Flow	TiO ₂ Power	SiO ₂ Power
	(Pa)	(sccm)	(sccm)	(W)	(W)
TiO ₂	1.35	0.3	14.7	125	-
ST - high	1.35	0.3	14.7	125	42
ST - med	1.35	0.3	14.7	125	75
ST - low	1.35	0.3	14.7	125	125
SiO ₂	0.67	0	15	-	100

TABLE 4.2: Thin films growth process parameters.

Characterization

The thicknesses of thin SiO_2 , TiO_2 , and of ST-high, ST-med, ST-low films used for the characterization, measured by profilometry (KLA-Tencor, P-7 Stylus Profiler), are listed in table 4.3.

Film Name	Thickne	ess (nm)	Thickness	Deposition
	Ellipsometer	Profilometer	discrepancy (%)	Rate (nm/min)
SiO ₂	125	126	0.8	1.9
ST-low	32	35	9.4	1.2
ST-med	27	29	7.4	0.7
ST-high	30	32	6.7	0.5
TiO ₂	23	25	8.7	0.4

TABLE 4.3: Thin films thickness and deposition rate.

Those values were compared with results obtained from the ellipsometric analysis: the two sets of measurements yielded very similar results (listed in table 4.3). The deposition rates were estimated from the thickness values measured using profilometry because of its high level of accuracy and reproducibility. For each sample the peak-to-valley height, measured over a distance of 100 μ m, was found to be lower than 6 nm, comparable with that of the substrate. Therefore, this suggest the flatness of the deposited films, demonstrating the feasibility of multilayer structures.

The ellipsometric measurements were performed using a spectroscopic ellipsometer (J. A. Woollam V-VASE UV-VIS-NIR), equipped with a detector that allows to analyze samples in the range of 250 to 2500 nm. Data were collected at an incident angle of 70° and were well fitted by the Cauchy dispersion formula [111],

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$
(4.4)

where λ is the wavelength, while A, B, and C are terms to be adjusted to match the refractive index for the material. Each fit performed on the single-layers returned thicknesses for the two roughness-equivalent layers ≤ 5 nm and a $\chi^2 \leq 5$ for each sample.



FIGURE 4.14: Measured dispersion curves of the sputtered thin films: refractive index (a) and extinction coefficient (b) of SiO₂ (black circles), TiO₂ (olive green squares), co-sputtered SiO₂/TiO₂ at various SiO₂ powers (red pentagon, blue rhombuses, and magenta triangles).

The measured dispersion curves of each deposited material are depicted in Fig. 4.14, in the range of 300-2500 nm. Fig. 4.14 (a) shows the real component of the refractive index, n, while Fig. 4.14 (b) shows the extinction coefficient, k, on a semi-logarithmic scale and in a narrower region, since elsewhere it is equal to zero. It is evident for co-sputtered materials that the increase in the SiO₂ power determines the decrease of the refractive index. The refractive index contrast calculated between the high- and low-index materials is high: $n_H/n_L = n_{TiO_2}/n_{SiO_2} \simeq 1.56$ at λ =632.8 nm, favoring the width of the reflection peak.

4.5.2 The SiO₂- and TiO₂-based IR mirror

As already mentioned in section 4.4.2, in the IR mirror design the layers have been arranged according to the scheme [ABCDEDCBA]², where the layer A is made of SiO₂, B of ST-low, C of ST-medium, D of ST-high, and E of TiO₂.

Results of measurements and simulation of the SIR filter designed using data displayed in Fig. 4.14 are shown in Fig. 4.15. Optical transmittance spectra were recorded over an ultra-broad spectral range, using a spectrophotometer (Lambda 950) in the range of 200 nm to 2500 nm and an FTIR Spectrometer (Thermo-Nicolet Nexus 670) in the region above 2000 nm. The simulated and measured transmittance spectra resulting from a 3 period SIR design is shown in Fig. 4.15 a). As expected, a dip in transmittance is observed around $\lambda = 2 \mu m$. The simulated and experimental data strongly agree, showing nearly identical shape. In the region between 2 and 2.5 μ m the result from Lambda 950 and FTIR measurements overlap, indicating a variation between the two data sets of less than 6%. The larger variation between experimental and simulated data in the region above $\lambda = 2 \mu m$ can be attributed to the two main factors that are responsible for the characteristic spectrum: refractive index and layer thickness. In fact, on the one hand, a larger error at wavelengths longer than 2.5 μ m is expected because of the lack of a direct measurement of the refractive index, in addition to the fact that ellipsometric measurements performed on test samples before and after the three-period multi-layer fabrication showed a change of $\pm 1\%$ in refractive index for all layers. On the other hand, a change in the deposition rates up to $\pm 7\%$ on the test samples preceding and following the multilayer

²As explained in the footnote 1, the actual scheme is ABCDEDCBA/BCDEDCBA/../BCDEDCBA. Therefore, while the fist period consists of 9 layers, all the others have 8 layers.



FIGURE 4.15: a) Spectral transmittance of a 3 periods rugate structure: simulation (red line) and measurements (blue and black lines). b) Layer number-dependent evolution of spectral transmittance: 41 layers (5 periods, blue line), 57 layers (7 periods, green line), 81 layers (10 periods, black line).

deposition was observed. This may be attributed to possible wear or degradation of the SiO₂ and/or TiO₂ targets during fabrication; in fact, a decrease in deposition rate after \sim 20% of a target's useful life is expected. Although the agreement between experimental and simulated data remains satisfying, the mitigation of these uncertainties is possible if a real-time deposition rate monitor, *in situ* ellipsometry, or fresher targets are used, which are readily available solutions at an industrial level. The figure 4.15 b) presents the layer-dependent evolution of the transmittance (T), similarly to the one showed in Fig. 4.11 b) for the IR mirror entirely made of layers of silicon nitrides. The analysis shows that 57 layers (corresponding to 7 repeated periods) are sufficient to reach a transmittance close to zero in a certain region of the mid-IR range.

Differently from what was observed in the case of the IR mirror made of SiN_x , in the present case the spectral absorption ($A(\lambda)$) is negligible, as demonstrated in Fig. 4.16. Therefore, the spectral reflectance can be obtained as $R(\lambda) = 1 - T(\lambda)$.



FIGURE 4.16: Normalized solar spectral irradiance (orange line) and absorption of the IR mirror made of SiO₂ and TiO₂ (black line).

4.6 Final considerations on the IR mirror

The IR mirror presented in the prior section is characterized by a very narrow stopband (approximately 0.5 μ m wide) centered at 2 μ m. Still, its average transmittance in the solar region is not maximum. Therefore, further work can be done to optimize the IR mirror. For instance, an higher transmittance in the visible region would benefit the amount of solar radiation hitting the SSA, and a broader reflection stopband would further increase system efficiency by recovering more of the radiative power lost by the heated absorber.

While the transmittance spectrum could be improved quite easily by using one of the processes described in section 3.4 (i.e. by introducing one or multiple matching layers and/or by using some optimization techniques), the filter stopband broadening is achievable by introducing *periodic chirping*, represented in Fig. 4.17 and defined as follows [45]:

$$x_{i} = x_{i-1} \cdot \left(\frac{1+\zeta}{1-\zeta}\right)^{\frac{1}{N_{p}-1}}$$
(4.5)

where x_i is the optical thickness of the i-th period, N_p the total number of layer periods and ζ denotes the chirp parameter. The different thickness of the layers involved in the design is crucial, in fact the layers with thickness *x* will reflect a certain wavelength, those with thickness *x*+*dx* will reflect a slightly longer wavelength, and so on, resulting in a mirror capable of reflecting a wider range of wavelengths.

The main drawback in the introduction of chirped layers is the need for increasing the number of periods, which leads to a bigger number of layers in the design.



FIGURE 4.17: Refractive-index profile of a chirped mirror.

The designed IR mirror is characterized by a glass substrate ($n \simeq 1.5$) and several stacked layers ending with SiO₂. Such material has a low refractive index, below 1.5, which is not too far from the refractive index of the external air (n_{air} =1.0). Therefore, the matching and apodization procedures would not lead to appreciable improvements, as illustrated in Fig. 4.18, where the spectrum of a standard SIR filter is compared with that of the same filter processed with the quintic polynomial apodization [71].



FIGURE 4.18: IR mirror: simulation of the rugate design with (red curve) and without (black line) apodization.

The only appreciable improvement is evident in the region around 2 μm , right before the main reflection peak. However, it also leads to an overall worsening of the spectrum and a slight reduction of the reflectance in the stopband, as anticipated in section 3.4.2. Furthermore, the layers considered in the simulation are made up of hypothesized materials, which have constant refractive indices and which do not really exist. In fact, it is not easy to find many existing transparent materials with refractive index values between 1.0 and 1.5. Therefore, the strong contribution in the optimization of the transmittance/reflectance comes from either the refinement of the layer thicknesses and the addition of new thin layers in selected positions along the entire designed structure (refinement and needle methods, respectively, described in section 3.4.2).

The combination of chirped layers and optimization leads to remarkable results: in Figure 4.19 is presented the result of simulation performed using the chirped rugate-like design as a starting point and applying a needle optimization to reach a target curve describing a filter with properties close to the ideal IR mirror (as defined in section 1.4.2). The periodic chirping has been realized by choosing $\zeta = 0.4$ and a design made of 40 periods, with a total of layers of 240. The spectrum showed in Fig. 4.19 demonstrates an enlargement of the main dip in the spectrum (Δ_{IRM}), reaching as high as $\Delta_{IRM} = 2.5 \ \mu m$. The mirror is characterized by an average reflectance, ρ_{avg} , of 0.97 in the range of 1.75 to 4.25 μm and by an average transmittance, τ_{avg} , of 0.91 in visible region, up to 1.75 μm .

Note that, as mentioned in section 3.4.2, the needle method works by adding new thin layers at a specific location in the design. Therefore, after the needle optimization, the number of total layers increases and passes from the initial value of 240 to 640. Furthermore, to ensure that the added layers were not too thin and impractical in reality, we limited the thickness of the needles to be at least 5 nm, which is a value close to the minimum thickness allowed by the most common sputtering tools. Also, to avoid adding new materials to the design, we set an additional constraint: all the additional layers must be selected from the materials already existing in the design.

Although it takes a long time to deposit hundreds and hundreds of layers, it is not impossible to achieve the final configuration if the sputtering tool used is



FIGURE 4.19: Spectral reflectance of optimized chirped IR mirrors based on SiO_2 and TiO_2 layers (blue line, right axis), compared with the solar spectrum (red filled area, left axis) and the emission spectrum of a commercial absorber working at 400 °C (black line, left axis).

automated and equipped with an *in situ* growth monitoring, both solutions easily applicable at an industrial level.

On the basis of the results illustrated in the Chapter 2 ([46]), it is easy to demonstrate that an IR mirror with such properties could lead to a non-negligible change in the high-vacuum solar thermal system efficiency, $\Delta \eta$. In fact, while the high-vacuum solar thermal collector without an IR mirror has a low thermal transfer efficiency at a working temperature of 400°C (η =0.130), the addition of a mirror with the same characteristics as the one presented in Fig. 4.19 b) results in an increase in the efficiency of $\Delta \eta = 0.176$ at the same working temperature. This finding indicates that the optimized IR mirror would represent a net benefit in high-vacuum flat solar thermal systems working at medium to high operating temperatures and low concentration. An ideal mirror (ρ =1 in the IR while τ =1 in the visible region) with the same bandwidth $\Delta_{IRM} = 2.5 \,\mu m$ would increase the efficiency change value up to the 30%. Of course, by broadening the bandwidth of the ideal mirror the efficiency improves even more, reaching values up to the 60% [46]. Note that the efficiency change values reported in this paragraph refer to peak efficiencies.

Even if it has been developed for a HVFP system, the approach is general enough that the IR mirror could potentially be extended to any emissive solar device. Therefore, it is interesting to investigate its performance for oblique incidence [112, 113], as the spectrum presented in Fig. 4.19 result from simulation performed at a normal incidence. Therefore, the IR mirror reflectance was studied at different wavelengths and incident angles, in 0-80°. The results of the analysis, schematically illustrated in Fig. 4.20, showed that the IR mirror has a very low angular dependence, keeping a high reflectance in the whole range of investigated angles of incidence, while a high transmittance in the VIS and near-IR regions up to 50°, where the flat panel considered here produces the considerable amount of energy. Therefore, this study demonstrates that considering only the normal incidence remains a good approximation when dealing with systems made of flat parallel plates, as schematically showed in Fig. 2.1.


FIGURE 4.20: Reflectance spectra of the chirped IR mirror as a function of the incident angle.

Chapter 5

Control of thermal emissions via selective multilayer

This chapter intends to provide a general overview of thermo-photovoltaic (TPV) systems, highlighting the key role of both high-vacuum insulation and selective emitters in the control of the thermal emissions and of the systems efficiency. The chapter is organized as follows: section 5.1 introduces the PhotoVoltaic (PV) cells operation, as it is the main component of a TPV system. The working principle of TPVs is described in details in section 5.2. Section 5.3 presents the state of the art of the development of selective emitters, while section 5.4 introduces the class of materials which can be involved in their design and presents the results of our approach in designing selective emitters.



5.1 PV cell operation

FIGURE 5.1: Working Principle of a PV Device. Image available in [114].

A photovoltaic (PV) cell, whose working principle is schematically shown in Fig. 5.1, is basically configured as a large-area p-n junction, i.e. n-type and p-type semiconductors put directly adjacent to each other to create a stronger carrier diffusion gradient. The mechanism that allows to convert solar energy into electricity is the *photovoltaic effect*: when the photons hit the cell, their energy is transferred to the electrons of an atom of the semiconducting material in the p-n junction, causing it to jump to a higher energy state (*conduction band*) and creating an electron-hole pair. Hence, these electrons are free to move through the material, and their motion towards the n-side of the juction creates an electric current in the cell, which is the key point of a working cell [115]. However, only photons with appropriate energy (equal to the bandgap energy, E_{bg} , of the semiconductor) participate to the process: photons with $E < E_{bg}$ are not able to create the electron-hole pair; photons with $E > E_{bg}$ can only create one electron-hole pair and their excess energy is dissipated as heat. Therefore, in both cases there is a loss of energy which limits the conversion efficiency of the PV cell, determined as the fraction of incident power which is converted to electricity and is defined as:

$$\eta_{PV} = \frac{P_{el}}{P_{in}}.$$
(5.1)

Hence, only a small part of the solar spectrum is useful for the conversion: for example, Fig. 5.2 shows that the available portion of the solar spectrum is reduced to the 33% in the case of a silicon solar cell, with E_{bg} =1.1 eV



FIGURE 5.2: Spectral analysis of the minimum losses for a silicon solar cell (bandgap = 1.1 eV): thermalization represents the largest loss in this analysis, and it increases for the higher energy portions of the solar spectrum [116].

Besides silicon, other semiconductors can be used in solar technologies: the most diffuse are listed in table 5.1, where their bandgap energy and wavelength (E_{bg} , λ_{bg}) are reported.

PV cells can be classified into four generations, depending on the materials which are used for their fabrication. They are illustrated in Fig. 5.3 [114]:

- first-generation cells, which include single- and multi-crystalline silicon;
- second-generation cells, which are based on thin films (the maximum film thickness was brought down to a few nanometers to tens of micrometers to reduce the high material usage and cost of the previous generation);
- **third-generation cells**, which include organic solar cells with nano-crystalline films;

Material	E_{bg} (eV)	$\lambda_{bg} (\mu m)$
GaInAsSb	0.53	2.34
Ge	0.66	1.88
GaSb	0.72	1.72
Si	1.12	1.11
GaAs	1.42	0.87
InGaSb	1.42 to 0.36	0.87 to 3.44
CdTe	1.45	855
CIGS	1.01 to 1.68 eV	0.74 to 1.23
Perovskites	1.3 to 2.3	0.54 to 0.95
InGaP	1.90	0.65

TABLE 5.1: Band-gap energy and wavelength of the semiconductors most used for PV cells. Note that the term *perovskite* indicates a class of compounds which have the same type of crystal structure as CaTiO₃, and the range of bandgap energies indicated in the table can be further extended. *CIGS* stands for Copper Indium Gallium Selenide.

• **fourth-generation cells**, which combine the low cost/flexibility of polymer thin films with inorganic nanostructures.



FIGURE 5.3: Schematic of the various generations of solar cells [114].

However, the most common solar cells available in the market are the first-generation solar cells.

Monocrystalline silicon solar cells Monocrystalline cells are made up of crystals grown along one plane from cylindrical shaped ingots which are sliced into small wafers. Impurity atoms are added to dope the silicon either to make it p-type or n-type. The high purity determines high costs but high efficiency (26.7% [117]).

Polycrystalline silicon solar cells Polycrystalline cells are made from raw silicon, melted and poured into a square mold, further cooled and cut into perfectly square

wafers. Therefore, the low purity and nonuniformity of the wafers determines a lower efficiency, which reach its maximum around the 24.4% [117].

5.2 The interest in TPV technologies

The recent growth of photovoltaic solar energy capacity worldwide, as well as the relatively high collection efficiency of solar thermal collectors, have brought the attention of many on the development of thermo-photovoltaic systems. A TPV system employs a PV module and a thermal collector and allows the direct conversion from the thermal radiation emitted from an object heated at temperatures tipically higher than 1000 K to electricity.

As a result of the PV cell operation (described in the prior section), it is crucial that the radiation incident on the PV cell matches its bandgap. Hence, the key role of the thermal emitter, a device which emits thermal radiation and for which selectivity is required: it must emit only the photons with energy included in the range of interest to make the PV cell work properly. Alternatively, a filter can be added in front of the PV cell to transmit only the photons with $E = \hbar \omega \simeq E_{bg}$, while the remaining photons with energy outside the range of energies admitted by the PV cell are reflected back and reabsorbed by the emitter. The filters are particularly useful when working with black body emitters or emitters not perfectly selective, but they mostly reflect a small percentage of light in the desired wavelengths range. Then, all the light that is not redirected to the emitter or to the PV cell is lost.



FIGURE 5.4: Schematic of TVP operation. Image available in [118].

The working principle of a TPV device is schematically illustrated in Fig. 5.4 and could be summarized as follows [119]: the thermal energy coming from any source heats up an emitter, which emits photons preferably with energy above the bandgap of the PV cell. At this point, the radiation emitted hits the PV cell and is converted into electricity.

Despite their design is complex, TPV systems have several advantages besides directly converting heat radiation into electricity: they are modular and lightweight, which means that existing systems can be expanded or adapted to the needs; their average lifetime is of 25 years; they require little maintenance, are silent and emissionfree [115]. The main advantage of TPV with respect to direct conversion by solar cells is that their spectral distribution can be tailored according to their sensitivity, thanks to the either the selectivity of the emitter and the filter. It also has a potentially higher efficiency and higher power densities (5-60 W/cm² compared with 0.1 W/cm² for solar cells), as the heat source and the PV cell are much closer in TPV compared to the distance from the Sun (1-10 cm Vs $\simeq 1.5 \cdot 10^{10}$ m).

However, the definition of efficiency in TPV systems is complex and strongly depends on the boundary conditions: the total input can be defined in different ways depending on the heat source, and the output could be either considered as exclusively electrical or electrical and thermal - in the case of Combined Heat and Power (CHP) systems. Fig. 5.5 illustrates a schematic of the energy flow of a general TPV system.



FIGURE 5.5: Energy flow of a TPV system (adapted from [119]).

Therefore, the overall efficiency of a TPV system, η_{TPV} , depends on the product of all partial efficiencies of the various part of the system [119], namely:

- η_{PV} is the PV cell efficiency, defined in Eq. 5.1;
- η_{source} is the heat source efficiency, defined as the ratio of emitter net heat transfer to the total input:

$$\eta_{source} = \frac{P_{net}}{P_{in}};\tag{5.2}$$

• η_{cavity} is the cavity efficiency, which in steady state is defined as ratio of the power incident on the PV cell to the net radiative heat flow:

$$\eta_{cavity} = \frac{P_{PV}}{P_{net}}.$$
(5.3)

The current estimate of the capital costs for PVT systems shows that it is approximately 30% higher than the cost of a PV and solar thermal system installed side by side, and the PVT collectors account for approximately the 60% of the total cost [120, 121]. But, as the cost of solar thermal systems is decreasing with a learning curve of 20% in Europe, similar to the decreasing production cost of crystalline silicon (c-Si) PV modules [122, 123], it would be not too risky to assume that a reduction of costs will also invest the TPV market. A first step in that direction certainly could be the development of innovative designs which increase the thermal efficiency and improve the cost-competitiveness of the system.

About this, a recent work [124] has proposed new high efficiency designs which reduced the emissivity of the solar cells in flat plate and evacuated TPVs. Those employs an evacuated glazing cavity combined with a low emissive coating (with and emissivity of ε =0.15). Compared to present commercial TPVs, this collector is projected to have double the thermal efficiency, and to provide 1.5 and 2 times the revenue or carbon savings of PV modules and solar thermal collectors, respectively [124]. Hence, the need to exploit the advantages of high vacuum insulation, already illustrated in the section 1.4 (Fig. 1.10).

Potentially, TPV systems can convert heat into electricity with Carnot efficiency. Hovewer, at the current stage of research, the highest estimation of efficiency for TPV systems working at 1300 K reaches the 70% of the Carnot's limit [125] if a selective emitters built from refractory metals is employed. It is therefore obvious that in such systems the control of thermal radiation through selective emitters becomes fundamental to reduce the amount of wasted heat.

In the next two sections we present the state of the art and propose new and easier designs of selective emitters.

5.3 Selective emitters: state of the art

We have learned that the interest in the control of thermal emissions in the IR range represents a crucial factor in reaching higher efficiency in various energy systems (as well as in other fields, involving applications like thermography [126], radiative cooling [127, 128], IR spectroscopy [129, 130], etc.). Emitters and their properties play a crucial role in that issue.

The ideal thermal emitter is a *selective emitter* (SE), characterized by a sharp transition from high- to low-emissivity. Considering the TPV systems operation, the transition has to happen in the position of the spectrum corresponding to a photon energy approximately equal to the bandgap energy of the associated PV cell.

Depending on their characteristics, they can be classified in *broadband emitters* and narrow-band emitters. Broadband emitters are characterized by an emissivity curve which is spectrally close to 1, leading to emission of photons across wide range of wavelengths. Silicon carbide (SiC) is for example one of the most used material for this application, as it determines an emissivity of approximately 0.9 over a large region of the spectrum. Their main advantages are the simplicity of fabrication and high durability [131], however their broad emission spectrum causes existing systems to have low efficiencies when applied to TPV systems, since the wavelength range of PV cells conversion is very small compared to the emitter spectral range. Therefore, to prevent unnecessary absorption of above-band gap photons and avoid losses, it is crucial to work on the properties of the emitter to obtain *narrow-band emitters*. In this case, the emitted photons should have energies slightly above the PV cell bandgap. Typically, broadband emitters yield higher output electrical power density while narrow-band emitters can increase the TPV conversion efficiency. The ideal spectral control of both broadband and narrow-band emitters is shown in Fig. 5.6 a), while Fig. 5.6 b) highlights the fraction of high-energy photons convertible



into electricity in a GaInAsSb cell. Several solutions of SE have been already devel-

FIGURE 5.6: a) Ideal spectral control of a broadband thermal emitter, where any in-band photons are preferentially emitted, and of a narrow-band emitter, where only photons with energy slightly above the bandgap are emitted. b) BB emission at 1273 K, where the fraction of high-energy photons convertible into electricity in a GaInAsSb cell is highlighted (cyan area). Adapted from [132, 133].

oped in the past. They are based on different designs, each having advantages and disadvantages:

- **bulk emitters**, which can be either *graybody emitters* [134] such as Si, SiC, or *metals* with [135] or without AR coatings [136]. Both are tipically inexpensive and easy to fabricate in large areas.
- **naturally selective emitters** [137], made from rare earth metals like erbium and ytterbium. They are easy to fabricate and thermally stable at high-temperatures, but their emission is not tunable.
- **metamaterials** [138]. They consists in engineered material made of periodic patterns that are smaller than the wavelength of interest and can produce or behave with characteristics that are not found in nature.
- **1D photonic crystals** [139–141], which consists of alternating layers of highand low-index materials. They can cause high emissions outside the region of interest.
- **2D photonic crystals** [142]. They consist of 2D array of features on top of or in a substrate: whether an emitter can be fabricated inexpensively with large area depends on the substrate.

Nevertheless, although some have very favorable characteristics, they all have in common two main disadvantages: high cost and complexity of fabrication, especially when considering that they need to be industrialized. Therefore, in the next section we propose simpler structures based on easy-to-fabricate multilayers which can be definitely extended to an industrial manufacturing.

Multilayers basically consist of alternating metal and dielectric layers of varying thicknesses. The layer thicknesses can be optimized to enable broadband or tight emissions. The main advantages are the good performance, the low fabrication cost, and the ability to fabricate in large scale. The only drawback could be that, in the

long run, the materials at the interfaces may intermix. Therefore, the materials must be chosen carefully and the absence of interdiffusion experimentally verified.

5.4 Design of multilayer-based selective emitters

In this section we define the steps towards the complete design of nearly ideal selective thermal emitters based on multilayer designs.

5.4.1 The choice of materials

Considering the high temperatures to which selective emitters are subject (typically between 1300 and 2000 K), the thermal stability and durability at high temperatures of the materials involved in the design must be considered. Therefore, it is essential to consider refractory materials, i.e. materials that withstand the high temperatures without contaminating other materials and that retain heat in the area where it is needed.

In table 5.2 are listed various materials which are easy to process and interesting for such application, as they have a very high melting point and, some more some less, are highly lossy in the visible and near-infrared region of the spectrum, which is useful to increase the emissivity of the SE in that region.

Among the materials listed in the prior table, for our study we have chosen Si, SiO₂, Cr_2O_3 , SiN_x as they are easily available in the laboratory and their refractive index has been experimentally determined [44, 79]. In addition, we have considered other materials like Pt, W, Nb₂O₅, and HfC because they have very interesting properties. In this case the refractive index data from the literature were considered [145]. However, the refractive index of hafnium carbide is still unknown in the literature, particularly for HfC in the form of thin films. Thanks to its very high melting point (3900 °C), it could find a large number of applications and it is surely of great interest in TPV and solar thermal applications. Therefore, we deposited and characterized various thin hafnium carbide films, thanks to a collaboration with Prof. Harish C. Barshilia from *Nanomaterials Research Laboratory, Surface Engineering Division, CSIR-National Aerospace Laboratories* and *Academy of Scientific and Innovative Research, CSIR-NAL Campus*, Bangalore, India. Results are shown in the next subsection.

5.4.2 HfC: study of the refractive index

To fill the lack of data on the refractive index of this material, we deposited and characterized various samples.

Deposition of HfC films Thin films of hafnium carbide were deposited using the PVD technique. Reactive DC magnetron sputtering of an Hf cathode was carried out in an argon and acetylene (C_2H_2) ambient at room temperature and at a pressure of approximately 10^{-4} Pa. Silicon was used as substrate, after an appropriate cleaning procedure. During the depositions, the argon flow rate is kept fixed (15 sccm), as well as the current (at 0.48 A), the pulsed DC power (at 100 W), and the frequency (at 100 kHz). The acetylene concentration was varied in the range of 2.5 to 5.0 sccm to investigate its influence on the properties of these films.

Optical characterization of HfC films The thicknesses of the HfC films were measured using a profilometer (KLA Tencor, P-15) and their values are listed in Table 5.3,

	Material	Melting Point (°C)
Metals	Au	1064
	Si	1410
	Pt	1772
	Rh	1966
	Nb	2468
	Mo	2617
	Ta	3017
	W	3410
Oxides	Nb ₂ O ₅	1485
	Fe ₂ O ₃	1565
	SiO ₂	1610
	SnO ₂	1630
	SiO	1702
	TiO ₂	1830
	Ta_2O_5	1872
	Al_2O_3	2072
	Cr_2O_3	2266
	ZrO ₂	2700
	HfO ₂	2758
	MgO	2852
Carbides	B ₄ C	2350
	SiC	2730
	TiC	3160
	TaC	> 3700
	HfC	3900
Nitrides	GaN	2500
et al.	TiN	2930
	GaAs	1238
	MgF ₂	1260

TABLE 5.2: Materials useful for application in selective emitters and their melting point[143, 144].

next to the ones obtained from the ellipsometric analysis. The table also shows the percentage discrepancy between these two sets of values, as well as the deposition rate for each film.

The refractive index of the samples was investigated using a spectroscopic ellipsometer (Horiba Jobin-Yvon, UVISEL), following the same technique already explained in section 3.2.3: measurements were conducted in the range of 280 to 1600 nm at an incident angle of 70° .

The schematic of the model used to fit the ellipsometric data is reported in Fig. 5.7: it includes two thin layers, useful to simulate the roughness at the interface between the substrate and the film and on the film surface.

Each fit returned negligible thicknesses for the two roughness-equivalent layers (\leq 5 nm) and the χ^2 was always \leq 1 for each sample. More details are listed in the Table 5.4.

Fig. 5.8 illustrates the complex refractive index of the HfC films, which was wellfitted by the *Forouhi-Bloomer* alias *Amorphous dispersion formula* [146, 147]. It shows a decreasing refractive index as the C_2H_2 flow rate increases.

C ₂ H ₂ flow rate	Thickness (nm)		Thickness	Dep. Rate
(sccm)	Profilometer	Ellipsometer	discrepancy (%)	(Å/s)
2.5	95	100	5.0	13.0
3.0	75	86	12.8	11.5
4.0	97	93	4.3	17.6
5.0	75	86	12.8	18.8

TABLE 5.3: Deposition rate, thickness of thin HfC films at different C₂H₂ flow rates, and percentage discrepancy between profilometric and ellipsometric thickness data.

HfC film	Air	Layer 3
HfC	Layer 2	
c-Si (111) substrate	Layer 1	
c-Si (111)		

FIGURE 5.7: Diagram of HfC samples (not to scale), including roughness-equivalent layers.



FIGURE 5.8: (a) Refractive index and (b) extinction coefficient (in semi-logarithmic scale) trends for samples produced at different C_2H_2 concentration.

Reflectivity measurements of each sample were performed by the integrating sphere (Ocean Optics ISP-REF) in the spectral range of 350-1750 nm, and were compared with the simulation results from *Open Filters* (Fig. 5.9).

The good agreement between the two sets of data confirms the goodness of the refractive indices obtained from ellipsometric measurements as well as of the measured thicknesses. These analyses are useful to deepen the knowledge of all the parameters (such as refractive index coupling and matching, deposition rate, adhesion) that determine the optical and physical properties of the material, and therefore are essential to design multilayer structures with the optical properties required for applications in the thermal energy field.

Experimental data will be presented at the International Conference on Metallurgical Coatings and Thin Films (ICMCTF) [148] in 2022 in an oral presentation entitled *Characterization of hafnium carbide thin film for thermal energy applications*.

5.4.3 Scheme of selective emitters

In this section we propose different types of selective emitters, all designed to lie in the near-IR ragion (1-2 μm wavelength), paving the way for structures compatible with low-bandgap PV cells [149, 150] with λ_{bg} below 2 μm (correspondent to $E_{bg} \simeq$

C ₂ H ₂ flow rate	Thickness (nm) χ^2		χ^2
(sccm)	Layer 1	Layer 3	
2.5	0.03	0.98	0.24
3.0	0.21	0.79	0.15
4.0	0.08	3.15	0.18
5.0	0.01	0.95	0.16

TABLE 5.4: Thickness of the two roughness-equivalent layers (referred to Fig. 5.7) and χ^2 values of the ellipsometric fit.



FIGURE 5.9: Reflectance measurements (black lines) and simulations performed with Open Filters software (red lines) on the various HfC samples.

0.60 eV). In this way, the most common and widespread PV cells are included in the study.

The optical simulations of multilayer structures working as selective emitters were carried out by means of Open Filters, and a slight optimization of the layer thicknesses has been performed by defining a target curve describing the specifications of an ideal emitter (high emissivity around 1 μm and low emissivity elsewhere) and applying the refinement method described in section 3.4.2.

The simulated absorption spectra obtained at normal incidence from different multilayer structures are depicted in Fig. 5.10. The emissivity spectrum of a 8-layer structure based on Si, SiO₂, Cr₂O₃ and W is represented in Fig. 5.10 a). It has a narrow emission peak (FWHM = 0.54 μ m) centered around 1 μ m with emissivity close to 1, while at wavelengths longer than 1.1 μ m the emissivity rapidly drops to values smaller than 0.1. Figure 5.10 b) shows the emissivity spectrum of a 8-layer structure based on Nb₂O₅, SiO₂, Cr₂O₃, Pt and W, with a tight peak centered at 1.07 μ m. The emissivity spectrum in 5.10 c) is obtained from a 3-layer structure made of Si, Cr₂O₃ and W. Its peak, centered at 1.01 μ m and with an FWHM of about 0.8 μ m, is less narrow than in the previous cases. But it still has good selectivity, as the emissivity quickly drops to negligible values. Figure 5.10 d) shows the emissivity spectrum of



FIGURE 5.10: Simulated emissivity of various selective emitters. Inset: schematic, not in scale, of the multilayer structures. The arrow indicates the layers growth direction.

a 5-layer structure based on SiO₂, W and HfC deposited with a C₂H₂ flow rate of 3.0 sccm. The peak has an FWHM of 0.92 μm and is centered at 0.92 μm . Figure 5.10 e) shows another example of selective emitter made of 8 layers, chosen among Pt, Nb₂O₅, SiO₂, W and the SiN_x film deposited at 400 W. Its peak is centered at 0.91 μm and reaches a height of 0.99. Finally, the selective emitter showed in Fig. 5.10 f) has a more complex structure, as it is made of 5 layers periodically repeated 5 times. The materials involved in this design are W, SiN_x deposited at 100 W, and HfC deposited with a C₂H₂ flow rate of 3.0 sccm organized as follows: ABCBA/BCBA/.../BCBA. This recall the rugate design we showed in the previous chapter. The emissivity spectrum shows a peak centered just below 1 μm with an FWHM of 0.97.

Despite the more complex structure, it has the advantage of being made of only 3

materials, which can be easily deposited in any sputtering tool consisting of 3 or more targets. The same applies to emitter **c**. The refractive indices of the materials involved in the design of the selective emitters presented above, as well as the thicknesses of the various layers are reported in detail in Appendix B.

In table 5.5 are listed the peaks position and height, the FWHM, and the value of emissivity at 2 μ *m* for each spectrum of Fig. 5.10. Despite all the emitters have a good selectivity, the ones with the narrower band are: emitter **a**, emitter **b**, and emitter **e**. The latter, in particular, also reaches the highest emissivity ($\varepsilon = 0.99$) in the proximity of the silicon bandgap.

Selective emitter	Peak position (μm)	FWHM (µm)	Height	ε @ 2 μm
а	1.05	0.54	0.97	0.05
b	1.07	0.41	0.98	0.12
с	1.01	0.78	0.98	0.14
d	0.92	0.92	0.96	0.24
e	0.91	0.42	0.99	0.11
f	0.98	0.99	0.97	0.27

TABLE 5.5: Peak position, FWHM, height and emissivity at 2 μm for various emitters.

Note that in all the optical simulations the wavelength dispersive character of the refractive index has been taken into account. Furthermore, although all the structures presented herein involve an Si substrate, it can be easily replaced by an appropriately chosen substrate that guarantees negligible transmissivity in the entire range of wavelengths investigated.

The performance of all the emitters presented above were investigated also at oblique incidence. The results, illustrated in Fig. 5.11, show a low angular dependence of each structure up to 70° , with the exception of the emitters **a** and **b**, which denote a greater angular dependence already at 60° or 50° , respectively.



FIGURE 5.11: Emissivity of the various emitters as a function of the incident angle.

The emission of the selective TPV emitters at various temperature have also been analyzed. Figure 5.12 shows the spectral radiation of the different emitters presented

in Fig. 5.10, calculated at 1273 K (Fig. 5.12 a)) and at 1773 K (Fig. 5.12 b)). Those are compared to that of the blackbody at the same temperatures. Each curve in the figure is normalized to the maximum of the blackbody emission, and both the wavelength (in μm) and the energy (in eV) have been reported on the *x*-axis for reference.



FIGURE 5.12: Normalized spectral radiation emitted by the BB (dash dotted line) and the various emitters (continuous colored lines) shown in Fig. 5.10, calculated at (a) 1223 K and (b) 1773 K.

At both temperatures it is evident that the emission spectrum of the selective objects occurs over a narrower region and is always lower than that of the blackbody at the same temperature. For example, emitter **f** (magenta lines in the figure) reaches a maximum spectral radiation of 0.4 at 1273 K (or 0.7 at 1773 K) and assumes negligible values already before 3 μm . Conversely, the blackbody at 1273 K radiates non-negligible fraction of radiation up to 10 μm and above (or up to 6 μm when working at 1773 K).

The Fig. 5.12 a) also shows that emitters **a**, **b**, and **e** working at 1273 K suffer from low selectivity. In general, the comparison of the emission curves at both temperatures shows that, while at 1273 K the normalized emission spectra are quite wide and cover the range from 1 to 3 μm , at higher temperatures the width of the emission peaks is reduced to approximately 1 μm , ensuring a greater selectivity.

Note that Fig. 5.12 b) shows the spectra of only 2 out of 6 emitters. Indeed, except for emitter **d** and emitter **f** of Fig. 5.10, the others are made of materials with a melting point lower than the temperature of 1773 K ($\simeq 1500$ °C). Hence, the importance of using materials stable at high temperatures.

Figure 5.13 shows the spectral radiation emitted by the selective emitters and by the BB, integrated over the range of 0 to 5 μm . Each curve is normalized to its own maximum. The analysis has been performed at two temperatures, 1273 K (Fig. 5.13 a)) and 1773 K (Fig. 5.13 b)). As already mentioned in the case of Fig. 5.12 b), Fig. 5.13 shows the spectra of the only 2 (out of 6) emitters which can actually work at such temperature.

The insets in the same figures show the comparison between the integrated radiation of the various emitters and of the blackbody at the two investigated temperatures: the absence of normalization puts in evidence that the radiation emitted by the selective emitters is much lower than that of the blackbody. As for the previous analysis on the spectral radiation, also the study of the integrated radiation highlights the selective behaviour of all the designed emitters, showing that the emitter **a** and the emitter **c** are the least and the most selective, respectively.



FIGURE 5.13: Normalized integrated radiation emitted by the BB (dash dotted line) and the various emitters (continuous colored lines) shown in Fig. 5.10, calculated at a) 1223 K and b) 1773 K. The integrated non-normalized radiation spectra are shown in the two insets.

The study conducted for designing novel selective thermal emitters is therefore promising and allows to choose among different designs that meet the requirements for the application in TPV technologies. Further studies are in progress to tune the emission peak at longer wavelength and to obtain an even more ideal emissivity curve, making use of other refractory materials. Such nearly ideal emitters could further increase the efficiency of a TPV system compared to what has been demonstrated in [151], and substantially help in the thermal energy storage [152].

Summary

In this thesis work the properties of High Vacuum Flat Plate (HVFP) collectors produced by the company TVP Solar have been analyzed and compared to that of the main types of solar collectors: unglazed collectors, traditional flat plate collectors, evacuated tubes and parabolic troughs. The analysis has highlighted the advantages due to both flat structure and vacuum encapsulation (pressure below 10^{-4} Pa) in HVFPs: no need for solar tracking, harvesting of direct and diffuse component of solar radiation and large acceptance angle, reduction of convective and conductive losses to negligible levels. The latter, in particular, brings the solar-to-thermal conversion efficiency at greater values and extends the temperature range of the panel operation above 200 °C. This allows the production of heat in the mediumhigh range of temperatures (250 °C - 350 °C) and offers great potential to further improve energy conversion efficiency.

Therefore, in the course of my Ph.D. program I worked on the i) design (using two optical simulation software, *Open Filters* and *Stanford Stratified Structure Solver*), ii) fabrication (through the reactive and non-reactive magnetron sputtering depositions) and iii) characterization (through the use of ellipsometry, profilometry, visible and infrared spectroscopy, etc.) of single layers and multilayers to obtain the desired optical properties for both infrared (IR) mirrors and selective emitters. Below is a brief analysis of the two approaches.

The IR mirror is conceived for recovering the infrared radiation emitted by the hot absorber in HVFP system. Therefore, high transmittance in the solar region and high reflectance in the IR region are required. The analysis conducted on various optical structures showed that the rugate design allows to achieve the aforementioned properties. Such design has been already investigated in the past but never experimentally implemented in solar thermal devices. However, because it consists of a continuous and sinusoidal variation of the refractive index with the filter thickness, is hardly manufacturable. Then, the IR mirror design has been approximated by a discrete number of layers with steps in the refractive indices, creating a *Stepped Index Rugate* (SIR) filter. To balance the benefits of high IR reflectance associated with a larger number of refractive indices with the experimental limitation of sputtering tools that allow for a smaller number of distinct materials, reactive sputtering and co-sputtering techniques have been considered [52, 80].

The first IR mirror, developed at ISASI in Naples, consists of a rugate filter entirely based on silicon nitride composites (SiN_x) , obtained from reactive sputtering of Si in argon and nitrogen ambient at different RF powers [79]. The layers have been arranged according to the scheme ABCDCBA/../BCDCBA, where A represents the lowest index layer (obtained from SiN_x deposited at 100 W) and D the highest index layer (SiN_x deposited at 350 W), ranging from a refractive index of 1.5 to one of 2.2. Unfortunately, its design determined a non-negligible and unwanted absorption of the solar radiation, which would cause a loss of absorption by the SSA.

The second design of IR mirror, produced at Purdue University, is instead based on

 SiO_2 (lowest index) and TiO_2 (highest index) [81]. The layers of the mirror are arranged as follows: ABCDEDCBA, where the A-layer represents the SiO_2 and the Elayer the TiO₂. The intermediate-index layers (B, C, D) are obtained by co-sputtering of TiO₂ and SiO₂, changing the SiO₂ deposition power. This IR mirror has been optimized through different techniques: addition of single and multiple matching layers or needles, refinement of the layer thicknesses and periodically chirped layers. The latter is useful to broaden the filter reflection band: our study demonstrated enlargements up to 2.5 μm , keeping a high average transmittance (τ_{avg}) in the visible region and a high average reflectance (ρ_{avg}) in the IR region. In particular, the IR mirror based on TiO₂ and SiO₂ has $\rho_{avg} \simeq 0.97$ in the range of 1.75 to 4.25 μm and τ_{avg} 0.91 in the solar region (up to 1.75 μ m). The analysis of the performance of evacuated panels equipped with an IR mirror highlighted the key role of the mirror, showing that the addition of a mirror with the same characteristics mentioned above ($\rho_{avg} \simeq$ 0.97, τ_{avg} 0.91, $\Delta_{IRM} \simeq 2.5 \ \mu m$) results in an increase in efficiency of approximately 0.18 at 400 °C [46]. An ideal mirror (ρ =1 in the IR while τ =1 in the visible region) with the same bandwidth Δ_{IRM} = 2.5 μm would increase the efficiency change value up to the 30%. Of course, by broadening the bandwidth of the ideal mirror the efficiency improves even more, reaching values up to the 60% at the same working temperature.

The reader should note that, even if the IR mirror described in this work has been developed for a HVFP system, the approach is general enough that the IR mirror could potentially be extended to any emissive solar device.

On the other hand, selective emitters are designed for improving the energy conversion efficiency in thermo-photovoltaic (TPV) systems. In fact, photovoltaic (PV) cells are devices that work properly only in the proximity of the bandgap energy (E_{bg}) of the material they are made of: they do not absorb photons with energy below E_{bg} and lose the excess energy of photons with energy higher than E_{bg} . Therefore, a considerable part of the solar spectrum is not absorbed or lost as heat, limiting the energy conversion efficiency of PV (and TPV) devices. Hence, in the design of thermal emitters for TPV, a sharp transition from high to low emissivity across the bandgap energy region is required. Throughout the work different materials and selective thermal emitters have been analyzed regarding their properties and emissivity spectrum. The aim was to balance the need for selectivity in thermal emissions and designs suitable for application in TPV systems and large-scale production, as the ones currently diffused include nanofabrication, metamaterials and complex structures. Therefore, after an insight into the general framework of TPV techonologies, six different selective emitters based on easy-to-fabricate multilayer designs involving refractory materials, all characterized by high melting temperatures, are discussed. The resulting spectra show high emissivity values (up to 0.99) in the range of interest and low emissivity outside, as required, making these emitters a good choice in the fabrication of TPVs.

Conclusions and perspectives

A large number of optical applications require spectral selectivity, including solar absorption, high-temperature radiation, hyperspectral sensors, and optical communications. Although many new materials have been developed, often their properties and/or production costs do not favor their use. The main purpose of this work is to increase the flexibility of optical materials by including periodic or more complex structures to obtain the desired functionality, but also to maintain a low production cost and a design that is reproducible on a large scale. In this work, we considered the problem of reducing losses for solar devices to improve their overall efficiencies. The concept investigated was to introduce selective coatings to improve the solar conversion efficiency in thermal or thermo-photovoltaic (TPV) devices.

Experimental measurements and simulations of the selective IR mirror indicate that it is significantly beneficial to add an IR mirror at the currently existing High Vacuum Flat Plate (HVFP) collectors with the aim of improving their efficiency in the mid temperature range (250 °C–350 °C): such temperatures open a path towards the use of solar energy in a large number of industrial applications requiring heat. For example, high-pressure steam generation represents a large fraction of current industrial heat demand that has not yet been addressed by widespread renewable energy solutions commercially available. Such improvements become more interesting considering that the easy installation of high vacuum flat solar thermal panels on flat roofs can save land area usage, which is particularly valuable in European countries and other high population density countries.

In a future study it would also be interesting to investigate the possible presence of accumulated stress due to the deposition of numerous layers within a single structure. Furthermore, the properties of the IR mirror (in particular of that made of SiN_x) could be improved by introducing oxygen gas into the process to form SiO_xN_y or SiO_2 . This would provide a further expansion of the current refractive index range, allowing for a lower or upper limit. In fact, as for SiN_x , also the refractive index of SiO_xN_y can be modified by varying the partial pressure ratios of oxygen and nitrogen.

Simulated emissivity spectra of selective emitters show promising results in terms of selectivity. Recent works on concentrated hybrid solar systems involves the use of selective mirrors to obtain a spectral splitting between the photons useful for conversion in PV cells and those useful for heat production. Therefore, this preliminary analysis on selective emitters, if confirmed at the experimental level, adds a valuable contribution to the growth of this new technology, which is at an earlier stage of development. Of course, the mechanism of interdiffusion of particles between each layer of the multilayer structure should be investigated to prevent an eventual alteration of the optical properties of the performances of the coatings.

The results of the study conducted during this Ph.D. program showed that the use of IR mirrors in evacuated flat solar thermal panels or selective thermal emitters in

TPV systems, together with low cost and ease of manufacture of the optical structure, could certainly play a key role in increasing and expansion of the solar energy market.Consequently, the mitigation of greenhouse gases in the atmosphere with the use of these technologies will ultimately benefit our planet and our health.

Appendix A

Further investigation on SiN_{*x*} samples

A deeper investigation on SiN_x samples was performed to highlight the many facets of a material that have been taken into account in numerous applications since the 80s: it has been involved in the fields of metallurgy [153], semiconductors [154], microelectronics and integrated circuits [155], optics [156], and solar cells [157].

Experimental setup

Atomic Force Microscopy

To investigate the morphology of a thin film, in addition to the profilometer one can use an Atomic Force Microscope (AFM), which generates a high-resolution threedimensional profile of the surface examined. The main component of an atomic force microscope is a flexible cantilevered, at the end of which is mounted a very small and sharp tip with a radius of curvature of the order of nanometers. While passing over the surface of the sample, the tip flexes and its movements are captured by a system that uses the reflection of a laser point from the top of the micro-lever towards a matrix of photodiodes or piezoresistive sensors. The sample is positioned on a piezoelectric tube which moves it around during the scan. The AFM can operates

- **in contact**, if the tip of the cantilever and the surface of the sample are "in contact" with each other (at a distance of a few angstroms);
- **contactless**, if the distance between the tip of the cantilever and the surface of the sample is of tens of angstroms.

Scanning Electron Microscopy

The Scanning Electron Microscope (SEM) is useful to observe the samples surface with magnification factors up to 100 KX and high resolution (of the order of a few nanometers). It mainly allows to obtain information about the surface of a solid sample and its chemical-physical composition; in addition, measurement of surface potentials and of potential contaminations are possible.

The working principle is based on the generation of a highly energetic electron beam in vacuum (10^{-2} Pa), which is then focused on a lens system and deflected to scan a certain area of the sample to be analyzed. The interaction between the electron beam and the sample causes the latter to emit numerous particles, including secondary electrons, creating signals which are acquired by appropriate detectors and then processed to form an image in gray scale, characterized by a high depth

of field. The sample must be made of conductive material, otherwise it produces electrostatic charges that disturb the detection of secondary electrons.

X-ray diffraction

The x-ray diffraction (XRD) is a non-destructive technique used to analyze the crystalline structure of a sample. The technique is based on the constructive interference of monochromatic x-rays and a crystalline sample: the x-rays generated by a cathode ray tube are directed toward and hit the sample; a detector record the intensity of the reflected beam at the same angle of incidence θ . The diffraction peaks generate when the path difference between the beams reflected from parallel planes is equal to an integer number of wavelengths, according to Bragg's law:

$$n\lambda = 2dsin\theta, \tag{A.1}$$

where *n* is an integer number that represents the "order" of reflection, λ the wavelength of the incident x-rays, *d* the interplanar spacing of the crystal. The resulting diffraction spectrum produces a series of reflections that are indicative of both the positions and intensities of the diffraction effects, useful for the identification of the material composition.

Energy Dispersive X-ray Spectrometry

The Energy Dispersive X-ray Spectrometry (EDS or EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample.

An electron beam is focused on a sample in order to stimulate the emission of characteristic X-rays from the material under investigation: the beam may excite and eject an electron of an inner shell creating a hole, which will be filled by an electron from an outer, higher-energy shell. The difference in energy between the higher-energy shell and the lower energy shell is then released in the form of an X-ray. The energy of the X-rays emitted from the sample is characteristic of the atomic structure of the emitting element, in fact each element has a unique atomic structure allowing the elemental composition of the sample.

Results of the measurements

Fig. A.1 shows the IR reflectance spectra of the three silicon nitride films taken into account earlier and deposited at different sputtering powers (150 W, 300 W, and 400 W). A strong absorption band was evident at approximately 830 cm⁻¹ in all samples, corresponding to the stretching vibration mode of the Si-N bond. The vibrations in the medium frequency range (500-750 cm⁻¹) can be attributed to vibrations of Si atoms in Si-N₄ tetrahedra [158]. The absence of additional peaks in the spectra suggests the absence of oxygen and hydrogen atoms in the chamber during deposition, which could have participated in formation of N-H, Si-H, and N-H2 bending or stretching modes that usually occurs in CVD depositions [159].

Morphological analysis was performed using the AFM (XE-70 Park System) with a scan rate of 0.8 Hz and a resolution of 1024 x 1024 pixels² over an area of 1 μm^2 . The AFM analysis showed flat samples, with average roughness values less than 1 nm. Fig. A.2 shows 2-D images of the samples over a sampling area of 1 μm x 1 μm . The analysis was performed using Gwyddion [160], a free and open-source



FIGURE A.1: IR reflectance spectra of silicon nitride films deposited at 150 W (blue line), 300 W (black line), and 400 W (red line) RF power. Inset: medium frequency region from $500-750 \text{ cm}^{-1}$.



X Range: 1 µm

FIGURE A.2: Atomic force micrographs of SiN_x films: 2-D topographic images over a $1x1 \ \mu m^2$ region for samples deposited at a sputtering power of (a) 150 W; (b) 300 W; (c) 400 W.

software for scanning probe microscopy data visualization and analysis. It returned average roughness values, R_a , of 0.46 nm for the film deposited at 150 W, 0.37 at 300 W, and 0.30 nm at 400 W. The root mean square (RMS) roughness was 0.75 nm at 150 W, 0.70 nm at 300 W, and 0.50 nm at 400 W. The analysis indicates that the surface roughness decreases as the sputtering power increases. One reason may be that at high power, the kinetic energy of the sputtered ions and the substrate temperature increase, resulting in enhanced ion mobility and diffusion, smoothing the growth front of the film [161].

The flatness of the samples, in addition to the reproducibility of the deposition process, demonstrate the feasibility of multilayer structure fabrication.

The samples were also analyzed using the SEM (Raith 150) with an accelerating voltage of 2 kV and an objective lens opening of 20 μ m. The analysis showed homogeneous and featureless surfaces for all samples (Fig. A.3), which is critical for the design of multilayer optical structures.



FIGURE A.3: SEM top view images of silicon nitride films deposited at 150 W (top row), 300 W (middle row), and 400 W (bottom row).

The films were also studied through x-ray diffraction (XRD) measurements performed with a Cu K α radiation x-ray source ($\lambda = 1.5406$ Å). The XRD patterns of the n-type Si (100) wafers used as substrates are shown in Fig. A.4 (a), with an intense peak at $2\theta = 69^{\circ}$ and two less intense peaks at 37.5° and 44°, enlarged in Fig. A.4 (c) and (d), respectively. The figure also shows the XRD spectra of three samples deposited at different sputtering powers: 150 W (red line), 300 W (blue line), and 400 W (magenta line). In addition to the three peaks caused by the substrate, an additional peak at $2\theta = 33^{\circ}$ (enlarged in Fig. A.4 (b)) was generated by the silicon nitride films. The films have a preferential growth orientation without a strict dependence on the deposition power. The absence of other peaks in the XRD spectrum does not allow establishment of an SiN_x crystallographic phase or the orientation of the lattice.

Finally, the elemental composition of the silicon nitride films was analyzed using the EDS with a Leo EVO 50 SEM equipped with an Oxford INCA Energy 300 EDS system. The EDS analyses were conducted at 20 kV and a microscope working distance of 8.5 mm, with an aperture size of 30 µm. To avoid strong silicon signal from the substrate, the SiN_x films were deposited on an MgO substrate, and an additional 10 nm Ag film was deposited on each sample. The recorded survey scans indicated variable weight percentages of Si and N in samples deposited at different powers, as shown in Fig. A.5. With the large signal originating from the substrate, the relative error in film composition is quite high; only the samples deposited at 150 W and 400 W are discussed. From the tables in the insets of Fig. A.5, the Si/N ratio increases as the RF power increases, and is 0.50 for the sample deposited at 150 W and 0.85 for the sample deposited at 400 W. These values are less and greater than the expected Si/N value of 0.75 for stoichiometric Si₃N₄ films, confirming the qualitative description reported earlier.



FIGURE A.4: a) XRD patterns of three thin SiN_x films deposited on a silicon substrate at different sputtering powers: 150 W (red line), 300 W (blue line), and 400 W (magenta line). The XRD diffraction pattern of the Si substrate is also shown as a black line. Enlarged view of the silicon nitride films peak at (b) $2\theta = 33^\circ$ and substrate peaks at (c) 37.5° and (d) 44° .



FIGURE A.5: EDS analysis results for SiN_x samples deposited at (a) 150 W and (b) 400 W. The inset tables show the atomic percentages of elements in the two SiN_x samples.

Appendix **B**

Details on the selective emitters design

Additional details on the structure of selective emitters described in Chapter 5 are given in this paragraph.

Different materials are involved in the design of selective emitters, each having different thickness, listed in Table B.1. Globally, we can list the materials used as follows: Si, SiO₂, Cr₂O₃, W, Nb₂O₅, Pt, HfC, and SiN_x. We should also remember that the latter material has been used in the form of low-index SiN_x (when deposited at 100 W) and high-index SiN_x (when deposited at 400 W). In Fig. B.1 the refractive index of all the materials mentioned are reported for reference.



FIGURE B.1: Refractive index (a) and extinction coefficient (b) of the materials involved in the design of selective emitters. SiN_x , SiO_2 , Cr_2O_3 , and HfC curves refer to experimental data, while data of W, Nb_2O_5 , Pt are taken from [145].

Emitter	Layer number	Material	Thickness (nm)
а	1	W	35
	2	Cr_2O_3	30
	3	W	25
	4	Cr_2O_3	80
	5	SiO_2	240
	6	Si	60
	7	SiO_2	78
	8	Si	20
b	1	W	116
	2	Pt	28
	3	W	11
	4	Cr_2O_3	37
	5	W	23
	6	Cr_2O_3	82
	7	SiO_2	312
	8	Nb_2O_5	44
С	1	W	177
	2	Cr_2O_3	25
	3	Si	28
d	1	SiO ₂	100
	2	HfC	50
	3	W	20
	4	HfC	50
	5	SiO_2	100
e	1	Pt	90
	2	SiO_2	104
	3	SiN_x - high	65
	4	W	13
	5	Pt	7
	6	SiO_2	44
	7	Nb_2O_5	39
	8	SiO ₂	6
f	1	$-\frac{-}{\text{SiN}_x - \text{low}}$	270
	2	HfC	230
	3	W	70
	4	HfC	46
	5	SiN_r - low	130

TABLE B.1: Details on the structure of selective emitters: materials and layer thicknesses.

Bibliography

- Ali Sayigh. "Renewable energy the way forward". In: *Applied Energy* (1999), p. 16.
- [2] Richard Perez and Marc Perez. "A fundamental look at energy reserves for the planet". In: 50 (Jan. 2009).
- [3] C. Lauterbach et al. "The potential of solar heat for industrial processes in Germany". In: *Renewable and Sustainable Energy Reviews* 16 (2012), pp. 5121–5130. DOI: 10.1016/j.rser.2012.04.032.
- [4] Amir Shahsavari and Morteza Akbari. "Potential of solar energy in developing countries for reducing energy-related emissions". In: *Renewable and Sustainable Energy Reviews* 90 (July 2018), pp. 275–291. DOI: 10.1016/j.rser. 2018.03.065.
- [5] Douglas J. Arent, Alison Wise, and Rachel Gelman. "The status and prospects of renewable energy for combating global warming". In: *Energy Economics* 33.4 (2011), pp. 584–593. DOI: 10.1016/j.eneco.2010.11.003.
- [6] Andrew J. Chapman, Benjamin C. McLellan, and Tetsuo Tezuka. "Prioritizing mitigation efforts considering co-benefits, equity and energy justice: Fossil fuel to renewable energy transition pathways". In: *Applied Energy* 219 (2018), pp. 187–198. DOI: 10.1016/j.apenergy.2018.03.054.
- [7] Rabia Akram et al. "Heterogeneous effects of energy efficiency and renewable energy on carbon emissions: Evidence from developing countries". en. In: *Journal of Cleaner Production* 247 (Feb. 2020), p. 119122. ISSN: 09596526. DOI: 10.1016/j.jclepro.2019.119122. URL: https://linkinghub.elsevier. com/retrieve/pii/S0959652619339927 (visited on 07/23/2020).
- [8] National Renewable Energy Laboratory. https://www.nrel.gov/research/ re-solar.html.
- [9] C. E. Kennedy. Review of Mid- to High-Temperature Solar Selective Absorber Materials. en. Tech. rep. NREL/TP-520-31267, 15000706. U.S. Department of Energy Office of Scientific and Technical Information, July 2002, NREL/TP-520– 31267, 15000706. DOI: 10.2172/15000706. URL: http://www.osti.gov/ servlets/purl/15000706-1i6DGF/native/ (visited on 07/23/2020).
- [10] P. Bermel et al. "Selective Solar Absorber". In: Annual Review of Heat Transfer 15 (2012), pp. 231–254. DOI: 10.1615/AnnualRevHeatTransfer.2012004119.
- [11] https://www.tvpsolar.com/.
- [12] Z. M. Zhang. Nano/Microscale Heat Transfer. Mc Graw Hill, 2007.
- [13] Anon. Overview of Spectroscopy. https://chem.libretexts.org/@go/page/70698, 2019.
- [14] M. Fox. *Optical Properties of Solids*. Oxford University Press, 2010.
- [15] F. P. Incropera et al. *Fundamentals of Heat and Mass Transfer*. John Wiley & Sons, 2007.

- [16] ASTM, ASTM G173: Standard Tables for Reference Solar Spectral Irradiance at Air Mass 1.5: Direct Normal and Hemispherical for a 37 Degree Tilted Surface. 2008.
- [17] C. G. Granqvist. "Solar energy materials: An overview". In: Appl. Phys. A Solids Surfaces 52 (1991), pp. 83–93.
- [18] Peter Bermel et al. "Design and global optimization of high-efficiency thermophotovoltaic systems". In: *Opt. Express* 18.S3 (2010), A314–A334. DOI: 10. 1364/0E.18.00A314.
- [19] Rockenbaugh, C., Dean J., Lovullo, D., Lisell, L., Barker, G., Hanckock, E., Norton, P. *High Performance Flat Plate Solar Thermal Collector Evaluation*. Prepared for the General Services Administration by the National Renewable Energy Laboratory.
- [20] Ashish Shukla et al. "A state of art review on the performance of transpired solar collector". In: *Renewable and Sustainable Energy Reviews* 16.6 (2012), pp. 3975– 3985. DOI: https://doi.org/10.1016/j.rser.2012.02.029.
- [21] M. Orosz and R. Dickes. "16 Solar thermal powered Organic Rankine Cycles". In: Organic Rankine Cycle (ORC) Power Systems. Ed. by Ennio Macchi and Marco Astolfi. Woodhead Publishing, 2017, pp. 569–612. ISBN: 978-0-08-100510-1. DOI: https://doi.org/10.1016/B978-0-08-100510-1.00016-8.
- [22] F. Calise et al. "Design and simulation of a prototype of a small-scale solar CHP system based on evacuated flat-plate solar collectors and Organic Rankine Cycle". In: *Energy Conversion and Management* 90 (2015), pp. 347–363. DOI: 10.1016/j.enconman.2014.11.014.
- [23] Weijing Dai et al. "Influence of gas pressure on the effective thermal conductivity of ceramic breeder pebble beds". In: *Fusion Engineering and Design* 118 (Mar. 2017), pp. 45–51. DOI: 10.1016/j.fusengdes.2017.03.073.
- [24] Nikolaus Benz and Thomas Beikircher. "High efficiency evacuated flat-plate solar collector for process steam production". In: *Solar Energy* 65 (Feb. 1999), pp. 111–118. DOI: 10.1016/S0038-092X(98)00122-4.
- [25] T. M. Letcher. Future Energy: Improved, Sustainable and Clean Options for our Planet. Elsevier, 2014.
- [26] P. Heller. *The performance of concentrated solar power (CSP) systems: analysis, measurement and assessment.* Woodhead Publishing, 2017.
- [27] ISO 9806:2017. Solar energy Solar thermal collectors Test methods International Organization for Standardization. Geneva, Switzerland.
- [28] A. Buonomano et al. "Experimental analysis and dynamic simulation of a novel high-temperature solar cooling system". In: *Energy Conversion and Man*agement 109 (2016), pp. 19–39.
- [29] K. Rajashekara. "Hybrid Fuel-Cell Strategies for Clean Power Generation". In: IEEE TRANSACTIONS ON INDUSTRY APPLICATIONS 41 (3) (2005). DOI: 10.1109/TIA.2005.847293.
- [30] Klaus Burlafinger, Andreas Vetter, and Christoph J. Brabec. "Maximizing concentrated solar power (CSP) plant overall efficiencies by using spectral selective absorbers at optimal operation temperatures". In: *Solar Energy* 120 (Oct. 2015), pp. 428–438.

- [31] Lee A. Weinstein et al. "Concentrating Solar Power". en. In: Chemical Reviews 115.23 (Dec. 2015), pp. 12797-12838. ISSN: 0009-2665, 1520-6890. DOI: 10.1021/acs.chemrev.5b00397. URL: https://pubs.acs.org/doi/10.1021/acs.chemrev.5b00397 (visited on 07/23/2020).
- [32] Feng Cao et al. "A review of cermet-based spectrally selective solar absorbers".
 en. In: *Energy & Environmental Science* 7.5 (2014), p. 1615. ISSN: 1754-5692, 1754-5706. DOI: 10.1039/c3ee43825b. URL: http://xlink.rsc.org/?DOI=c3ee43825b (visited on 07/23/2020).
- [33] Carl M. Lampert. "Coatings for enhanced photothermal energy collection I. Selective absorbers". en. In: Solar Energy Materials 1.5-6 (June 1979), pp. 319–341. ISSN: 01651633. DOI: 10.1016/0165-1633(79)90001-7. URL: https://linkinghub.elsevier.com/retrieve/pii/0165163379900017 (visited on 07/23/2020).
- [34] Masanori Okuyama et al. "Selective absorber using glow-discharge amorphous silicon for solar photothermal conversion". In: *Solar Energy Materials* 3 (1980), pp. 405–413. DOI: 10.1016/0165-1633(80)90029-5.
- [35] A. Donnadieu and B. O. Seraphin. "Optical performance of absorber–reflector combinations for photothermal solar energy conversion". In: *Journal of the Optical Society of America* 68 (1978), 292–297. DOI: 10.1364/J0SA.68.000292.
- [36] C. D'Alessandro et al. "Solar Selective Coating for Thermal Applications". In: Key Engineering Material 813 (2019), pp. 316–321. URL: https://www.scientific.net/KEM.813.316.
- [37] Nicholas P. Sergeant et al. "Design of wide-angle solar-selective absorbers using aperiodic metal-dielectric stacks". In: *Optics Express* 17.25 (2009), p. 22800.
 DOI: 10.1364/0E.17.022800. (Visited on 07/23/2020).
- [38] Feng Cao et al. "Enhanced Thermal Stability of W-Ni-Al₂O₃ Cermet-Based Spectrally Selective Solar Absorbers with Tungsten Infrared Reflectors". en. In: Advanced Energy Materials 5.2 (2015), p. 1401042. DOI: 10.1002/aenm. 201401042.
- [39] Michael H. Huang et al. "Room-Temperature Ultraviolet Nanowire Nanolasers". en. In: Science, New Series 292.5523 (2001), pp. 1897–1899. URL: http://www.jstor.org/stable/3083931.
- [40] Jia Zhu et al. "Optical Absorption Enhancement in Amorphous Silicon Nanowire and Nanocone Arrays". In: *Nano Letters* 9 (Jan. 2009), pp. 279–282. DOI: 10. 1021/n1802886y.
- [41] Ivan Celanovic, Natalija Jovanovic, and John Kassakian. "Two-dimensional tungsten photonic crystals as selective thermal emitters". en. In: *Applied Physics Letters* 92.19 (May 2008), p. 193101. ISSN: 0003-6951, 1077-3118. DOI: 10.1063/1.2927484. URL: http://aip.scitation.org/doi/10.1063/1.2927484 (visited on 07/23/2020).
- [42] Pengfei Li et al. "Large-Scale Nanophotonic Solar Selective Absorbers for High-Efficiency Solar Thermal Energy Conversion". In: *Advanced Materials* 27.31 (2015), pp. 4585–4591. DOI: 10.1002/adma.201501686. (Visited on 07/23/2020).
- [43] https://alanod.com/en/industries/solar/absorbent-surfaces.
- [44] Davide De Maio et al. "A Selective Solar Absorber for Unconcentrated Solar Thermal Panels". In: *Energies* (2021). DOI: 10.3390/en14040900.

- [45] O. Ilic et al. "Tailoring high-temperature radiation and the resurrection of the incandescent source". In: *Nature Nanotechnology* 11 (2016), pp. 320–324.
- [46] Carmine D'Alessandro et al. "Performance analysis of evacuated solar thermal panels with an infrared mirror". In: *Applied Energy* 288 (2021), p. 116603. DOI: 10.1016/j.apenergy.2021.116603.
- [47] Roberto Grena. "Efficiency Gain of a Solar Trough Collector Due to an IR-Reflective Film on the Non-Irradiated Part of the Receiver". In: *International Journal of Green Energy* 8.7 (2011), pp. 715–733. DOI: 10.1080/15435075.2011. 602154.
- [48] Marie C. Cyulinyana and Phil Ferrer. "Heat efficiency of a solar trough receiver with a hot mirror compared to a selective coating". In: *South African Journal of Science* 107.11/12 (2011), 7 pages. DOI: 10.4102/sajs.v107i11/12. 524.
- [49] V. S. Kaluba and P. Ferrer. "A model for hot mirror coating on solar parabolic trough receivers". In: *Journal of Renewable and Sustainable Energy* 8.5 (Sept. 2016), p. 053703. DOI: 10.1063/1.4965252.
- [50] C. D'Alessandro et al. "Measurements of Spectrally Averaged Absorptivity and Emissivity for a Selective Solar Absorber in High Vacuum Under Direct Solar Illumination". In: *Journal of Physiscs: Conference Series* 1599 (2020). DOI: 10.1088/1742-6596/1599/1/012027.
- [51] https://www.thorlabs.com/newgrouppage9.cfm?objectgroup_id=139.
- [52] Daniela De Luca et al. "Rugate filter window coating for improvement of vacuum solar thermal absorber efficiencies". In: *Proc. SPIE 11496, New Concepts in Solar and Thermal Radiation Conversion III* (Aug. 2020). DOI: 10.1117/12. 2574604.
- [53] Kraus A. D. Bejan A. Heat Transfer Handbook. Wiley, June 2003. 1496 pp. URL: https://www.wiley.com/en-us/Heat+Transfer+Handbook-p-9780471390152.
- [54] K. Xu et al. "Thermal emittance of Ag films deposited by magnetron sputtering". In: *Vacuum* 174 (2020). DOI: 10.1016/j.vacuum.2020.109200.
- [55] D. De Maio et al. "Thermal Efficiency of a Concentrating Solar Collector Under High Vacuum". In: *Journal of Physiscs: Conference Series* 1599 (2020). DOI: 10.20944/preprints202001.0072.v1.
- [56] COMSOL Multiphysics, v. 5.6. www.comsol.com. COMSOL AB, Stockholm, Sweden.
- [57] R.W. Moss et al. "Performance and operational effectiveness of evacuated flat plate solar collectors compared with conventional thermal, PVT and PV panels". In: *Applied Energy* 216 (2018), pp. 588–601. DOI: 10.1016/j.apenergy. 2018.01.001.
- [58] M. Eck et al. "Guidelines for CSP Yield Analysis Optical Losses of Line Focusing Systems; Definitions, Sensitivity Analysis and Modeling Approaches". In: *Energy Procedia* 49 (2014). Proceedings of the SolarPACES 2013 International Conference, pp. 1318–1327. DOI: https://doi.org/10.1016/j.egypro.2014.03.141.
- [59] JRC Photovoltaic Geographical Information System (PVGIS) European Commission. 2020. URL: https://re.jrc.ec.europa.eu/pvg_tools/it/#DR (visited on 08/07/2020).

- [60] https://emsliegroup.mcmaster.ca/orf-re/ald/images-for-websitepvd-and-cvd.png/view.
- [61] K.S. Sree Harsha. *Principles of physical vapor deposition of thin films*. Elsevier Science, 2006.
- [62] http://www.semicore.com/what-is-sputtering.
- [63] Dong-Hyeok Lee and Nahm Gyoo Cho. "Assessment of surface profile data acquired by a stylus profilometer". In: *Measurement Science & Technology -MEAS SCI TECHNOL* 23 (Oct. 2012). DOI: 10.1088/0957-0233/23/10/ 105601.
- [64] https://jascoinc.com/learning-center/theory/spectroscopy/fundamentalsftir-spectroscopy/.
- [65] Victor Liu and Shanhui Fan. "S⁴: A free electromagnetic solver for layered periodic structures". In: *Computer Physics Communications* 183.10 (2012), pp. 2233 –2244. ISSN: 0010-4655. DOI: 10.1016/j.cpc.2012.04.026. URL: http://www.sciencedirect.com/science/article/pii/S0010465512001658.
- [66] S. Larouche and L. Martinu. "Open Filters: open-source software for the design, optimization, and synthesis of optical filters". In: *Appl. Opt.* 47 (2008), pp. C219–C230. DOI: 10.1364/A0.47.00C219.
- [67] L. Li. "New formulation of the Fourier modal method for crossed surfacerelief gratings". In: *J. Opt. Soc. Amer. A* 14 (1997). DOI: 10.1364/JOSAA.14. 002758.
- [68] D. M. Whittaker and I. S. Culshaw. "Scattering-matrix treatment of patterned multilayer photonic structures". In: *Phys. Rev. B* 60 (1999). DOI: 10.1103/ PhysRevB.60.2610.
- [69] L. Li. "Formulation and comparison of two recursive matrix algorithms for modeling layered diffraction gratings". In: J. Opt. Soc. Amer. A 13 (1996). DOI: 10.1364/JOSAA.13.001024.
- [70] H. A. Macleod. *Thin-Film Optical Filters*. CRC Press, Taylor & Francis Group, 2001.
- [71] W. H. Southwell and Randolph L. Hall. "Rugate filter sidelobe suppression using quintic and rugated quintic matching layers". In: *Appl. Opt.* 28.14 (1989), pp. 2949–2951. DOI: 10.1364/A0.28.002949.
- [72] William H. Southwell. "Using apodization functions to reduce sidelobes in rugate filters". In: *Appl. Opt.* 28.23 (1989), pp. 5091–5094. DOI: 10.1364/A0. 28.005091.
- [73] V.S.R.S.P. Kumar et al. "Design and optimization of high reflectance graded index optical filter with quintic apodization". In: *International Conference on Optics and Photonics 2015.* Ed. by Kallol Bhattacharya. Vol. 9654. SPIE, 2015, pp. 65–70. DOI: 10.1117/12.2181732.
- [74] Eric W. Weisstein. Bartlett Function. https://mathworld.wolfram.com/ BartlettFunction.html.
- [75] Eric W. Weisstein. Gaussian Function. https://mathworld.wolfram.com/ GaussianFunction.html.
- [76] P. Baumeister. "Design of multilayer filters by successive approximations". In: J. Opt. Soc. Am. 48 (1958), pp. 955–958.

- [77] J. J. Moré. "The Levenberg-Marquardt algorithm: implementation and theory". In: Lect. Notes Math. 630 (1978), 105–116.
- [78] A. V. Tikhonravov. "A method of synthesis of optical coverings which uses the necessary optimality conditions". In: *Vestn. Mosk. Univ. Fiz. Astronomiya* 37 (1982), 108 –110.
- [79] Daniela De Luca et al. "Tuning silicon nitride refractive index through radiofrequency sputtering power". In: *Thin Solid Films* 737 (2021), p. 138951. DOI: https://doi.org/10.1016/j.tsf.2021.138951.
- [80] Daniela De Luca et al. "Rugate filters for evacuated thermal collectors: IR mirror for improvement of energy conversion efficiency". In: *New Concepts in Solar and Thermal Radiation Conversion IV*. Ed. by Peter Bermel and Jeremy N. Munday. Vol. 11824. International Society for Optics and Photonics. SPIE, 2021, pp. 28–32. DOI: 10.1117/12.2594497.
- [81] Daniela De Luca et al. "An ultra-thin sputter-deposited infrared rugate mirror for enhancing solar to thermal energy conversion". In: Optics Letters (2021). DOI: 10.1364/0L.442839.
- [82] Carl M. Lampert. "Heat mirror coatings for energy conserving windows". In: Solar Energy Materials 6.1 (1981), pp. 1–41. ISSN: 0165-1633. DOI: https: //doi.org/10.1016/0165-1633(81)90047-2.
- [83] B. Karlsson et al. "Materials for solar-transmitting heat-reflecting coatings". In: Thin Solid Films 86.1 (1981), pp. 91–98. ISSN: 0040-6090. DOI: https://doi.org/10.1016/0040-6090(81)90162-0. URL: https://www.sciencedirect.com/science/article/pii/0040609081901620.
- [84] E. Valkonen, B. Karlsson, and C.G. Ribbing. "Solar optical properties of thin films of Cu, Ag, Au, Cr, Fe, Co, Ni and Al". In: *Solar Energy* 32 (1984), pp. 301– 11.
- [85] I. Hamberg and G. C. Granqvist. "Evaporated Sn-doped In₂O₃ films: Basic optical properties and applications to energy-efficient windows". In: *Journal* of Applied Physics 60 (1986), R123–160. DOI: https://doi.org/10.1063/1. 337534.
- [86] V.S. Kaluba, Khaled Mohamad, and P. Ferrer. "Experimental and simulated performance of hot mirror coatings in a parabolic trough receiver". In: *Applied Energy* 257 (2020), p. 114020. DOI: 10.1016/j.apenergy.2019.114020.
- [87] J. C. C. Fan and F. J. Bachner. "Transparent heat mirrors for solar-energy applications". In: *Applied Optics* 15 (1976), p. 1012. DOI: 10.1364/A0.15.001012.
- [88] D.R. Sahu and Jow-Lay Huang. "High quality transparent conductive ZnO/Ag/ZnO multilayer films deposited at room temperature". In: *Thin Solid Films* 515.3 (2006), pp. 876–879. DOI: https://doi.org/10.1016/j.tsf.2006.07.049.
- [89] B. G. Bovard. "Rugate filter theory: an overview". In: Appl. Opt. 32 (1993), pp. 5427–5442.
- [90] C. J. Tang et al. "Residual Stress in *Ta*₂O₅-*SiO*₂ composite Thin-Film Rugate Filters Prepared by Radio Frequency Ion-Beam Sputtering". In: *Appl. Opt.* 47 (2008), pp. C167–C171.
- [91] C. K. Carniglia. "Comparison of several shortwave pass filter designs". In: *Appl. Opt.* 28 (1989), pp. 2820–2823.
- [92] P. Baumeister. "Utilization of Kard's Equation to Suppress the High-Frequency Bands of Periodic Multilayers". In: *Appl. Opt.* 24 (1985), pp. 2687–2689.

- [93] P. Baumeister. "Simulation of a Rugate Filter via a Stepped-Index Dielectric Multilayer". In: *Appl. Opt.* 25 (1986), pp. 2644–2645.
- [94] E. S. Sakr, Z. Zhou, and P. Bermel. "High efficiency rare-earth emitter for thermophotovoltaic applications". In: *Appl. Phys. Lett.* 105 (2014), p. 111107.
- [95] L. Thomas, G. N. Aliev, and P. A. Snow. "Hypersonic rugate filters based on porous silicon". In: *Appl. Phys. Lett.* 97 (2010), p. 173503.
- [96] A. G. Imenes and D. R. McKenzie. "Flat-topped broadband rugate filters". In: *Appl. Opt.* 45 (2006), p. 7841.
- [97] Jan Kischkat et al. "Mid-infrared optical properties of thin films of aluminum oxide, titanium dioxide, silicon dioxide, aluminum nitride, and silicon nitride". In: Appl. Opt. 51.28 (2012), pp. 6789–6798. DOI: 10.1364/A0.51.006789.
- [98] M.A. Signore et al. "Deposition of silicon nitride thin films by RF magnetron sputtering: a material and growth process study". In: Optical Materials 34.4 (2012), pp. 632-638. ISSN: 0925-3467. DOI: https://doi.org/10.1016/j. optmat.2011.09.012. URL: https://www.sciencedirect.com/science/ article/pii/S0925346711004587.
- [99] M. Vila et al. "Characterization of Si3N4 thin films prepared by r.f. magnetron sputtering". In: Surface and Coatings Technology 151-152 (2002). Proceedings of Symposium C on Prtoective Coatings and Thin Films, pp. 67–71. ISSN: 0257-8972. DOI: https://doi.org/10.1016/S0257-8972(01)01600-0.
- [100] F. Gao, Q.N. Zhao, and Y.H. Zhao X.J.and Dong. "Influence of Substrate Temperature on Silicon Nitride Films Deposited by R.F. Magnetron Sputtering." In: Advanced Materials Research 150-151 (2010). Proceedings of Symposium C on Prtoective Coatings and Thin Films, 1391–1395. DOI: https://doi.org/ 10.4028/www.scientific.net/amr.150-151.1391.
- [101] S. Guruvenket et al. "Characterization of bias magnetron-sputtered silicon nitride films". In: *Thin Solid Films* 478.1 (2005), pp. 256–260. ISSN: 0040-6090. DOI: https://doi.org/10.1016/j.tsf.2004.10.031.
- [102] E. Sarhammar et al. "A study of the process pressure influence in reactive sputtering aiming at hysteresis elimination". In: *Surf. Coat. Tech.* 232 (2013), pp. 357–361. DOI: 10.1016/j.surfcoat.2013.05.035.
- [103] K. Strijckmans, R. Schelfhout, and D. Depla. "Tutorial: Hysteresis during the reactive magnetron sputtering process". In: J. App. Phys. 124) (2018), pp. 241101– 1, 241101–29. DOI: 10.1063/1.5042084.
- [104] P. S. Nayar. "Refractive index control of silicon nitride films prepared by radio-frequency reactive sputtering". In: J. Vac. Sci. Tech. A 20 (2002), p. 2137. DOI: 10.1116/1.1513637.
- [105] M. K. Mustafa, U. Majeed, and Y. Iqbal. "Effect on Silicon Nitride thin Films Properties at Various Powers of RF Magnetron Sputtering". In: Int. J. Eng. Tech. 7 (2018), pp. 39–41. DOI: 10.14419/ijet.v7i4.30.22000.
- [106] J. Y. Horiba. *Tauc-Lorentz Dispersion Formula*. Tech. rep. 2006.
- [107] G. E. Jellison and F. A. Modine. "Parameterization of the optical functions of amorphous materials in the interband region". In: *Appl. Phys. Lett.* 69 (1996). DOI: 10.1063/1.118064.
- [108] K. Luke et al. "Broadband mid-infrared frequency comb generation in a Si₃N₄ microresonator". In: Opt. Lett. 40 (2015), pp. 4823–4826. DOI: 10.1364/0L.40. 004823.
- [109] W.J. Gunning et al. "Codeposition of continuous composition rugate filters". In: *Appl. Opt.* 28 (1989), pp. 2945–2948.
- [110] J-S. Chen et al. "Mixed films of TiO₂-SiO₂ deposited by double electron-beam coevaporation". In: *Appl. Opt.* 35 (1996), pp. 90–96.
- [111] https://www.jawoollam.com/resources/ellipsometry-tutorial/opticalconstants.
- [112] S. Joseph and A. K. Hafiz. "Omnidirectional reflector using one-dimensional dispersive photonic heterostructure". In: Optik 125 (2014), pp. 2734–2738. DOI: 10.1016/j.ijleo.2013.11.071.
- [113] F. Wu et al. "Broadband wide-angle multilayer absorber based on a broadband omnidirectional optical Tamm state". In: *Optic Express* 29 (2021), p. 23976. DOI: 10.1364/0E.434181.
- [114] "Chapter 41 Engineered Nanomaterials for Energy Applications". In: Handbook of Nanomaterials for Industrial Applications. Ed. by Chaudhery Mustansar Hussain. Micro and Nano Technologies. Elsevier, 2018, pp. 751–767. ISBN: 978-0-12-813351-4. DOI: https://doi.org/10.1016/B978-0-12-813351-4.00043-2. URL: https://www.sciencedirect.com/science/article/pii/B9780128133514000432.
- [115] S. Krauter. *Solar Electric Power Generation Photovoltaic Energy Systems.* Berlin-Heidelberg, Germany: Springer-Verlag, 2006.
- [116] Octavi Semonin, Joseph Luther, and Matthew Beard. "Quantum Dots for Next-Generation Photovoltaics". In: *Materials Today* 15 (Nov. 2012). DOI: 10. 1016/S1369-7021(12)70220-1.
- [117] https://www.ise.fraunhofer.de/content/dam/ise/de/documents/ publications/studies/Photovoltaics-Report.pdf.
- [118] Veronika Rinnerbauer et al. "Recent developments in high-temperature photonic crystals for energy conversion". In: *Energy Environ. Sci.* 5 (10 2012), pp. 8815–8823. DOI: 10.1039/C2EE22731B.
- [119] T. Bauer. *Thermophotovoltaics Basic Principles and Critical Aspects of System Design*. Springer, 2011.
- [120] María Herrando and Christos Markides. "Hybrid PV and solar-thermal systems for domestic heat and power provision in the UK: Techno-economic considerations". In: *Applied Energy* 161 (Jan. 2016), pp. 512–532. DOI: 10.1016/ j.apenergy.2015.09.025.
- [121] Ilaria Guarracino et al. "PERFORMANCE ASSESSMENT AND COMPARI-SON OF SOLAR ORC AND HYBRID PVT SYSTEMS FOR THE COMBINED DISTRIBUTED GENERATION OF DOMESTIC HEAT AND POWER". In: July 2016.
- [122] Wolfram Sparber et al. "Strategic Research and Innovation Agenda for RHC, 2013". In: (Mar. 2013).
- [123] Arnaud de La Tour, Matthieu Glachant, and Yann Ménière. "Predicting the costs of photovoltaic solar modules in 2020 using experience curve models". In: *Energy* 62.C (2013), pp. 341–348. DOI: 10.1016/j.energy.2013.09..
- [124] Alexander Mellor et al. "Roadmap for the next-generation of hybrid photovoltaicthermal solar energy collectors". In: *Solar Energy* 174 (Sept. 2018), pp. 386–398. DOI: 10.1016/j.solener.2018.09.004.

- [125] Sakib Hassan, Chloe Doiron, and Gururaj Naik. "Optimum selective emitters for efficient thermophotovoltaic conversion". In: *Applied Physics Letters* 116 (Jan. 2020), p. 023903. DOI: 10.1063/1.5131367.
- [126] Carosena Meola and Giovanni M Carlomagno. "Recent advances in the use of infrared thermography". In: *Measurement science and technology* 15.9 (2004), R27.
- [127] Aaswath P Raman et al. "Passive radiative cooling below ambient air temperature under direct sunlight". In: *Nature* 515.7528 (2014), pp. 540–544.
- [128] Norman Nan Shi et al. "Keeping cool: Enhanced optical reflection and radiative heat dissipation in Saharan silver ants". In: *Science* 349.6245 (2015), pp. 298–301.
- [129] Barbara H Stuart. *Infrared spectroscopy: fundamentals and applications*. John Wiley & Sons, 2004.
- [130] Yannick De Wilde et al. "Thermal radiation scanning tunnelling microscopy". In: *Nature* 444.7120 (2006), pp. 740–743.
- [131] Wan Rashid et al. "Recent Development of Thermophotovoltaic System for Waste Heat Harvesting Application and Potential Implementation in Thermal Power Plant". In: *IEEE Access* PP (June 2020), pp. 1–1. DOI: 10.1109/ ACCESS.2020.2999061.
- [132] Reyu Sakakibara et al. "Practical emitters for thermophotovoltaics: a review". In: *Journal of Photonics for Energy* 9.3 (2019), pp. 1–20. DOI: 10.1117/1.JPE.
 9.032713. URL: https://doi.org/10.1117/1.JPE.9.032713.
- [133] Ivan Celanovic, Peter Bermel, and Marin Soljaić. "Thermophotovoltaic power conversion systems: current performance and future potential". In: 2011.
- [134] Yang Wenming et al. "Research on micro-thermophotovoltaic power generators with different emitting materials". In: *Journal of Micromechanics and Microengineering* 15 (2005). DOI: 10.1088/0960-1317/15/9/S11.
- [135] L. Fraas et al. "Antireflection coated refractory metal matched emitters for use with GaSb thermophotovoltaic generators". In: *Conference Record of the Twenty-Eighth IEEE Photovoltaic Specialists Conference - 2000 (Cat. No.00CH37036).* 2000, pp. 1020–1023. DOI: 10.1109/PVSC.2000.916059.
- [136] V. M. Andreev et al. "Solar Thermophotovoltaic Converters Based on Tungsten Emitters". In: *Journal of Solar Energy Engineering* 129.3 (2006), pp. 298– 303. DOI: 10.1115/1.2734576.
- [137] B. Bitnar et al. "Characterisation of rare earth selective emitters for thermophotovoltaic applications". In: *Solar Energy Materials and Solar Cells* 73.3 (2002), pp. 221–234. DOI: https://doi.org/10.1016/S0927-0248(01)00127-1.
- [138] Pavel N Dyachenko et al. "Controlling thermal emission with refractory epsilonnear-zero metamaterials via topological transitions". In: *Nature communications* 7.1 (2016), pp. 1–8.
- [139] Jean-Jacques Greffet et al. "Coherent emission of light by thermal sources". In: *Nature* 416.6876 (2002), pp. 61–64.
- [140] B. J. Lee, C. J. Fu, and Z. M. Zhanga. "Coherent thermal emission from onedimensional photonic crystals". In: *Appl. Phys. Lett.* 87 (2005), p. 071904. DOI: 10.1063/1.2010613.

- [141] D. Bierman, A. Lenert, and W. et al Chan. "Enhanced photovoltaic energy conversion using thermally based spectral shaping". In: *Nat Energy* 1 (2016), p. 16068. DOI: https://doi.org/10.1016/S0927-0248(01)00127-1.
- [142] Veronika Rinnerbauer et al. "Metallic Photonic Crystal Absorber-Emitter for Efficient Spectral Control in High-Temperature Solar Thermophotovoltaics".
 In: Advanced Energy Materials 4 (2014), p. 1400334. DOI: 10.1002/aenm.201400334.
- [143] Kurt J. Lesker Company. https://www.lesker.com/.
- [144] The Royal Society of Chemistry. https://www.rsc.org/periodic-table/ element/45/rhodium.
- [145] *RefractiveIndex.INFO*. https://refractiveindex.info/.
- [146] A. R. Forouhi and I. Bloomer. "Optical dispersion relations for amorphous semiconductors and amorphous dielectrics". In: *Phys. Rev. B* 34 (10 1986), pp. 7018–7026. DOI: 10.1103/PhysRevB.34.7018. URL: https://link.aps. org/doi/10.1103/PhysRevB.34.7018.
- [147] A. R. Forouhi and I. Bloomer. "Optical properties of crystalline semiconductors and dielectrics". In: *Phys. Rev. B* 38 (3 1988), pp. 1865–1874. DOI: 10.1103/PhysRevB.38.1865. URL: https://link.aps.org/doi/10.1103/PhysRevB.38.1865.
- [148] https://icmctf2022.avs.org/.
- [149] Matteo Bosi and Claudio Pelosi. "'The Potential of III-V Semiconductors as Terrestrial Photovoltaic Devices'". In: Progress in Photovoltaics: Research and Applications 15 (Jan. 2007), pp. 51–68. DOI: 10.1002/pip.715.
- [150] V. Avrutin, N. Izyumskaya, and H. Morkoç. "Semiconductor solar cells: Recent progress in terrestrial applications". In: *Superlattices and Microstructures* 49.4 (2011), pp. 337–364. ISSN: 0749-6036. DOI: https://doi.org/10.1016/j. spmi.2010.12.011.
- [151] Zunaid Omair et al. "Ultraefficient thermophotovoltaic power conversion by band-edge spectral filtering". In: *Proceedings of the National Academy of Sciences* 116.31 (2019), pp. 15356–15361. DOI: 10.1073/pnas.1903001116.
- [152] Caleb Amy et al. "Thermal energy grid storage using multi-junction photovoltaics". In: *Energy Environ. Sci.* 12 (1 2019), pp. 334–343. DOI: 10.1039/ C8EE02341G.
- [153] Z. Krstic and V. D. Krstic. "Silicon nitride: the engineering material of the future". In: J. Mat. Sci. 47 (2012), 535–552. DOI: 10.1007/s10853-011-5942-5.
- [154] C. E. Morosanu. "The preparation, characterization and applications of silicon nitride thin films". In: *Thin Solid Films* 65 (1980), pp. 171–208. DOI: 10. 1016/0040-6090(80)90254-0.
- [155] M. D. Dange, J.Y. Lee, and K. Sooriakumar. "New applications of low temperature PECVD silicon nitride films for microelectronic device fabrication". In: *Microelec. J.* 22 (1991), pp. 19–26. DOI: 10.1016/0026-2692(91)90010-K.
- [156] Q. Wilmart et al. "A Versatile Silicon-Silicon Nitride Photonics Platform for Enhanced Functionalities and Applications". In: *Appl. Sci.* 9(2) (2019), p. 255. DOI: 10.3390/app9020255.
- [157] M. Lipinski. "Silicon nitride for photovoltaic application". In: *Arc. Mat. Sc. Eng.* 46(2) (2010), pp. 69–87.

- [158] D. Legut, U. D. Wdowik, and P. Kurtyka. "Vibrational and dielectric properties of α-Si₃N₄ from density functional theory". In: *Mat. Chem. Phys.* 147.1-2 (2014). DOI: 10.1016/j.matchemphys.2014.03.058.
- [159] G. N. Parsons, J. H. Souk, and J. Batey. "Low hydrogen content stoichiometric silicon nitride films deposited by plasmaenhanced chemical vapor deposition". In: J. Appl. Phys. 70 (1991), p. 1553. DOI: 10.1063/1.349544.
- [160] D. Necas and P. Klapetek. "Gwyddion: an open-source software for SPM data analysis". In: *Cent. Eur. J. Phys.* 10 (1) (2012). DOI: 10.2478/s11534-011-0096-2.
- [161] V. Bhatt and S. Chandra. "Silicon Nitride Films Deposited by RF Sputtering for Microstructure Fabrication in MEMS". In: J. El. Mat. 38 (2009), pp. 1979– 1989. DOI: 10.1007/s11664-009-0846-8.