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ANALYSIS OF DIFFERENT SELECTIVE THERMAL EMITTER DESIGNS FOR
INCREASING THE EFFICIENCY OF THERMOPHOTOVOLTAIC SYSTEMS

BY

LAURA LIN

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

IN

MECHANICAL ENGINEERING AND APPLIED MECHANICS

UNIVERSITY OF RHODE ISLAND

2015

MASTER OF SCIENCE IN MECHANICAL ENGINEERING
OF
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2015

ABSTRACT

The research regarding more efficient renewable energy, including heat recovery is of great importance. Thermophotovoltaic (TPV) converts heat directly into electricity and thus, has great potential for efficient heat recovery. However, at the current stage of research the conversion efficiency of TPV systems is still low and it is uncertain which efficiencies can be achieved. Selective thermal emitters give the opportunity to improve the efficiency of TPV systems if the emission of photons in a certain spectral range matches with a specific TPV cell. Therefore, different dielectric materials and the effects of different design structures are analyzed by calculating the resulting emissivity distributions. The aim is to find a material structure that generates a high emissivity matching the quantum efficiency of the TPV cell.

The physical principles of radiation heat transfer, the Maxwell-Garnett-Mie theory and the Effective-Medium theory are implemented into MATLAB to generate a code for calculating the spectral emissivity of different thin films, doped materials and surface gratings. Furthermore, the optical data of suitable materials are implemented in the code to obtain their dielectric functions. The calculation of the spectral emissivity for different design structures shows that materials doped with nanoparticles of reflective metals show a great enhancement of the emissivity in the wavelength range of interest. Developed selective thermal emitter designs of Silicon Carbide or Silicon Dioxide doped with Tungsten nanoparticles and surface gratings of those materials reach emissivity values of up to 0.9 between 0.4 μm and 2 μm .

ACKNOWLEDGMENTS

Writing my Master's Thesis as part of the Dual Degree Program between the URI and the TU Braunschweig would not have been possible without the contribution, cooperation, and support from several people. Therefore, I would like to take the opportunity to thank the following people and acknowledge their help and guidance throughout completing my Master's Degree.

First of all, I want to give my sincere thanks and heartfelt gratitude to my major advisor Dr. Yi Zheng for his continuous help, encouragement and guidance throughout this project. He is always up to date regarding the state of art and assisted me with his invaluable suggestions. Especially, I would like to thank Alok Ghanekar. He showed me that everything is possible due to hard work and consistency. Without his good ideas, I could not have reached this goal.

Thanks to the members of my committee: Dr. Yi Zheng, Dr. Zongqin Zhang, Dr. Tao Wei and my defense chair Dr. Ying Zhang. I am very grateful and honored that you all accepted to review my work and thesis.

Lastly, I am grateful to my parents and family for their support and continuous love. That gave me the opportunity to focus only on my work. Without them, I would not have been able to accomplish what I have today. I would also like to deeply thank my boyfriend, Christian Gasthaus, for being by my side throughout this year; his positive thinking gave me the strength to finish this project.

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LIST OF ABBREVIATIONS

Ag	Silver
AlN	Aluminium Nitride
ATR	Attenuated Total Reflectance
Au	Gold
BDRF	Bidirectional Reflectance Function
BEM	Boundary Element Method
BN	Bor Nitride
CHP	Combined Heat and Power
Co ₃ O ₄	Cobalt(II,III) Oxide
Cu	Copper
EMT	Effective Medium Theory
EQE	External Quantum Efficiency
Er ₂ O ₃	Erbium(III) Oxide
FDTD	Finite Difference Time Domain
FEM	Finite Element Method
FTIR	Fourier Transform Infrared

GaSb	Gallium Antimonide
Ge	Germanium
InGaAs	Indium Gallium Arsenide
InGaAsSb	Indium Gallium Arsenide Antimonide
IQE	Internal Quantum Efficiency
IR	Infrared
MgO	Magnesium Oxide
NiO	Nickel(II) Oxide
NO _x	Nitrogen Oxide
PhC	Photonic Crystal
PV	Photovoltaic
QE	Quantum Efficiency
RCWA	Rigorous Coupled Wave Analysis
SEM	Scanning-Electron-Microscopy
Si	Silicon
SiC	Silicon Carbide
SiO ₂	Silicon Oxide
SPhP	Surface Phonon Polariton
SPP	Surface Plasmon Polariton

SR	Spectral Response
TE	Transverse-Electric
TM	Transverse-Magnetic
TPV	Thermophotovoltaic
UV	Ultraviolet
VO ₂	Vanadium Dioxide
W	Tungsten
wt	Weight
Yb ₂ O ₃	Ytterbium(III) Oxide
YSZ	Ytria-Stabilized Zirconia

LIST OF SYMBOLS

A	Surface Area	m^2
b	Wien's Displacement Constant	mK
B	Magnetic Flux Density	Wb/m^2
c	Speed of Propagation	m/s
c_0	Speed of Light	m/s
d	Distance/Thickness	m
d_p	Penetration Depth	m
D	Electric Displacement	C/m^2
e	Elementary Charge of an Electron	As
E	Electric Field	V/m
E_0	Amplitude Vector of the Electric Field	V/m
f	Volume Fraction	-
h	Planck's Constant	$\text{m}^2\text{kg/s}$
h_1	First Order Spherical Hankel Function	-
H	Magnetic Field	A/m
j_1	First Order Spherical Bessel Function	-

J	Electric Current Density	A/m ²
J_{ph}	Incident Photon Flux	μmol/m ² s
J_{max}	Max. Photon Current Density	μmol/m ² s
k	Wave Vector	1/m
k_{ρ}	In-Plane Wave Vector	1/m
k_x	X-Component of the Wave Vector	1/m
k_z	Z-Component of the Wave Vector	1/m
L	Grating Period	m
m	Effective Mass of Electrons	kg
m_0	Effective Optical Mass Factor of Electrons	-
m_w	Molecular Weight	kg/mol
n	Refractive Index	-
N	Density of Conduction Electrons	1/m ³
N_a	Avogadro's Constant	1/mol
p	Polarization	-
P_{el}	Electricity Output	W
P_{input}	Total Power Input	W
P_{net}	Net Heat Transfer	W

P_{PV}	Net Heat Flow Incidenting the PV Cell	W
q_i	Incident Power Density per Wavelength	W/m ³
Q_{rad}	Radiation Heat Transfer	W/m ²
r	Radius	m
$\mathbf{r}$	Position Vector	m
$R_{i,i+1}^{(p)}$	Fresnel Reflection Coefficient	-
$\tilde{R}_{i,i+1}^{(p)}$	Generalized Reflection Coefficient	-
t	Thickness	m
t	Time	s
T	Temperature	K
T_{∞}	Ambient Temperature	K
$T_{i,i+1}^{(p)}$	Fresnel Transmission Coefficient	-
vf	Volume Fraction	-
x_m	Size Parameter of Matrix	-
x_{np}	Size Parameter of Nanoparticles	-

Greek Symbols

α	Absorptance	-
α_1	First Electric Mie Coefficient	1/m

α_c	Absorption Coefficient	1/m
α_λ	Spectral Absorptivity	-
α_{MGM}	Electric Dipole Polarizability	-
Γ	Damping Factor	-
ϵ	Emissivity	-
ϵ_λ	Spectral Emissivity	-
ϵ	Relative Permittivity/Dielectric Function	-
ϵ_0	Permittivity of Vacuum	F/m
ϵ_m	Absolute Permittivity	F/m
ϵ_∞	High-Frequency Dielectric Constant	-
η_{cavity}	Cavity Efficiency	-
$\eta_{maintain}$	Efficiency Reduction due to Maintenance	-
η_{PV}	PV Cell Efficiency	-
η_{source}	Heat Source Efficiency	-
θ	Incident Angle	rad
κ	Extinction Coefficient	-
λ	Wavelength	m
Λ	Grating Period	m

μ	Relative Permeability	-
μ_0	Permeability of Vacuum	N/A ²
μ_m	Absolute Permeability	N/A ²
ξ_1	First Order Riccati-Bessel Function	-
ρ	Reflectance	-
ρ_e	Electric Charge Density	C/m ³
ρ_d	Density	Kg/m ³
ρ_λ	Spectral Reflectivity	-
σ	Stefan-Boltzmann Constant	W/m ² K ⁴
τ	Transmittance	-
τ_r	Relaxation Time	s
ϕ	Filling Factor	-
ψ_1	First Order Riccati-Bessel Function	-
ω	Angular Frequency	rad/s
ω_L	Frequency of Traversal Optical Phonons	eV
ω_p	Plasma Frequency	eV
ω_T	Frequency of Longitudinal Optical Phonons	eV

CHAPTER 1 – INTRODUCTION

Scarcity of resources, environmental pollution, and climate change are important topics that engage today's society. The increasing energy demand as well as local and global environmental impacts result in an increased interest in green energy resources and the efficient use of fossil fuels. The share of renewable energy is still very low compared to the total energy demand, which makes the research in more efficient energy usage, generation, and conversion inevitable.

Thermophotovoltaic (TPV) is a promising technology for heat recovery and is an attractive alternative to existing electricity generation technologies. A TPV system consists of an emitter that receives thermal energy and a TPV diode cell that generates electricity by absorbing incident photons from the emitter. Although TPV is environmentally friendly, low conversion efficiency and power generation interferes with its further propagation. Therefore, selective thermal emitters can be applied to enhance the efficiency of TPV systems. This recent research field started only 20 years ago and gained much attention in the last years. Many different selective thermal emitter structures with different optical properties were investigated. The difficulties of this research result from the limitation of the macroscopic formulation because the dimensions of selective thermal emitter structure are comparable to the molecular mean free path.

Selective thermal emitters can increase the efficiency of TPV cells, so that less energy is wasted, by creating high emissivity peaks at specific wavelengths dependent

on the material. Photonic crystals (PhCs) are already applied as selective emitters for TPV cells. However, the efficiency of these TPV systems still has room for improvement. One important aspect is the need for investigations of different materials and layer thicknesses to optimize the emissivity. Therefore, different selective thermal emitter designs are analyzed in this study with the aim to find a new enhanced design applicable for TPV systems.

To contribute to the development of more efficient TPV cells, different dielectric materials and the effects of different layer thicknesses are analyzed by calculating the resulting emissivity distributions. The aim is to find a material structure that generates high emissivity values at the specific band-gap of the TPV cell's material. To give an insight into the general framework and the basic physical principles of this study, the fundamentals of thermal radiation as well as the functionality and the composition of selective thermal emitters and TPV systems in general are described. Furthermore, the current state of the art of selective thermal emitters in TPV systems is summarized. Based on the physical principles and calculation methods, a MATLAB code is generated to calculate the spectral emissivity of different selective thermal emitter designs consisting of various materials and structures. The different analyzed structures are thin films of single materials, materials doped with nanoparticles, and surface gratings. Subsequently, the results are compared to the characteristic wavelength regions of different TPV cells. Furthermore, simple selective thermal emitter samples are generated to compare their experimentally determined emissivity spectrum to the calculated results. At last, a short conclusion summarizes the study and gives a critical appraisal and outlook to possible future work.

CHAPTER 2 – REVIEW OF LITERATURE

For a better understanding of this research study, the following chapter gives a review of the fundamentals of thermal radiation, including electromagnetic waves, radiative properties, and the interaction of electromagnetic waves with matter. Furthermore, the physical principals and different designs of selective thermal emitters are introduced. Then, the functionality of TPV systems, their different components and efficiencies, as well as the spectral control concepts are presented. Moreover, the state of the art of the application of selective thermal emitters for TPV systems as a promising technology for enhancing the energy conversion efficiency is reviewed.

2.1. Fundamentals of Thermal Radiation

In general, thermal radiation is wavelength and temperature dependent. The nature of radiation can be described as electromagnetic waves or a collection of particles also known as photons (Wave-Particle-Duality-Theory). Radiation is originated from matter that emits through complicated mechanisms (e.g. molecular vibration in gases or electron and lattice vibrations in solids). Thermal radiation means that the emission is directly related to the temperature of the matter. [1]

In the following section, the basic principals of thermal radiation, including electromagnetic waves, radiative properties, and the interaction of light with matter are presented.

2.1.1. Electromagnetic Waves

Light consists of electromagnetic waves; hence, the oscillation of an electric and magnetic field at rates of the magnitude 10^{14} Hz. Since electromagnetic waves of different wavenumber carry different amounts of energy, their behavior varies. Depending on this behavior, electromagnetic waves have been grouped into a number of different categories, as shown in Figure 1. Visible light has only a small wavelength range between $0.4\ \mu\text{m}$ and $0.7\ \mu\text{m}$. Thermal radiation includes a small part of the ultraviolet, the visible, and the near- as well as the mid-infrared (IR) radiation. Electromagnetic waves with very high energies, like gamma rays, x-rays, and ultraviolet radiation, which occur in solar energy systems, as well as electromagnetic waves with very low energies, like far-infrared radiation, and microwaves, usually do not occur in TPV systems. [2]

Figure 1: Electromagnetic wave spectrum in vacuum [2]

The thermal radiation propagates by electric and magnetic fields exchanging energy following Ampere's and Faraday's laws. The magnetic and electric fields are perpendicular to each other. The propagation of these waves can be described by the Maxwell's equations, which give the time dependence of the electric field $\mathbf{E}$ and the

magnetic field $\mathbf{H}$ and their interaction with optical media. The macroscopic differential forms of the Maxwell's equations are given as:

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (2.1)$$

$$\nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \quad (2.2)$$

$$\nabla \cdot \mathbf{D} = \rho_e \quad (2.3)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (2.4)$$

where $\mathbf{B}$ is the magnetic flux density, $\mathbf{J}$ electric current density, $\mathbf{D}$ electric displacement, ρ_e electric charge density, and t is time. Equation (2.1) expresses Faraday's law of induction and states that a time varying magnetic field produces an electric field in a coil. The general Ampere's law is given by Equation (2.2), which states that there is an electric current density and/or an electric displacement current through any closed magnetic field line. Equation (2.3) describes that the electric field diverges from the electric charge density (Gauss's law). Equation (2.4) gives the analogy to Gauss's law for a magnetic field. [3,4]

For an isotropic medium, the electric and magnetic flux densities depend on the electric and magnetic field. The electric and magnetic constants of the material are given by:

$$\mathbf{D} = \epsilon_m \mathbf{E} \quad (2.5)$$

$$\mathbf{B} = \mu_m \mathbf{H} \quad (2.6)$$

The absolute electric permittivity or dielectric constant is given by ϵ_m and the absolute magnetic permeability is given by μ_m . The values of the material constants for free

space or vacuum are given by $\epsilon_0 = 8.854 \times 10^{-12} \text{ F/m}$ and $\mu_0 = 4\pi \times 10^{-7} \text{ N/A}^2$. [1]

The wave equation can be derived from Maxwell's equations given by Equation (2.7) for the electric field.

$$\nabla^2 \mathbf{E} = \mu_m \epsilon_m \frac{\partial^2 \mathbf{E}}{\partial t^2} \quad (2.7)$$

There exist an infinite number of solutions for the wave equation. For a monochromatic wave, the solution is given by:

$$\mathbf{E} = \mathbf{E}_0 e^{-i(\omega t - \mathbf{k} \cdot \mathbf{r})} \quad (2.8)$$

where $\mathbf{E}_0$ is the amplitude vector, ω the angular frequency, $\mathbf{r}$ the position vector and $\mathbf{k}$ the wave-vector. If Equation (2.8) is substituted into the Maxwell's equations, they can be written as:

$$\mathbf{k} \times \mathbf{E} = \omega \mu_m \mathbf{H} \quad (2.9)$$

$$\mathbf{k} \times \mathbf{H} = \omega \epsilon_m \mathbf{E} \quad (2.10)$$

When ϵ_m and μ_m are positive, $\mathbf{E}$, $\mathbf{H}$, and $\mathbf{k}$ are orthogonal to each other and the surface of the electromagnetic wave, also called wave-front, travels with a phase speed. This speed of propagation c is given by:

$$c = \frac{\omega}{k} = \frac{1}{\sqrt{\epsilon_m \mu_m}} \quad (2.11)$$

If the wave-front is perpendicular to the x-direction, k will be the x-component of the wave-vector, named as the wave number, which can be calculated by:

$$k = \frac{2\pi}{\lambda} = \frac{\omega}{c} \quad (2.12)$$

where λ indicates the wavelength of the electromagnetic wave. In free space, the speed of light is $c_0 = \frac{1}{\sqrt{\epsilon_0 \mu_0}} = 2.998 * 10^8 \text{ m/s}$. [3,5]

The specific wavelength and speed of propagation in a medium is dependent on the refractive index of the material, given in Equation (2.13) and (2.14). The refractive index n is given in Equation (2.15) and is usually temperature-dependent and changing with the wavelength if the material is dispersive.

$$c = \frac{c_0}{n} \quad (2.13)$$

$$\lambda = \frac{\lambda_0}{n} \quad (2.14)$$

$$n = \sqrt{\frac{\mu_m \epsilon_m}{\mu_0 \epsilon_0}} = \sqrt{\mu \epsilon} \quad (2.15)$$

where ϵ is the relative permittivity or dielectric constant and μ is the relative permeability, which is the ratio of the absolute permittivity/permeability in the matter to the one in free space. A linearly polarized electromagnetic wave and its parameters are shown in Figure 2. [4,6]

Figure 2: Linearly polarized electromagnetic wave [1]

Previously, the relative permittivity was assumed to be a scalar, but due to a complex refractive index for absorbing materials, the dielectric function is also complex. In this study only non-magnetic materials ($\mu = 1$) are considered. Therefore, the focus is set on the relative permittivity or dielectric function. The dielectric function is defined by the optical constants, which generally change with the wavelength. The dielectric function is given by: [1,7,8]

$$\varepsilon = \varepsilon' + i\varepsilon'' = (n - i\kappa)^2 \quad (2.16)$$

where $n - i\kappa$ represents the complex refractive index and κ is called the extinction coefficient. For a free space, the optical constants are given by $n = 1$ and $\kappa = 0$, and thus, $\varepsilon = 1$. [1]

The dielectric function is the response of a medium to an external electric field. Therefore, it is of great importance for the study of electromagnetically coupled modes, e.g. the plasmon-, phonon-, and exciton-polaritons, which will be described in more detail in section 2.1.3. [9]

2.1.2. Radiative Properties

If a plane wave incidents from one medium to another, this wave will be partly reflected, partly transmitted, and partly absorbed. Thus, the three fundamental radiative properties reflectance ρ , absorptance α , and transmittance τ are defined as following:

$$\rho = \frac{\text{reflected part of incoming radiation}}{\text{total incoming radiation}} \quad (2.17)$$

$$\alpha = \frac{\text{absorbed part of incoming radiation}}{\text{total incoming radiation}} \quad (2.18)$$

$$\tau = \frac{\text{transmitted part of the incoming radiation}}{\text{total incoming radiation}} \quad (2.19)$$

These radiative properties are non-dimensional and vary between 0 and 1. All radiation is either reflected, transmitted, or absorbed. Therefore, it can be stated that:

$$\rho + \alpha + \tau = 1 \quad (2.20)$$

If all radiation that passes into the medium is absorbed and no radiation is transmitted, the medium is called opaque. In case, that no radiation is reflected and the absorptance $\alpha = 1$, the medium is called a blackbody, which makes a blackbody a perfect absorber. [10]

All media also emits thermal radiation, which can escape from the surface. Depending on the temperature, the maximum thermal radiation can be emitted from a blackbody, so that a blackbody is also a perfect emitter. Therefore, Kirchhoff's law states that the directional-spectral emissivity ϵ_λ of a surface equals directional-spectral absorptivity α_λ at thermal equilibrium. The emissive power spectrum of a blackbody for different temperatures is shown in Figure 3. [2]

The peak emissive power at different temperatures shifts to different wavelengths. Wien's displacement law states this and the maximum wavelength λ_{max} at each temperature T is given by:

$$\lambda_{max,T} = \frac{b}{T} \quad (2.21)$$

where b is called Wien's displacement constant with a value of 2.897810×10^{-3} mK. This so-called thermal wavelength also defines where far-field radiation is valid. For large distances where the distance d is large compared to the thermal wavelength $\lambda_{max,T}$ ($d > \lambda_{max,T}$), the heat flux is independent of the distance and can be

calculated spectrally. It is similar to a blackbody spectrum, with distinct modulations given by the spectral emissivity of the materials. If the distance is reduced to $d < \lambda_{max,T}$ (less than 10 μm under ambient conditions/temperatures around 300 K), the heat flux increases significantly. In this regime, the heat transfer is dominated by the near field effects that are generated by evanescent waves interacting near the material interface. [10,11]

Figure 3: Blackbody emissive power spectrum [2]

Therefore, the emissivity ϵ is another non-dimensional radiative property, that is defined as the ratio of the energy emitted by the surface of a medium to the emitted energy of a blackbody at the same temperature, as shown in Equation (2.22). Thus, the emissivity value also varies between 0 and 1, where the latter is the emissivity value of a blackbody. [2]

$$\epsilon = \frac{\text{energy emitted from a surface}}{\text{energy emitted from a blackbody}} \quad (2.22)$$

The emissivity is a value that varies with the wavelength of the radiation. Therefore, the emissivity over the whole wavelength spectrum is called spectral emissivity $\epsilon(\lambda)$. The average over all wavelengths is called total emissivity. Furthermore, the radiation angle is important. The emissivity in one direction is called directional emissivity, where the average over all directions is called hemispherical emissivity. The same terminology can be used for the other three radiative properties as well. [10]

The overall radiation heat transfer Q_{rad} for a body at a certain temperature T is calculated according to the Stefan-Boltzmann law:

$$Q_{rad}(\lambda, T) = \epsilon(\lambda)\sigma A(T^4 - T_{\infty}^4) \quad (2.23)$$

The radiation heat transfer is proportional to $T^4 - T_{\infty}^4$ and T_{∞} is the ambient temperature, so that radiation becomes the dominant mode of heat transfer at high temperatures. A is the surface area of the radiating body, σ is the Stefan-Boltzmann constant and $\epsilon(\lambda)$ is the spectral emissivity of the material, that varies with the corresponding wavelength. [12]

2.1.3. Electromagnetic Waves Interacting with Matter

The characteristics of these waves are dependent on the radiative properties of the medium. Assuming that the interface of the two media is planar and extends to infinity as well as that the media is homogeneous and isotropic, then, the electric and magnetic response can be characterized by the relative permittivity and permeability. The reflection and transmission at an interface of two media are shown in Figure 4. Depending on the direction of the electric and magnetic field, the wave is either called transverse electric (TE) or transverse magnetic (TM) wave. [1]

Figure 4: Illustration of reflection and transmission at an interface [1]

Resulting from the boundary condition, that the tangential components of the electric and magnetic field must be continuous at the interface, the x-components of the wave-vector of the incident, reflected and transmitted wave are equal. Thus, Shell's law can be applied for the angle of the incident wave θ_1 and the reflected or transmitted wave θ_2 , given by:

$$\sin\theta_2 = \frac{k_x}{k_2} = \frac{n_1 \sin\theta_1}{n_2} \quad (2.24)$$

Then, the reflectivity and the transmission can be calculated from the Fresnel reflection and transmission coefficients $R_{1,2}^{(p)}$ and $T_{1,2}^{(p)}$. These are dependent of whether the TE (s-polarized) or the TM (p-polarized) waves are calculated. The formula for $R_{1,2}^{(p)}$ and $T_{1,2}^{(p)}$, with the polarization $p = TE, TM$, are shown in Equation (2.25) to (2.28). [13]

$$R_{1,2}^{TE} = \frac{k_{z1}\mu_2 - k_{z2}\mu_1}{k_{z1}\mu_2 + k_{z2}\mu_1} \quad (2.25)$$

$$R_{1,2}^{TM} = \frac{k_{z1}\varepsilon_2 - k_{z2}\varepsilon_1}{k_{z1}\varepsilon_2 + k_{z2}\varepsilon_1} \quad (2.26)$$

$$T_{1,2}^{TE} = \frac{2k_{z1}\mu_2}{k_{z1}\mu_2 + k_{z2}\mu_1} \quad (2.27)$$

$$T_{1,2}^{TM} = \frac{2k_{z1}\varepsilon_2}{k_{z1}\varepsilon_2 + k_{z2}\varepsilon_1} \quad (2.28)$$

From Equation (2.12), the z-components of the wave-vectors k_{zn} for the different media $n = 1, 2, 3 \dots N$ are calculated by:

$$k_{zn} = \sqrt{k_n^2 - k_\rho^2} = \sqrt{\varepsilon_n \frac{\omega^2}{c^2} - k_\rho^2} \quad (2.29)$$

where k_ρ is the magnitude of the in-plane wave-vector of the medium. If only a 2D case is considered, k_ρ corresponds to the x-component of the wave-vector k_x . [14]

For structures with multiple layers of different media (see Figure 5), the generalized reflection coefficient has to be calculated. It is assumed, that there is no transmission for infinite media because the thickness is much greater than the radiation penetration depth. Therefore, the formula for the generalized reflection coefficient $\tilde{R}_{i,i+1}^{(p)}$ of a medium $i+1$ with the thickness $d_{i+1} - d_i$ is given by:

$$\tilde{R}_{i,i+1}^{(p)} = \frac{R_{i,i+1}^{(p)} + \tilde{R}_{i+1,i+2}^{(p)} e^{i2k_{zi+1}(d_{i+1}-d_i)}}{1 + R_{i,i+1}^{(p)} \tilde{R}_{i+1,i+2}^{(p)} e^{i2k_{zi+1}(d_{i+1}-d_i)}} \quad (2.30)$$

where the reflection coefficient $R_{i,i+1}^{(p)}$ is calculated according to Equation (2.25) or (2.26). The generalized reflection coefficient $\tilde{R}_{i+1,i+2}^{(p)}$ between medium $i+1$ and $i+2$ is calculated the same way as $\tilde{R}_{i,i+1}^{(p)}$. There is no generalized reflection coefficient needed for the last interface between medium $N-1$ and N . Therefore, the reflection coefficient $R_{N-1,N}^{(p)}$ is calculated for $\tilde{R}_{N-1,N}^{(p)}$. [13]

Figure 5: Reflection and Transmission in a multilayered medium

The spectral reflectivity ρ_λ is defined as the ratio of the reflected and the incident energy flux. The (directional) spectral reflectivity for a certain incident angle is given by: [1]

$$\rho_\lambda(k_x) = \left| \tilde{R}_{1,2}^{(p)} \right|^2 \quad (2.31)$$

For the analysis of different selective thermal emitter designs, the emissivity is the most important object of study. Regarding Kirchhoff's law and the previous assumption of a sufficient thick layer, so that no radiation is transmitted, the spectral emissivity is given by: [1]

$$\epsilon_\lambda = \alpha_\lambda = 1 - \rho_\lambda \quad (2.32)$$

Hence, the spectral emissivity of a selective thermal emitter designs with multiple thin layers (1D PhC) can be calculated by the reflection coefficient. The hemispherical emissivity is computed by Equation (2.33). The integral includes the radiation from different angles into the calculation. If the radiation incidents the sample perpendicularly, the integral is not necessary. [14]

$$\epsilon(\lambda) = \frac{\lambda^2}{4\pi^2} \int_0^{2\pi/\lambda} k_x \sum_{p=TE,TM} (1 - |\tilde{R}_{1,2}^{(p)}|^2) dk_x \quad (2.33)$$

2.2. Review of Selective Thermal Emitter

The aim of selective thermal emitters is to generate or modify the emissivity spectrum of a material or material combination by different nano- or micro-scale structures. Therefore, they have many different applications for energy conservation and conversion, as well as for bio- or biochemical sensing. Depending on the optical properties of the material and the structure, different surface effects result in a modified spectral emissivity. A graphical illustration of an emissive power spectrum resulting from a modified emissivity spectrum is shown in Figure 6. This figure points out how a blackbody emitter and a selective emitter can have the same total integrated emissive power of 144,000 W/cm², however, the emitted radiation of the selective emitter is much more useful in the range between 1.0 μm and 2.0 μm. [14]

Figure 6: Emissivity of selective thermal emitter [15]

Selective thermal emitters can be generated by PhCs, which can consist of periodic multilayer thin films (1D PhC), as well as different 2D and 3D structures, or metamaterials and plasmonics. The different materials and structures of selective thermal emitters, as well as different effects that result in spectral emissivity modifications are introduced in the next sections. [14]

2.2.1. Materials

All phenomena related to electromagnetic waves are based on their interaction with matter. Therefore, the radiative properties and thus, the spectral emissivity strongly depends on the given material or material combinations. The material constants are changing periodically throughout the structure of PhCs and the small structural dimensions result in surface effects that interact with each other. These surface effects make the suppression and enhancement of the spectral emissivity possible and are described in more detail in the following. [16]

The interaction of an electromagnetic wave with matter results in the excitation of internal degrees of freedom. This is a “quasi-particle” excitation that is called polariton. A polariton means that the photon, as the quantum of an electromagnetic field, is coupled with a dipole-active elementary excitation depending on the medium (e.g. plasmon, phonon, exciton). Thus, the dielectric and optical properties of the medium are needed to define the basic characteristics of polaritons. Furthermore, the term surface polaritons refers to mixed electromagnetic modes within a few wavelengths of a surface. Their amplitude is maximal at the surface and attenuates with the distance from the surface. The characteristics of the surface polariton depend

on the material properties as well. However, the focus of this study lies on far field effects, which are not influenced by surface waves. [9]

The energy quantum of a lattice vibration or an elastic wave due to an excitation of a polar crystal or dielectric is known as a phonon. If a photon incidents a polar crystal and is coupled to a phonon, this mixed mode is a phonon polariton. Surface effects due to the interaction of a photon with dielectric material are called surface phonon polaritons (SPhPs). In metals, the excitation of the conduction electron gas results in a plasma oscillation or a collective electron wave. This quantum of energy is called a plasmon and the propagation of an electromagnetic wave in plasma is called plasmon polariton. If near-field effects are taken into account, the interaction of photons with the electron gas of metals is called surface plasmon polaritons (SPPs). When a photon incidents a semiconducting material, it excites an electron-hole pair. This excitation is resulting in a bound electron-hole pair and is called an exciton. These excitons can travel in the semiconductor as a polarization wave and therefore, radiate electromagnetic waves. These electromagnetic waves can again result in excitons. Because there is a frequent conversion of energy between photons and excitons, these two waves, which are called exciton polariton, cannot be separated. The basic behavior of these different excitations is shown in Figure 7. [7,9]

PhC usually consist of dielectric materials or semiconductors, while selective thermal emitter structures of metallic materials are normally called plasmonics. These are based on the generation, manipulation and transfer of SPPs. However, composite nanostructures play an important role in terms of tuning optical properties and enabling various potential applications. Metal-metal coupled structures largely

enhance the electromagnetic field. Metal-dielectric composite structures make the plasmonic properties more tunable because the SPPs depend on the dielectric environment. Furthermore, metal-semiconductor nanostructures can modify the optical properties by the interactions between plasmons and excitons. [17]

Figure 7: Excitations a) Phonon – Transverse elastic wave, b) Exciton – Polarization wave, c) Plasmon – Collective electron wave [7]

Besides PhC structures of dielectrics, metals, or semiconductors, another possibility to create a selective thermal emitter is to use metamaterials, which are man-made materials with properties, that do not occur in nature, like a negative refractive index. Most materials usually present positive values for the dielectric permittivity and for the magnetic permeability. Certain materials can either have a negative dielectric function or a negative permeability. However, these two conditions are never simultaneously satisfied in a given material. Neutral non-collisional plasma, certain metals, or semiconductors may have a negative permittivity under specific conditions and for a limited range of frequencies. For a negative permeability, only antiferromagnetic and strongly anisotropic systems may provide this property. As regards, the aim is to create an artificial material with negative values for both, permittivity and permeability. [18] The research in these complex materials has become very important for different fields, like electromagnetics, optics, and material

science amongst others in the past decade. A view on the history and evolution of metamaterials is given in [19].

2.2.2. Structures

Photonic crystals are natural or artificial periodic structures of materials with different refractive indices. The spatial period is defined as the lattice constant, which scale has to be on the order of the electromagnetic wave. The characterization of PhCs regarding the geometry of their structure separates them into one-, two- and three-dimensional structures. Example structures are shown in Figure 8. [20]

Figure 8: Schematic illustration of 1D, 2D and 3D PhC [20]

The permittivity only changes in one direction for a 1D PhC. The structure of the other two directions is uniform. Examples for this kind of PhC are Bragg gratings or anti-reflecting coatings. 2D PhC have a periodic changing permittivity in two directions and are uniform in one direction. Therefore, the variety of configurations is much larger. Examples of 2D PhCs are porous silicon with periodically arranged voids or a periodically arranged system of dielectric rods in air. Furthermore, the pattern of a butterfly's wing is also caused by a 2D microstructure. If a structure is periodic in all

three directions and, thus, has even more configuration possibilities, it is called a 3D PhC. A natural example for this kind of PhC is a stone opal. [3]

The properties of a PhC are defined by its structure, which is a periodical configuration of their refractive index profile. Wave optics and interference result from the same length scale of the device and the light wavelength. In general, PhC are ideal structures with strict periodicity. Structures that are not strictly periodic are referred to as photonic structures. Therefore, just a thin film or a multilayer thin film structure can also generate simpler selective thermal emitter structures. Furthermore, 2D or 3D surface gratings also have the effect of modifying the spectral emissivity. Examples of these structures are shown in Figure 9. [21]

Figure 9: Simple selective thermal emitter structures

2.3. Review of TPV Systems

TPV systems generate electricity from the thermal radiation emitted from a hot body. Therefore, the same basic principles are used as a conventional PV cell. Solar PV converts mostly visible radiation, while TPV runs with lower temperatures. In the following sections, the functionality and the advantages of TPV systems are described.

The two main components (the radiator/emitter and the PV cell) are explained in more detail. Finally, the efficiency of a TPV systems and different spectral control concepts are discussed.

2.3.1. Functionality of TPV Systems

TPV conversion can use a variety of heat sources, like chemical energy, nuclear energy, solar energy, or waste heat. More specific examples for heat sources can be the combustion of gas, or wood for combined heat and boiler systems, or in off-grid locations, diesel combustion for mobile power sources, high-temperature waste heat or heat from the sun for solar TPV applications. Typical temperatures for TPV lie in the range of 1,000–2,000 K. Therefore, most of the radiation occurs in the infrared spectral range. Temperatures below that aggravate achieving reasonable efficiencies, while higher combustion temperatures result in the emission of nitrogen oxides (NO_x) that exceed safe limits. [22]

Figure 10: Schematic illustration of a TPV system [23]

The design of a TPV system requires the selection and design of the heat source, the radiator, and the PV cell, as well as a spectral control concept (see Figure 10). In

general, the source heats up the radiator or emitter. The emitted radiation incidents the PV cell, which converts it into electricity or a combination of electricity and heat. [23]

The spectral control has the task of spectrally matching the incident radiation on the PV cell in accordance to the cell band-gap. Alternatively to additional components, like filters, the spectrum can be spectrally controlled by selective thermal emitters, which are the focus of this study. [23]

2.3.2. Advantages of TPV Systems

TPV system design is complex, but has several advantages besides directly converting heat radiation into electricity. A practical advantage is, that these systems are modular and lightweight. Therefore, existing systems can be expanded or adapted to the needs. Furthermore, they have a lifetime up to 25 years and need only little maintenance. They operate silent and emission-free as well as steadily in terms of intensity, spectrum, and angle of radiation as well as PV cell temperature. Moreover, TPV systems can be used as power sources on their own, as well as in combined heat and power (CHP) generation systems. [8,22,23,24]

Comparing TPV to solar PV, TPV has potentially higher efficiency and heat source flexibility, although, lower heat source temperatures result in a difficulty to achieve high efficiencies. On the other hand, the heat source and the PV cell are much closer to each other in TPV ($\sim 1\text{-}10\text{ cm}$) compared to the distance to the sun ($\sim 1.5 \times 10^{10}\text{ m}$). This fact makes much higher power densities possible, which can be around $5\text{-}60\text{ W/cm}^2$ compared with 0.1 W/cm^2 for solar cells. Another difference of PV and TPV is that TPV only converts thermal radiation in contrast to the whole spectrum of the sunlight. Therefore, PV cells that cover a higher wavelengths

spectrum are needed for TPV. Moreover, the emitter of a TPV system can be controlled and thus, helps to increase the system efficiency. [22]

2.3.3. Radiator/Emitter

Radiators or emitters have different properties based on which they can be classified. A broad classification is to distinguish emitters in spectrally broadband and selectively emitting, or into metal and ceramic radiators. Broadband emitters should have a spectral emissivity close to unity. Therefore, Silicon Carbide (SiC) is mostly used for this application because its emissivity is approx. 0.9 over a large range of wavelengths and can withstand temperatures up to 1900 K. In contrast, selective emitters have a variable spectral emissivity. [4,25]

Some possible characterization aspects are the optical properties, like the spectral and angular emissivity, the thermal properties (e.g. the upper operation temperature, and thermal conductivity), the material and material composition, and the physical structure (e.g. bulk, porous, filaments, film and micro-structured surface). Moreover, several requirements need to be considered for the design of the radiator/emitter:

- Thermal stability in the selected atmosphere (e.g. air, inert gas, or vacuum)
- Good thermal shock resistance (important for the start-up and cooling-down process), which can be achieved by low thermal expansion materials
- High thermal conductivities (uniform temperature distribution of the radiators)
- High emissivity for short wavelength (in-band) radiation (high radiative heat transfer rate, which results in a high electrical power density). [23]

Furthermore, other emitter properties have been the focus of recent research studies, like surface area and size of the emitter and their influence on the energy output with the same given energy input. [26,27]

2.3.4. Photovoltaic Cell

The functionality of a TPV system is similar to a solar PV system. Except from infrared (heat) radiation, that mainly incidents the PV cell instead of the whole solar spectrum. Thus, the peak emission wavelength is longer and materials with lower band-gap energy have to be applied for the PV cell. The PV cell is a diode of semiconducting material. Semiconductors are crystalline or amorphous and their electrical conductivity can be altered by a change in temperature or by changing the impurity content of the material as well as by incident radiation on the semiconductor. [6]

The main characteristic of the PV cell is the p-n junction that is created by doping the crystal with additional impurities. The n-region is doped with atoms that have more electrons than necessary. Thus, there are a majority of mobile and free electrons/negative charges in this region. In contrast, the p-region consists of a crystal doped with atoms missing an electron for a complete binding. The term “hole” refers to this missing electron/positive charge. Hence, these two regions create an electrical field. If matching incident radiation on the PV cell generates an electron-hole pair, it is separated by the electrical field and the electron or hole diffuses either to the p- or n-region. As a result, electrical power is dissipated between the contacts on both sides. [8,28]

Consequent properties for the semiconducting material of a PV cell are the specific band-gap, diffusion length of current carriers, the chemical composition and structure of the PV cell, as well as the doping concentration of the homo-junctions amongst others. A schematic illustration of the functionality of a PV cell is shown in Figure 11. [29]

Figure 11: Schematic illustration of a PV cell [28]

In the following, some of the most common semiconducting materials for PV cells are introduced and described in further detail. Silicon (Si) and Germanium (Ge) are part of the group of IV semiconductors. Si-cells are commonly used for solar PV systems. However, Silicon has an indirect band-gap at 1.12 eV or 1.11 μm , which is regarded high for TPV conversion. Germanium substrates have very low costs, but Ge-cells suffer from poor cell performance. Its band-gap lies at 0.66 eV or 1.88 μm . Another group of PV cells are based on III-V semiconductors, which currently have the highest conversion efficiencies. For TPV conversion, Gallium Antimonide (GaSb), Indium Gallium Arsenide (InGaAs), and Indium Gallium Arsenide Antimonide (InGaAsSb) are of most interest because of their low band-gaps. GaSb has a band-gap of 0.72 eV or 1.72 μm . The band-gap of InGaAs can be varied in a range between 1.42 eV and 0.36 eV, which corresponds to wavelength between 0.87 μm to 3.44 μm ,

depending on the different concentrations of In and Ga. InGaAsSb cells have band-gaps between 0.29 eV and 0.72 eV or 1.72 μm and 4.28 μm . The different semiconductor materials that are mostly used for PV cells in TPV systems with their corresponding band-gaps are also listed in Table 1. [23]

Table 1: Band-gap energy and wavelength of different semiconductors

PV-cell	Band-gap energy	Band-gap wavelength
Si	1.12 eV	1.11 μm
Ge	0.66 eV	1.88 μm
GaSb	0.72 eV	1.72 μm
InGaSb	1.42 to 0.36 eV	0.87 to 3.44 μm
InGaAsSb	0.29 to 0.72 eV	1.72 to 4.28 μm

2.3.5. Efficiency

TPV converts heat directly into electricity and thus, has great potential for efficient heat recovery. The conversion of heat into electricity could be conducted with Carnot efficiency. This fact makes TPV an attractive alternative to existing electricity generation technologies. However, at the current stage of research it is uncertain which efficiencies TPV systems can achieve. [23]

Defining TPV efficiency is complex because the general definition of the efficiency as useful output to total input is ambiguous for TPV systems. The total input can be defined in different ways depending on the heat source. Furthermore, the useful output can be either solely electrical or electricity and heat for CHP systems. Therefore, the efficiency of a TPV system depends on how the system boundaries are defined. A schematic illustration of the energy flow within a general TPV system is

shown in Figure 12. To identify and to maximize the overall efficiency of a TPV system, the efficiencies of the different stages have to be identified and maximized. [23]

Figure 12: Energy flow of a TPV system [23]

The total input depends on the heat source and e.g. can be measured as a heat flux (W/m^2) for radioisotope, solar or waste heat. Thus, the heat source efficiency η_{source} can be calculated from the radiator net heat transfer P_{net} to the total input P_{input} (e.g. product of fuel flow rate and calorific value). [23]

$$\eta_{source} = \frac{P_{net}}{P_{input}} \quad (2.34)$$

Radiation takes the main part of heat transfer in the cavity, where convection and conduction heat transfer should be minimized. The latter appears through gas conduction and possibly free convection. It can be reduced by using a suitable gas or reducing the pressure (vacuum) in the cavity. Ideally no radiation is lost because the radiator and PV cells are close together. However, heat can be lost through the insulation to the surroundings (cavity heat losses), especially in small systems with large surface-to-volume ratio. In steady-state there will be a net radiative heat flow

which incidents the PV cell P_{PV} . This heat flux includes short wavelength or in-band radiation that is convertible by the PV cell and additionally, the long wavelength or out-of-band radiation that is not convertible by the PV cell. Thus, the cavity efficiency η_{cavity} can be defined as: [23]

$$\eta_{cavity} = \frac{P_{PV}}{P_{net}} \quad (2.35)$$

The electricity output P_{el} of the PV cell depends on different conditions and the losses in a PV cell can be divided into fundamental and technological loss factors as shown in Table 2. [24]

Table 2: Loss factors of a PV cell [24]

Fundamental loss factors	<ul style="list-style-type: none"> • Loss by long wavelength photons • Loss by excess energy of photons • The voltage factor • The fill factor
Technological loss factors	<ul style="list-style-type: none"> • Loss by reflection • Loss by metal coverage • Loss by incomplete absorption • Collection efficiency

Photons with long wavelengths, so that their energy is smaller than the band-gap energy of the PV cell, cannot create an electron-hole-pair. Therefore, their energy is lost. As a photon can only generate one electron-hole-pair, the excess energy larger than the band-gap energy is also lost and dissipated as heat. To work against these two loss factors and increase the efficiency, the spectral radiation distribution can be influenced by spectrally matching the radiator and the PV cell with a selective thermal emitter. The voltage factor is defined as the ratio of the open circuits voltage to the band-gap voltage. High radiation densities can increase the voltage factor. Furthermore, the temperature of the PV cell influences the voltage factor. The fill

factor is defined as the ratio of the maximum electrical power density to the product of the photocurrent density and the open circuit voltage. Besides these fundamental loss factors, there are technological loss factors, like the loss by reflection, which can be reduced by surface treatments or anti-reflective coatings. Furthermore, due to the metal contacts, that cover part of the front surface, there is a loss by metal coverage. [24]

Two important and related quantities to describe the PV cell performance are the quantum efficiency (QE) and the spectral response (SR). The QE of a PV cell refers to the quantity of electrons and holes collected per absorbed photon. If reflection losses are included, it is called external quantum efficiency (EQE), while the reflected radiation of the cell surface is excluded for the internal quantum efficiency (IQE). The IQE is the maximum possible current density J_{max} that can be produced by the incident photon flux J_{ph} . Therefore, the IQE and EQE can be calculated as following:

$$IQE(\lambda) = \frac{J_{ph}}{J_{max}} \quad (2.36)$$

$$EQE(\lambda) = (1 - R)IQE(\lambda) \quad (2.37)$$

where R represents the reflection losses of the incident radiation. The SR is defined as the ratio of the produced photon current density per wavelength J_{ph} to the incident power density per wavelength q_i .

$$SR(\lambda) = \frac{J_{ph}}{q_i} = \frac{e\lambda}{hc} EQE(\lambda) \quad (2.38)$$

where e is the charge of an electron and h the Planck's constant. If every incident photon at a certain wavelength produced current, then the EQE would be one. Therefore, the QE depends on the wavelength, and is a PV cell property, which is

independent of the radiation source. The collection efficiency is the spectral average of the EQE. [4]

Subsequently, the overall PV cell efficiency η_{PV} can be calculated according to:

$$\eta_{PV} = \frac{P_{el}}{P_{PV}} \quad (2.39)$$

Additionally, it has to be decided if the output power includes the power that is needed for maintaining the system (for example fuel pump or electric control). The efficiency reduction due to this power $\eta_{maintain}$ is given in by: [23,30]

$$\eta_{maintain} = \frac{P_{el,net}}{P_{el}} \quad (2.40)$$

Regarding the fact, that all those efficiencies of the subsystems are less than unity, the overall efficiency must be relatively low. Even if the efficiencies of the heat source, the cavity, the PV cell, and the power maintenance system are assumed to be 90%, the overall efficiency would be less than 66%. However, more realistic component efficiencies will reduce the total efficiency significantly to less than 20%. [25]

2.3.6. Spectral Control

One main approach to increase the efficiency of a TPV system is to control the radiation spectrum that incidents the PV cell, so that it matches the EQE of the PV cell. The most widespread technique is using a filter. However, in the last decade, the use of selective thermal emitters has been the focus of many researches. Due to its promising benefits regarding the efficiency performance, the spectral control with selective thermal emitters is advantageous for TPV applications. Schematic illustrations of both spectral control concepts are shown in Figure 13. [22]

Figure 13: Spectral control concept a) with a filter and b) with a selective thermal emitter [31]

So far, the most common spectral control concept is to filter all photons with less than the band-gap energy. To reach higher system efficiencies than with just a blackbody source, these photons have to be returned to the radiator, so that the heat is recovered and their energy is conserved. This can be realized by including e.g. plasma filters, dielectric stacks, or black surface reflectors. Therefore, using a filter can increase the overall efficiency. However, the power density, which is just influenced by photons with higher energies than the band-gap, stays the same. [25]

Contrary to TPV systems including a filter, no blackbody emitter is necessary for the spectral control with a selective emitter. This emitter directly radiates quasi-monochromatic radiation that matches the PV cell. Therefore, less energy will be lost due to photons with higher or lower energy than the band-gap. Thus, the efficiency limit is increased and additionally, this concept has a simpler device configuration. An example for a matching emissivity spectrum of a selective thermal emitter made of metamaterial and the EQE spectrum of a GaSb-cell is shown in Figure 14. The selective thermal emitter only emits over the range of wavelength, where the PV cell generates electron-hole pairs. The aim is to reach a spectral emissivity close to one in

this wavelength range. Contrary, the spectral emissivity should be close to zero for the remaining wavelengths, so that no photon energy is lost. [31,32]

Figure 14: Matching selective thermal emitter- and EQE-spectrum [32]

Nefzaoui, Drevillon, and Joulain compared the efficiency of TPV systems with a blackbody emitter without any spectral control, with an additional filter and with a selective thermal emitter instead of a blackbody emitter. The emitters were all heated up to a temperature of 5800 K. The efficiency is defined as the ratio of the electric power by the incident radiative power and the results over the wavelength are shown in Figure 15. The blackbody emitter reaches the lowest efficiency due to the loss factors mentioned before. For the filter concept, an assumption has to be made, that the filtered radiative power is recovered to reach a higher efficiency than a blackbody emitter without a filter. The selective emitter almost doubles the efficiency of the TPV system because of the matching emissivity spectrum. Furthermore, it can be observed that the efficiency curve is also narrower than the other two curves, which points out

that the emissivity spectrum has to be well matched to the PV cell to obtain this high efficiency values. [31]

Figure 15: Efficiency of a TPV device with a blackbody emitter, a filtered blackbody radiation and a selective thermal emitter over the wavelength at 5800 K [31]

2.4. State of the Art: Selective Thermal Emitter for TPV Applications

Selective thermal emitters give the opportunity to improve the efficiency of TPV systems if the emission of photons in a certain spectral range matches with a specific TPV cell. This result is due to the fact, that TPV cells only generate electricity if the emitted energies are higher than the band-gap of the semiconductor material of the TPV cell. However, much higher photon energies lower the conversion efficiency because of the loss of excess energy. Depending on the material, the highest efficiency

is achieved by using a selective thermal emitter with the emissivity peak at the wavelength of the specific band-gap of the TPV cell. As the normal emitter radiates energies in a broad spectral region, wavelength-selective emitters can improve the conversion efficiency and power generation of TPV systems. [33]

Because of its promising benefits, selective thermal emitters have been the focus of numerous recent research papers. One major target is to determine the emissivity dependent on different materials and material structures. Different studies already chose specific materials and material structures to suggest design enhancements of TPV energy conversion systems.

Recently, different 1D and 2D selective thermal emitter structures of Tungsten (W) and Silicon Oxide (SiO_2) were analyzed. These thin film/grating structures were proposed to enhance the efficiency of TPV systems in combination with matching TPV cells. Zhao et al. studied 2D grating/thin-film nanostructures of SiO_2 and W and also investigated the effect of azimuthal and polar angles on the emissivity spectra. [33] Chen and Zhang had a critical look at 1D W-complex-gratings by the superposition of two simple W-gratings with different periods and filling factors. Thus, a wider emissivity peak near 1 between $0.8\ \mu\text{m}$ and $1.7\ \mu\text{m}$ could be calculated that is almost constant over all angles. This enhancement could be explained by the excitation of surface SPPs coupled with the grating microstructures. [34] Both, simple and complex gratings of SiO_2 and W have been analyzed by Wang and Zhang, who predicted emissivity values over 0.8 in the wavelength region from $0.62\ \mu\text{m}$ to $1.98\ \mu\text{m}$ and below 0.2 at wavelengths longer than $2.4\ \mu\text{m}$ for these nano-engineered structures. [35] Furthermore, using the Rigorous Coupled Wave Analysis (RCWA)

method for calculating the spectral emissivity generated all the results of these studies. [33,34,35]

Nefzaoui, Drevillon, and Joulain studied the design and optimization of more simple structures. The resulting structures are composed of two or four layers of metals and semiconductors. The two-layer structure consists of a Ge-anti-reflection coating and a second layer of either SiC, Bor Nitride (BN) or Aluminium Nitride (AlN), which have strong lattice resonances in the mid IR. The four-layer structure consists of Silver (Ag) or Gold (Au) doped Si. Efficiency calculations have been conducted for the different structures. The usual PV device efficiency limit lies around 30% for crystalline Silicon under solar radiation (according to Shockley-Queisser model) and could be increased up to 60% with the new emitter structures. [31]

Another study by Kohiyama et al. reported the design of the quasi-monochromatic thermal emitter based on the micro-cavity effect and the design of the configuration of a solar-TPV system using this multi-layer emitter based on W and Yttria-Stabilized Zirconia (YSZ). The system efficiency and electric power density of the selective emitter design is 16.6% and 2.9 W/cm^2 , respectively. [36]

Because of their high thermal stability, numerous studies focus on the use of rare earth oxides for selective thermal emitters. Bitnar et al. fabricated and measured the emissivity of selective radiation emitters made from Ytterbium (III) Oxide (Yb_2O_3) and Erbium (III) Oxide (Er_2O_3). The maximum emissivities of the selective peaks were 0.85 at 1.27 eV for the Yb_2O_3 emitter and 0.82 at 0.80 eV for the Er_2O_3 emitter. [37] Diso et al. tested ceramic composites containing alumina and zirconia fibres at different erbium concentrations to obtain a radiation between $1.4 \mu\text{m}$ and

1.6 μm to realize a selective thermal emitter with a good functional as well as a good structural performances for TPV applications. [38] Furthermore, Wang, Hong, and Zhang developed an Er_2O_3 coating-type selective emitter with good stability at 1400 $^\circ\text{C}$ with an emissivity peak at 1.55 μm , which matches a GaSb cell. [39]

Other studies also take the requirement of a high temperature resistance into account. For a 2D PhC selective thermal emitter made of Vanadium Dioxide (VO_2), Ye, Wang, and Cai reached a spectral emissivity of 0.95 within the convertible wavelength range of the InGaAs cells, whereas the emissivity for non-convertible wavelengths were less than 0.3. The simulated results were generated by the Finite Difference Time Domain (FDTD) method and the highest radiative efficiency of 54.11% was predicted at 1500 K. As a result, the efficiency of the whole TPV system increased from 8.43% to 12.37%. Additionally, they explained the influences of the radius and depth of the grating cavities on the emissivity based on the coupled-mode theory. [40]

Various different material structures and grating dimensions have to be analyzed in order to optimize the efficiency of TPV systems. Therefore, Chen, and Tan presented a method to systematically and efficiently search for matching selective emitter structures of 3D periodic W-nanostructures. The optimization of structure depth, periods, and filling ratios has been carried out using the orthogonal array from the Taguchi method with four variations each. The spectral emissivity from the optimized structures lies above 0.9 at wavelengths between 1.0 μm and 2.0 μm , but the emissivity lies below 0.2 at wavelengths between 2.0 μm and 4.0 μm . [41]

Besides grating structures, other research studies also propose doped materials for generating selective thermal emitter. A low infrared emissivity Magnesium Oxide (MgO) host doped with Cobalt (II,III) Oxide (Co_3O_4) or Nickel (II) Oxide (NiO) at concentrations of 2-4 wt.% was developed by Ferguson, and Dogan, that matched very well to the response of GaSb cells. The peak emissivity is nearly 0.9 at a wavelength between 1 μm and 1.9 μm at temperatures of 1700 K. These results have been experimentally measured. [15]

Moreover, Lui et al. analyzed selective thermal emitters made of metamaterials for TPV applications. They experimentally generated a narrow band mid-IR thermal emitter as well as a dual-band mid-IR emitter made of multiple metamaterial sublattices matching the EQE of a GaSb-cell. [32]

Other research studies also propose an emissivity measurement combination of selective emitter and filter. Therefore, the best spectral efficiency result of 87.86% was generated for a W-SiO₂ emitter-filter combination. [42] Moreover, selective emitter made of nano-fibers can also be used for TPV applications. Tomera et al. reported that erbia-modified electrospun titania nano-fibers emit selectively in the range of approx. 1.4 μm to 1.7 μm . [43]

Schemeya, and Vandervelde proposed to install the thermal selective emitter directly on the top surface of the TPV diode stage. Simulations lead to a potential efficiency enhancement of 81% for a GaSb TPV cell with a two-dimensional photonic crystal consisting of Si₃N₄ rods in an ohmic contact material. [44] Park et al. also examined the effects of near-field radiation on the photon penetration depth, photocurrent generation, and quantum efficiency. [45]

CHAPTER 3 – METHODOLOGY

In the following sections, the basic methodology for the design and analysis of the selective thermal emitter structures will be described. Afterwards, the principles of the numerical calculations necessary for the spectrum of emissivity and the analysis and selection of materials applicable for enhancing the TPV efficiency will be presented. Furthermore, a description of the implementation of the calculations in MATLAB will follow. After presenting the different designs and materials to be analyzed, different measuring methods necessary for the experimental verification of the calculated results are introduced.

3.1. Basic Methodology: Characterization and Analysis

The basic methodology of this study will include the following steps: The analysis of the relevant materials already used for TPV cells and possible new materials, including the optical data of the materials needed for the calculations as well as the numerical calculation of the spectral emissivity for different design structures, like thin films, surface gratings and layers of materials doped with nanoparticles. These calculations will be implemented in a MATLAB calculation model to analyze the selective thermal emitter designs and possibly find matching designs for different PV cells and their EQE-spectrum. The basic methodology of this study is illustrated in Figure 16.

Figure 16: Basic methodology for analyzing selective thermal emitter designs

3.1.1. Design Methodology

He et al. characterized the design methodology for selective thermal emitters with six properties: Doping, surface roughness, texture, and periodicity as well as coating thickness, and nano-composite coatings. [46]

Doping means intentional introduction of impurities into an extremely pure material. As mentioned before, according to Wien's displacement law and Planck's law most black body energy at high temperature is radiated in the wavelength range of 1-5 μm . However, many materials have a weak intrinsic absorption and therefore, a low emissivity within this range. Thus, the total and spectral emissivity has to be enhanced and this can be realized by doping the material. Different mechanisms to enhance the

emissivity for doped materials are e.g the free carrier absorption mechanism or the distortion of the crystal lattice. [46]

Figure 17 shows the absorption coefficient over the wavelength for SiC with three different doping concentrations. It can be stated, that higher impurity concentrations result in a higher absorption. Thus, the spectral emissivity enhances accordingly. [46]

Figure 17: Absorption coefficient for Silicon Carbide with different impurity concentrations [46]

Hence, doping plays an important role in modifying the spectral emissivity; doped materials will be included in the analysis of different selective thermal emitter designs.

The **surface roughness** usually appears for all real surfaces, whereas ideal surfaces are characterized as optically smooth. The spectral emissivity of optically smooth surfaces can be determined by the Fresnel's equation and Kirchhoff's law as described in Chapter 2. The surface roughness of real surfaces can be separated into three regions according to the optical roughness, which is defined as the ratio between

surface roughness σ and wavelength λ : the specular region ($0 < \frac{\sigma}{\lambda} < 0.2$), intermediate region ($0.2 < \frac{\sigma}{\lambda} < 1$) and the geometric region ($\frac{\sigma}{\lambda} > 1$). Then, the spectral emissivity calculations have to be adapted. For the specular region, the spectral emissivity can be calculated by the Gaussian distribution of surface heights. For the intermediate region, the bidirectional reflectance function (BDRF) and for the geometric region, the geometrics optics can be applied. [46]

However, there does not exist a universal model for the influence of the surface roughness on the emissivity. Therefore, all material surfaces will be assumed ideal and thus, optically smooth.

The **surface texture** is known, in material science, as the distribution of crystallographic orientations of a sample in materials science. Different orientations often originate during coating deposition and have an important effect on radiative scattering. Different studies found, that a surface texture with high aspect ratio (height to width ratio) provides higher emissivity values, in comparison to a randomly oriented surface texture. However, the effect of different surface textures and how to apply them in predicting the spectral emissivity is still controversial. [46]

Because of that, the surface texture will not be included in the calculation model for the spectral emissivity of this study.

The **surface periodicity** refers to the periodical nano-structures that affect the motion of photons. Therefore, PhCs are composed of periodic dielectric or metallo-dielectric nano-structures to manipulate the propagation of electromagnetic waves. This physical effect is based on diffraction. Thus, the periodicity of the selective

thermal emitter has to be of the same length-scale as half of the wavelength of electromagnetic waves. [46]

Because the surface periodicity has a great impact on the modification of the spectral emissivity, surface gratings are included in the analysis of different selective thermal emitter designs for this study.

The **coating thickness** is strongly related to the spectral emissivity of a selective emitter. For a free-standing thin film, the film has to be thicker than the penetration depth d_p , which is defined as inverse of the absorption coefficient α_c , so that no transmittance occurs:

$$d_p = \frac{1}{\alpha_c} = \frac{\lambda}{4\pi\kappa} \quad (3.1)$$

where the extinction coefficient κ of the material should be as low as possible to get high emissivity of coatings. For multiple layers, optical interference will occur if the layer thicknesses are of the same order of magnitude as the wavelength of the incident radiation. [46]

Selective thermal emitters of different structures will be analyzed regarding their spectral emissivity. Furthermore, the relationship between emissivity and layer thickness will be investigated to find the optimal coating thicknesses for different materials and material combinations.

The last property is defined as **nano-composite coatings**, which have a higher spectral emissivity than single component materials. Nano-composite coatings consist of at least two phases: a crystalline phase and an amorphous phase, or two different crystalline phases. Furthermore, nano-composite coatings can obtain other properties

such as mechanical properties, thermal shock resistance, and oxidation resistance, which are necessary for high temperatures. [46]

This property will be taken into account by analyzing not only thin films of single materials, but also of doped materials, and surface gratings.

3.1.2. Selective Thermal Emitter Requirements

The aim of this study is to analyze different selective thermal emitter designs to enhance the efficiency of TPV systems. Therefore, the fundamentals of thermal radiation, as well as the functionality of selective thermal emitters and TPV systems have been reviewed. Moreover, the basic methodology of this research study has been described and a design methodology for selective thermal emitters has been presented. As a result, different selective thermal emitter requirements have been defined, that have to be fulfilled by the drafted designs.

1. Far-field radiation: From Section 2.1.2, it is known that far-field radiation is only valid, if $d > \lambda_{max,T}$, which corresponds to approx. 10 μm under ambient conditions (temperatures around 300 K). Otherwise, near field effects dominate the spectral emissivity calculations. As the distance of the emitter and the TPV cell is about 10 cm (Section 2.3.1), only far-field radiation will be taken into account.

2. Matching spectral hemispherical emissivity and EQE-spectrum: As mentioned before, matching the emitter radiation to the EQE of the PV cells improves the TPV efficiency significantly because there is no loss due to photons with lower energies and excess energies of photons with higher energies. Therefore, the ideal selective thermal emitter only emits photons with energies corresponding to the band gap of the PV cell. [4] As the two basic mechanisms for spectral alteration of the

emissivity are the material composition and the physical structure, those will be the variable input parameters of this study. Furthermore, the spectral emissivity is also dependent on the angle besides being wavelength-dependent. Thus, the spectral hemispherical emissivity will be the main optimization criteria of this study. [23]

3. Design methodology: As described in the previous section, coating thickness, surface periodicity, and doping will be included in the analysis of the selective thermal emitter designs. Therefore, the calculations of thin film structures, surface gratings and doped materials are the main parts of the MATLAB model. Furthermore, the surface will be assumed as optically smooth and the surface texture to be homogeneous.

4. Simple design structure: Recently, many different selective emitter design structures have been developed and analyzed to increase the TPV efficiency. However, the majority of those structures are very complex, e.g. a large number of layers or complex 2D and 3D PhC structures. If industrial fabrication processes are taken into account, the production costs will be too high to establish them in the market. [31] To consider the fabrication costs, simple 1D structures and surface gratings are the focus of this analysis.

5. Material requirements: Concluding from Section 2.3.3 the following main material properties are required for the radiator/emitter: High thermal stability, good thermal shock resistance (low thermal expansion materials), and high thermal conductivities. Furthermore, in this study, only non-magnetic materials ($\mu_m = \mu_0$), like most metals, dielectrics and semiconductors are considered. Therefore, only the dielectric function is needed to characterize the materials electromagnetic behavior. [1] Moreover, the focus will be set on nano-composite coatings with

multiple components or multilayered structures because they are promising to reach high emissivity values with excellent mechanical or thermal properties. [46]

3.2. Calculation Methods for Different Materials

In Section 2.1.1, the dielectric function has been identified as the main material property that influences the spectral emissivity of a selective thermal emitter. This assumption requires that the material is non-magnetic. The calculation of the dielectric function is important to model the different electromagnetically coupled modes (see Section 2.2.1) that are responsible for the wavelength selectivity of an emitting material. The dielectric function from Equation (2.16) can be used for measured values of n and κ of any material. The Drude model and the Lorentz model can be used to calculate the dielectric function of some metals and dielectric materials. [1]

3.2.1. The Drude Model

The free electrons that interact with the incoming electromagnetic waves cause the absorption in metals. Without an electromagnetic field, free electrons move randomly. The electromagnetic field causes the electrons to move at a nonzero average velocity, which results in an electric current that oscillates at the same frequency as the electromagnetic field. Furthermore, the carriers collide with stationary atoms, ionized impurities, phonons, other carriers or interfaces etc. These collisions act as a damping force on the motion of carriers, which is proportional to their velocity. The oscillatory movement of an electron resulting from a harmonic field and the damping force is described by:

$$\varepsilon(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma} \quad (3.2)$$

This equation is also called the Drude model and describes the frequency-dependent conductivity of metals and can be extended to free carriers in semiconductors. Here, ε_{∞} is the high-frequency dielectric constant, ω_p is the plasma frequency and the damping factor is indicated by Γ . [1]

3.2.2. The Lorentz Model

The Lorentz model takes the contribution of bound electrons into account. The lattice vibrations or bound electrons absorb light due to the existence of electric dipoles formed by the lattice. When the frequency equals the vibrational mode of the dipole, the absorption is maximal. This usually occurs in the mid- to far-infrared region of the spectrum. The Lorentz oscillator model assumes that a bound charge e is accelerated by the local electric field E . These vibrations of the lattice ions and bound electrons contribute to the dielectric function. The formula to define the dielectric function directly dependent on the wavelength is given by:

$$\varepsilon(\omega) = \varepsilon_{\infty} \left(1 + \frac{\omega_L^2 - \omega_T^2}{\omega_T^2 - \omega^2 - i\omega\Gamma} \right) \quad (3.3)$$

where ε_{∞} is the high-frequency dielectric constant, Γ the damping factor, ω_L the frequency of the longitudinal optical phonons and ω_T the frequency of transversal optical phonons. [1]

3.3. Calculation Methods for Different Design Structures

In Section 3.1.2, thin film structures, surface gratings and doped materials have been determined to be the focus of the design analysis. To generate the MATLAB model for calculating the spectral emissivity of those designs, the different calculation approaches used in this study are presented in the following sections.

3.3.1. Thin Films

The most simple selective thermal emitter structure is a thin film of polar material of less than 1 μm . For a better handiness, this thin film has to be deposited onto a substrate. In order to shield the emissivity of the polar material from the emissivity of the substrate, a layer of reflective metal should be deposited between them. Two or three layers of different materials can be deposited on top of each other to receive different thin layer designs. One example of a two-layer selective thermal emitter is shown in Figure 18. [14]

Figure 18: Two-layer selective thermal emitter design

As the transmission can be neglected, the Fresnel reflection coefficients for the TM and TE waves are calculated according to Equation (2.25) and (2.26). For a multi-layered thin film structure, the generalized reflection coefficient of the whole structure

is calculated according to Equation (2.30). In case of a two-layer structure, the generalized reflection coefficient from vacuum to the first material is:

$$\tilde{R}_{1,2}^{(p)} = \frac{R_{1,2}^{(p)} + \tilde{R}_{2,3}^{(p)} e^{i2k_{z2}t_1}}{1 + R_{1,2}^{(p)} \tilde{R}_{2,3}^{(p)} e^{i2k_{z2}t_1}} \quad (3.4)$$

The generalized reflection coefficient from the first to the second material is calculated respectively. The reflective metal prevents the reflection from the substrate from interfering with the emitter structure. Therefore, the generalized reflection coefficient $\tilde{R}_{3,4}^{(p)}$ equals the Fresnel reflection coefficient from the second material to the reflective metal $R_{3,4}^{(p)}$. To obtain the Fresnel reflection coefficient for each interface, the z-component of the wave-vector has to be calculated for every layer according to Equation (2.23). In this case, k_{z1} is the z-component of the wave-vector in vacuum, k_{z2} in Material 1, k_{z3} in Material 2, and k_{z4} in the reflective metal. After all necessary parameters have been obtained; the spectral emissivity of this two-layer structure can be calculated according to Equation (2.33). [14]

3.3.2. Surface Gratings

The conversion efficiency of TPV systems can also be enhanced by the use of micro/nanostructured gratings as wavelength-selective emitters. There exist a number of research studies that modeled the radiative properties of different grating structures and compared the results to experimental measurements. As a result of the surface grating, the first layer is now an inhomogeneous region (see Figure 19). The surface grating is periodic in one-dimension (x-direction) and the first layer consists of material 1 and free space, so that in this region, the dielectric function is a periodic function of x with a grating period Λ . The filling ratio of material 1 is ϕ , and the

grating is assumed to extend to infinity. Therefore, the permittivity and the permeability are spatial functions and the Maxwell equations become more complex. Thus, numerical methods are required to solve the wave equations. [30,47]

Figure 19: Thin film structure with periodic surface grating of period Λ and filling factor ϕ

One of the most common methods to obtain the spectral emissivity is the Rigorous Couple Wave Analysis (RCWA). Further methods are the Finite Difference Time Domain (FDTD), the Finite Element Method (FEM), Boundary Element Method (BEM), as well as the volume integral method. Another approach is to use the Effective Medium Theory (EMT), which calculates the spectral emissivity via approximating the inhomogeneous medium with an effective homogenous permittivity and permeability. [1]

In the following section, the RCWA method will be presented because it is an effective and accurate numerical tool to obtain the optical properties of periodic gratings. Furthermore, RCWA is faster than e.g. the FDTD method. Subsequently, the method of homogenization will be described as a different approach to calculate the spectral emissivity. This method is based on the EMT and is commonly used to obtain the permittivity and permeability of inhomogeneous media. Moreover, EMT requires

much less computation time because the emissivity of the surface gratings can still be solved with thin film optics. [1]

Rigorous Coupled Wave Analysis

The RCWA is a common method and efficient tool to analyze layered dielectric structures that are periodic on the scale of a wavelength. The analysis is rigorous because there are no approximations made to the Maxwell's equations. For this method, the wave equation is solved analytically in the longitudinal direction, so that structures of arbitrary length can be modeled. Furthermore, the method can include waves with different angles of incidence into its calculations. [48]

For a structure of layers uniform in the longitudinal direction, RCWA formulates a Fourier expansion of fields in each grating layer and then forms a set of coupled space harmonics. Thus, the wave equation is a set of ordinary differential equations and can be solved as an eigenvalue problem. To satisfy the boundary conditions, the phase of these field harmonics are matched over all grating layer interfaces, so that the method is compatible with the transmittance matrix approach and RCWA gives a stable numerical solution. [49]

Because a complete set of eigenmodes must be computed within each segment, RCWA is most efficient to analyze layered problems with minimal volumetric complexity. Arbitrarily shaped structures must be divided in many thin segments ("stair-case" approximation). Therefore, it becomes very computationally intensive because a complete set of eigenmodes must be solved in every segment. Periodic structures of low index contrast and without fine features can be described well by Fourier series with few terms and RCWA is very fast and efficient. Although the

formulation of RCWA seems more cumbersome and complicated than other methods, it is very simple and compact to implement. [48]

Effective Medium Theory

The EMT was first formulated by Maxwell Garnett to calculate the effective dielectric function of metal particles embedded in a dielectric material. However, Rytov first applied EMT for a periodic grating structure to obtain the effective optical constants. The zeroth-order EMT is considered to be applicable when the period-to-wavelength ratio is small, so that an assumption can be made that the electromagnetic fields do not vary spatially within a given material. Therefore, the zeroth-order EMT has been used for the design of surfaces with antireflection and selective radiative properties. The expression has to be extended to include higher-order terms for one- and two-dimensional gratings when the grating periods are only several times smaller than the incident wavelength and/or when the permittivity of the substrate material is large compared to the permittivity of the incident medium. Therefore, the second-order EMT is applied to calculate the spectral emissivity of selective thermal emitter structures with surface gratings. [50]

Moreover, the effective medium formulation for surface gratings is polarization-dependent. Therefore, effective permittivity is calculated differently if the electric field $\mathbf{E}$ is perpendicular to the wave vector $\mathbf{k}$ (TE or y polarization), or if $\mathbf{E}$ is parallel to $\mathbf{k}$ (TM or x polarization). The formula to calculate the effective dielectric function according to the zeroth-order EMT ($\varepsilon_{TE,0}$ and $\varepsilon_{TM,0}$) as well as the second-order EMT ($\varepsilon_{TE,2}$ and $\varepsilon_{TM,2}$) are given below:

$$\varepsilon_{TE,0} = \phi\varepsilon_A + (1 - \phi)\varepsilon_B \quad (3.5)$$

$$\varepsilon_{TM,0} = \left(\frac{\phi}{\varepsilon_A} + \frac{1-\phi}{\varepsilon_B} \right)^{-1} \quad (3.6)$$

$$\varepsilon_{TE,2} = \varepsilon_{TE,0} \left(1 + \frac{\pi^2}{3} \left(\frac{\Lambda}{\lambda} \right)^2 \phi^2 (1-\phi)^2 \frac{(\varepsilon_A - \varepsilon_B)^2}{\varepsilon_{TE,0}} \right) \quad (3.7)$$

$$\varepsilon_{TM,2} = \varepsilon_{TM,0} \left(1 + \frac{\pi^2}{3} \left(\frac{\Lambda}{\lambda} \right)^2 \phi^2 (1-\phi)^2 (\varepsilon_A - \varepsilon_B)^2 \varepsilon_{TE,0} \frac{\varepsilon_{TM,0}}{\varepsilon_A \varepsilon_B} \right) \quad (3.8)$$

where the permeability of the grating material and the vacuum in between are indicated by ε_A and ε_B , respectively. It can be seen, that in the case of a small filling ratio ϕ , the second-order term can be neglected. The second-order correction is calculated to improve the useful range of the EMT. After the calculation of the effective dielectric function for the grating region, the surface grating can be treated as a homogeneous material for the respective polarization. [47]

Comparison of RCWA and EMT

Both RCWA and EMT are widely used for calculating the emissivity spectrum over different wavelengths and incident angles. A direct comparison of both methods is shown in Table 3. The table shows if the corresponding method performs better (+) or worse (-) for each criterion.

Table 3: Direct comparison of the RCWA- and EMT-method

	RCWA	EMT
Accuracy of results	+	-
Mathematical complexity	-	+
Simulation speed	-	+
Applicability	-	+
Possible design complexity	+	-

RCWA gives a more accurate solution, especially for very complex periodic structures because no approximations are made to Maxwell's equations or to the

theoretical modeling of the structure itself. However, one main advantage of the application of EMT for surface gratings is, that it is about 1000 times faster than RCWA. The latter is more complex due to its large number of matrix elements. The effective medium formulation is not as accurate, but can be easily applied to calculate the effective optical properties when the grating region can be approximated as isotropic and homogeneous. The second-order EMT is an extension of zeroth-order EMT to achieve additional accuracy of the calculated results. [50]

Raguin and Morris compared the results of RCWA and the zeroth- and second-order EMT and showed that the results calculated by the zeroth-order EMT can differ substantially from the second-order EMT results and are particularly inaccurate when IR transmissible substrates are analyzed. The second-order EMT corresponds with the results of RCWA, especially for the TE-polarization. However, the results just have been compared for periodic structures in one dimension because no closed-form EMT exists for structures, which are periodic in two or even three dimensions. [47]

As only non-magnetic materials are analyzed in this study and one selective thermal emitter requirement is to obtain a simple design structure; the EMT is assumed to be sufficient for the calculation of the effective dielectric function. Additionally, EMT is less complex because the method of homogenization simplifies surface gratings to planar multilayer structures and thus, it is suitable for this research study and can be easily applied.

3.3.3. Doped Materials

Besides thin layers or surface gratings of one material, wavelength selectivity can also be achieved by doping materials with nanoparticles. Such a selective thermal emitter design is shown in Figure 20.

Figure 20: Thin film structure doped with nanoparticles of radius r and volume fraction vf

To calculate the spectral emissivity, the effective dielectric function of the matrix and the nanoparticles is required instead of the dielectric function of each layer material. This effective dielectric function ϵ_{eff} can be obtained by the Clausius-Mossotti equation: [51,52]

$$\epsilon_{eff} = \epsilon_m \left(\frac{r^3 + 2\alpha_{MGM}(r)vf}{r^3 - 2\alpha_{MGM}(r)vf} \right) \quad (3.9)$$

where the dielectric function of the matrix material is given by ϵ_m . Furthermore, r is the radius and vf the volume fraction of the nanoparticles. The electric dipole polarizability α_{MGM} can be calculated according to the Maxwell Garnett Mie theory: [53]

$$\alpha_{MGM}(r) = \frac{3jc^3}{2\omega^2\epsilon_m^{3/2}} a_1(r) \quad (3.10)$$

To solve this equation, the first electric Mie coefficient $a_1(r)$ has to be calculated. Therefore, the dielectric functions of the matrix ε_m and the nanoparticles ε_{np} are needed, as well as the Riccati-Bessel functions of the first order ψ_1 and ξ_1 of the size parameters of the matrix x_m and the nanoparticles x_{np} . The Riccati-Bessel function of first order is calculated from the first order spherical Bessel functions j_1 and the first order spherical Hankel functions $h_1^{(1)}$. [51]

$$a_1(r) = \frac{\sqrt{\varepsilon_{np}}\psi_1(x_{np})\psi'_1(x_m) - \sqrt{\varepsilon_m}\psi_1(x_m)\psi'_1(x_{np})}{\sqrt{\varepsilon_{np}}\psi_1(x_{np})\xi'_1(x_m) - \sqrt{\varepsilon_m}\xi_1(x_m)\psi'_1(x_{np})} \quad (3.11)$$

$$\psi_1(x) = xj_1(x) \quad (3.12)$$

$$\xi_1(x) = xh_1^{(1)}(x) \quad (3.13)$$

$$x_m = \frac{\omega r \sqrt{\varepsilon_m}}{c} \quad (3.14)$$

$$x_{np} = \frac{\omega r \sqrt{\varepsilon_{np}}}{c} \quad (3.15)$$

3.4. Computer-aided Calculation and Simulation

The computer-aided calculation and simulation include the implementation as well as the simulation and validation of the model. The implementation of the model is conducted with MATLAB and will be described in the following sections as well as the application of the simulation and its validation.

3.4.1. Implementation in MATLAB

The calculations of the spectral emissivity for different selective thermal emitter structures are implemented in MATLAB, which involves an intuitive user language,

an interactive environment, and various mathematical as well as graphical functions. For these reasons, MATLAB is often applied, especially for technical calculations. In addition, no variable declaration of a particular data type is required, so that the assignment can be of any type and be changed in between. Although, the amount of time to carry out a simulation is often longer compared to other simulation programs, the simulation model will not be as complex for this to be relevant. [54]

The material composition and the physical structure are the defining components of the selective thermal emitter design. Therefore, the material constants of the selected materials and the structural dimensions are the input parameters of the calculation model. Hence, the emissivity is dependent on the wavelength and the incident angle; the spectral hemispherical emissivity is set to be the output of the model (see Figure 21).

Figure 21: Input and output of the calculation model

In more detail, when the simulation is started, it loads all information given by the user. This includes the design parameters, like layer thickness and layer number, the physical constants necessary and the materials selected for the different layers. Then, it will be distinguished if the layer consists of one single material, a matrix material doped with nanoparticles or a surface grating. For the doped material or surface grating, further design parameters, like the radius and volume fraction of the nanoparticles or the period and filling ratio of the surface grating, are necessary. After that, either the dielectric function of the single material, or the effective dielectric

function for the doped material, or surface grating will be calculated for each wavelength. Afterwards, the wave vector and reflection coefficients will be calculated for each wavelength and incident angle. The numerical integration over all incident angles results in the emissivity value for one wavelength. This procedure is repeated over the whole defined wavelength spectrum, so that the results can be evaluated and plotted in the end. The described structure of the MATLAB simulation is illustrated in Figure 22.

Figure 22: Structure of MATLAB simulation

The actual MATLAB code is divided into various scripts and functions that can be activated according to the chosen design of the selective thermal emitter. These will be described in more detail in the following.

Main_emissivity is the main script and defines all input parameters (see A.1). At first, the incident wavelength spectrum is specified because the emissivity is calculated for a specific wavelength spectrum in a defined number of steps. Therefore, a vector from the minimal to the maximal value of the wavelength spectrum to be analyzed is specified or distinct wavelength values from a data-file are loaded. If a design should be calculated consisting of materials with only data values for the dielectric function, the data table with more values has to be interpolated over the spectrum. Furthermore, the script *f_parameter* is opened (see A.2). In this script all physical constants are defined and all parameters are allocated that are needed for the calculations.

After that, the selective thermal emitter design is specified. For every layer, the layer thickness t , the permeability m (1, for non-magnetic materials) and the dielectric function e has to be determined. For the different materials either a function *e_material* (e.g. *e_SiC*, *e_Au...*) has to calculate the dielectric function over the wavelength spectrum or a data-file with different values for n and κ are given for each wavelength from which the value for the dielectric function can be calculated.

The effective dielectric functions for a material doped with nanoparticles are given by *e_np* and for a surface grating by *e_grating* (see A.3 and A.4). The input parameters for a layer of doped material are the matrix material *e_m*, the material of the nanoparticles *e_np*, the particle radius r , and the volume fraction of the

nanoparticles γf . Out of this, the effective dielectric function can be calculated from the Maxwell-Garnett-Mie-Theory. For a surface grating, different effective dielectric functions have to be calculated for the TE and TM wave by the second-order EMT. Here, the input parameters are the grating material e_a , the filling material (usually air or vacuum) e_b , the grating period L , and the filling ratio ϕ .

The function f_{int} calculates the emissivity of the design for one wavelength over all incident angles (see A.5). Here, it is assumed, that the y-component of the in-plane wavevector is zero. k_x is set in the interval $[0 ; 2 \cdot \pi \cdot \lambda]$ for a defined number of steps, so that the results can be numerically integrated over k_x . Then, the z-component of the wavevector k_z and the Fresnel reflection coefficients for the TE and TM wave are calculated for every interface for every k_x . After that, the generalized reflection coefficients for the TE and TM wave are calculated backwards from the last interface, so that they can be plugged into the equation for the previous interface. After the emissivity is calculated from the generalized reflection coefficient of the surface (interface of vacuum and first layer) and numerically integrated over all incident angles, the value is given back to $main_emissivity$.

As a surface grating results in different effective dielectric functions for the TE and TM wave, another function $f_{int_grating}$ was written (see A.6). It has the same structure as f_{int} , but uses these different effective dielectric functions for the calculation of the z-component of the wavevector and the Fresnel reflection coefficients.

To satisfy the requirement of a simple design structure of the selective thermal emitter and reduce the complexity of the code, only designs with one or two layers on

top of a reflective metal are analyzed. Therefore, another function *f_int_four* (vacuum – layer 1 – layer 2 – reflective metal) was written to calculate the emissivity of such a structure (see A.7).

Finally, all emissivity values for each wavelength are given back to *main_emissivity*. Then, the calculation results can be plotted over the wavelength spectrum.

3.4.2. Simulation and Validation of the Calculation Model

The simulation and visualization follow the implementation of the calculations in MATLAB. In general, simulation is known as the execution of one or more computer-aided calculations to solve a mathematical problem. Because normally a high number of parameters will be obtained, especially for complex calculations, the visualization of the results is of great importance to help the user with the interpretation of the results. [55]

The spectral emissivity for the different selective thermal emitter designs will be calculated as described before. After the material and design parameters are specified, the simulation calculates the spectral emissivity. The results are plotted over the defined wavelength spectrum.

After the simulation and visualization, the calculation model has to be validated. This is conducted by comparing the results with different publications. Three different design structures have to be validated: selective thermal emitter designs consisting of a thin film of just one material, a thin film of a matrix material doped with nanoparticles of another material, and a thin film with a surface grating.

Firstly, the simulation model is tested for thin films of SiC. The dielectric function of SiC is calculated with the Lorentz model, which is given in Equation (3.3). The values for ε_∞ , ω_L , ω_T and Γ are given by 6.7, 0.12 eV, 0.0983 eV, and $5.9 \cdot 10^4$ eV, respectively. The real and imaginary part of the refractive index of SiC are plotted in Figure 23. The results for a thin film of SiC of different thicknesses t on top of a 1 μm layer of Gold are shown in Figure 24. [14]

The dielectric function of Au is given by the Drude model from Equation (3.2) with the following values for ω_p and Γ : 9.06 eV and 0.077 eV, respectively. These values can be calculated by the data and formula from Johnson and Christy; the approach will be described further in Section 3.5.2. [56]

The emissivity spectrum of the 4 mm thin film can be seen as the emissivity of bulk SiC because the absorption depth is less than 0.4 mm. The spectral emissivity is close to zero between 10 μm and 13 μm , which is called the Reststrahlen band. The thin layers of 0.2 μm and 0.4 μm have emissivity peaks at 10.33 μm and approx. 13 μm . The latter varies with the thickness of the film. The wavelength of the first peak is called λ_{ZIM} for zero-index material because the absolute value of the dielectric function is minimal at this wavelength and would reach zero without dissipation. The second peak can be explained by a very large n and very small κ of the refractive index. The real and imaginary part of the refractive index is shown in Figure 23. These results are correspondent to the results of Narayanaswamy, Mayo, and Canetta. [14]

Figure 23: Real and imaginary part of the refractive index of SiC

Figure 24: Thin film of SiC on a layer of Au of various thicknesses

Furthermore, the spectral emissivity for a 0.4 μm thin film of polystyrene doped with a volume fractions $v_f = 10\%$ of Au nanoparticles of different radii has been calculated and validated by comparing them to the results of Ghanekar et al. (see Figure 25). The results show, that the emissivity increases for smaller radii of the nanoparticles at the same volume fraction. [51]

The dielectric function of Polystyrene is calculated by:

$$\varepsilon(\omega) = 1 + \sum_{i=1}^4 \frac{f_i}{(\omega_i^2 - \omega^2 - jg_i\omega)} \quad (3.16)$$

where the parameters f_i , ω_i and g_i are given by $f_i = [14.6, 96.9, 44.4, 136.9]$, $\omega_i = [6.35, 14.0, 11.0, 20.1]$ and $g_i = [0.65, 5.0, 3.5, 11.5]$. All values are given in the units of eV. [51]

Another dielectric function has to be applied for Au nanoparticles than for a thin film of Gold. The nanoparticles are considered homogeneous and spherical, and they also have a complex dielectric function similar to the Drude model. However, the mean free path of the free electrons is limited because of the small size of the particles. Therefore, the rate of scattering from the surface of the nanoparticle increases extremely compared to bulk scattering. To account for this effect, the Drude model is enhanced by a damping factor Γ and a surface scattering rate ω_s :

$$\omega_s = \frac{Av_f}{r} \quad (3.17)$$

where v_f is the Fermi velocity, which has the value of 1.4×10^6 m/s for Au, r is the radius of the nanoparticle, and A is a proportionality factor with a magnitude of unity. The dielectric function for Au nanoparticles that takes the size of the particle into account can then be obtained from:

$$\varepsilon(\omega, r) = \varepsilon_b(\omega) + \frac{\omega_p^2}{\omega^2 + j\omega\Gamma} - \frac{\omega_p^2}{\omega^2 + j\omega\left(\Gamma + \frac{Av_f}{r}\right)} \quad (3.18)$$

where $\varepsilon_b(\omega)$ represents the dielectric function of Au bulk material and the value for the plasma frequency of Gold ω_p is given by 9.03 eV. If the radius of the particle becomes very large, the surface scattering rate becomes zero and the dielectric function gives the same results as the dielectric function for bulk material. [57]

Figure 25: Polystyrene mixed with Au nanoparticles of various radii ($vf = 10\%$)

At last, the calculation of a surface grating of SiO_2 implemented in a layer of Si has been simulated with the generated MATLAB code. Chen, Zhang and Timans used the data for the refractive index and the extinction coefficient of Si from Palik. [58]

Then, the dielectric function can be calculated according to Equation (2.16). The dielectric function of SiO₂ for the examined wavelength region is given by: [59]

$$\varepsilon_{SiO_2}(\lambda) = 1 + \frac{0.6962\lambda^2}{\lambda^2 - 0.06840^2} + \frac{0.4079\lambda^2}{\lambda^2 - 0.1162^2} + \frac{0.8974\lambda^2}{\lambda^2 - 9.896^2} \quad (3.19)$$

The grating layer is 0.35 μm thick, the grating period is 0.24 μm and the filling ratio is 25%. The results match the results of Chen, Zhang and Timans and are plotted in Figure 26. The spectral emissivity for the TE- and TM-wave are plotted separately and only for an incident angle perpendicular to the surface. [50]

Figure 26: Surface grating of SiO₂ in Si-layer calculated for TE- and TM-wave with 0th and 2nd order EMT

The simulation model for the calculation of the spectral emissivity generates the same results presented in previous research and therefore, has been validated for these three different design structures and will be used in the following to analyze different selective thermal emitter designs for the application in TPV.

3.5. Analyzing Different Designs

To analyze different selective thermal emitter designs, the EQE of different TPV cells has to be determined. Then, the spectral region that needs to be matched by the emitter can be identified. Furthermore, the dielectric functions of possible emitter materials, and material combinations have to be determined, so that the spectral emissivity of different designs can be modeled.

3.5.1. EQE of Different TPV Cells

The EQE of the different PV cells is of great importance to this study because it indicates which selective emitter design is suitable for increasing the efficiency of the TPV system. Figure 27 shows the different EQE over the wavelength for different PV cells based on VI and III-V semiconductors. The EQE of most PV cells has high values in the region from near the band-gap to lower wavelengths. The PV cells with high EQE values in the lowest wavelength region are Si- and GaAs-cells (from 0.4 μm to 1.1 μm and from 0.4 μm to 0.9 μm). GaSb- and InGaAs- cells have a broader EQE spectrum between 0.4 μm and 1.8 μm . However, their highest values lay between approx. 1 μm and 1.8 μm . Ge-cells have lower EQE values between 1 μm and 1.6 μm . [60,61,62]

A study from Ferrari et al. regarding the state of the art in TPV research indicates that GaSb- and Si-cells are mainly used for TPV prototypes. In conclusion, a high emissivity spectrum in the range from 0.4 μm to 1.8 μm is interesting for this study. [63]

Figure 27: EQE of different PV cells [61,62]

3.5.2. Optical Properties of Selected Materials

According to a study from Ferrari et al., the most common materials for TPV prototypes with selective thermal emitters are rare earth metals and SiC. Rare earth metals itself already emit selectively in a suitable range for the TPV application, so that they are not analyzed in different design structures for this study. Furthermore, different existing studies about selective thermal emitters for TPV applications have been presented in Section 2.4. From that, the following materials have been selected for this study to be analyzed further in different combinations and structures: Si, SiC, SiO₂, Au, Ag, Copper (Cu) and W. [31,33,34,35,60]

The optical constants and/or the dielectric function of these materials and how they were obtained will be described in the following. The refractive index of SiC and therefore the dielectric function are already known from Section 3.4.2. The values for

the optical constants of Si, SiO₂, and W are obtained from Palik and the dielectric function has been calculated according to Equation (2.16). [58]

Palik compared and averaged the measured values of Si for n and κ from different investigators. The group of investigators, whose values were included, was chosen by different criteria, e.g. the quality of the sample or the accuracy of the reported values (third decimal place). The data reaches from 1.12 to 588 μm and was measured with the angle of minimum deviation technique for the near-IR and with the channel spectra technique for the far-IR. [58]

Figure 28: Real and imaginary part of the refractive index of Si

The real and imaginary part of the refractive index of Si calculated from these values for the optical constants are shown in Figure 28. It can be seen that both the real and imaginary part of the dielectric function have a high peak below 0.5 μm and

then have constant values at higher wavelengths, where the imaginary part even reaches zero.

The optical constants for crystalline SiO_2 are well studied in the IR spectral region. In contrary, there is less accurate data available in the ultraviolet (UV) region because they are generally calculated from the Kramers-Kronig analysis of the reflectance data. The data is precise between the UV and IR spectrum because it can be derived from prism data. Figure 29 shows the real and imaginary part of the refractive index of SiO_2 calculated from the values of n and κ provided by Palik. [58]

Figure 29: Real and imaginary part of the refractive index of SiO_2

Palik states, that the measured optical constants for W mostly agree with each other. From $2818 \text{ \AA}$ to $8.3 \text{ }\mu\text{m}$ the data was obtained by a calorimetric technique. The measured values might be influenced by oxidation, which however, has not been studied. Tungsten could be treated as a free-electron metal above approx. $3 \text{ }\mu\text{m}$.

However, there does not exist a definite wavelength limit at which the Drude parameters (plasma frequency and damping factor) are not influenced by the interband transition anymore. Figure 30 shows the obtained data of the real and imaginary part of the refractive index of Tungsten. [58]

Figure 30: Real and imaginary part of the refractive index of W

To implement the effect of electron scattering due to the size of nanoparticles for Tungsten, the dielectric function for W bulk material $\varepsilon_b(\omega)$ has been enhanced according to Equation (3.18). The values for the plasma frequency ω_p and the damping factor Γ are given by 5.9503 eV and 0.0537 eV, respectively. The Fermi velocity v_f is calculated from the Fermi energy of W and given by 1.4×10^{12} $\mu\text{m/s}$. [64]

The dielectric functions of the noble metals Cu, Ag, and Au can be calculated according to Johnson, and Christy. They provided the electron masses m_0 and relaxation times τ_s for these materials (see Table 4). [56]

Table 4: Optical masses m_0 and relaxation times τ for Cu, Ag, and Au [56]

	m_0 (electron masses)	τ (sec)
Copper	$(1.49 \pm 0.06)m$	$(6.9 \pm 0.7) \cdot 10^{-15}$
Silver	$(0.96 \pm 0.04)m$	$(31 \pm 12) \cdot 10^{-15}$
Gold	$(0.99 \pm 0.04)m$	$(9.3 \pm 0.9) \cdot 10^{-15}$

The optical masses of the conduction electrons is calculated by the factor given in Table 4 multiplied by the effective mass of electrons $m = 9.109 \times 10^{-31} kg$. Then, the plasma frequency ω_p and the damping factor Γ can be calculated from these values by the following equations: [56]

$$\omega_p = \sqrt{\frac{Ne^2}{\epsilon_0 m_0}} \quad (3.20)$$

$$\Gamma = \frac{1}{\tau} \quad (3.21)$$

In Equation (3.20), the value has to be divided by the permittivity of free space because the relative permittivity should be calculated. N represents for the density of conduction electrons. Johnson, and Christy assume that there is one free electron per atom. So, N is the same number as the number of atoms per unit volume and can be calculated according to:

$$N = \frac{N_a \rho_d}{m_w} \quad (3.22)$$

where N_a is the Avogadro's number, and ρ_d and m_w are the density and the molecular weight of the material, respectively. The values of these parameters are given in Table 5 for Cu, Ag, and Au. [56]

Table 5: Molecular weight m_w and density ρ_d of Cu, Ag, and Au

	m_w (kg/mol)	ρ_d (kg/m ³)
Copper	0.06355	8,950
Silver	0.10787	10,500
Gold	0.19697	19,500

From this, the plasma frequency and the damping factor are calculated. Although, Johnson, and Christy give a range for the electron masses and relaxation times, the average value has been used in this study. Then, the calculated results for the plasma frequency and damping factor have to be converted from rad/s to eV by dividing them by $h/2\pi$. The values for Copper, Silver, and Gold are listed in Table 6. [56]

Table 6: Plasma frequency ω_p and damping factor Γ for Cu, Ag and Au

	ω_p (eV)	Γ (eV)
Copper	8.8598	0.0954
Silver	29.0184	0.0212
Gold	9.0662	0.0708

Johnson, and Christy state, that the Drude model for the dielectric function is only valid for wavelength above approximately 1.9 μm . For higher energies, they provide a table with the measured values for the optical constants n and κ to obtain the dielectric function. This is also implemented in the MATLAB calculations involving Copper, Silver, and Gold. The real and imaginary part are plotted in Figure 31 for Au. [56]

Figure 31: Real and imaginary part of the refractive index of Au

3.5.3. Selective Thermal Emitter Designs

As described in Section 3.3, the three design structures that can be simulated are thin films of single materials as well as doped materials and surface gratings. As one of the selective thermal emitter requirements is a more simple design structure to decrease the fabrication complexity, the focus will lie on doped materials rather than surface gratings.

The emissivity spectrum will be simulated for different thin film structures of the selected materials. Furthermore, the materials will be doped with nanoparticles to analyze the change of spectral emissivity. The aim is to reach a design that has a high emissivity between $0.4 \mu\text{m}$ and $1.8 \mu\text{m}$ and a very low emissivity at all other wavelengths.

3.6. Experimental Measuring Methods

There are only few experimental investigations of the spectral emissivity to verify the numerical calculations. These experimental examinations are important to ensure the practicability of selective thermal emitters in various applications. At first, four basic measuring methods are presented. Then, the Fourier Transform Infrared (FTIR) spectroscopy is described as a common experimental setup to measure the spectral emissivity.

3.6.1. Basic Measuring Methods

There exist many different methods to measure the spectral emissivity. However, none of the developed methods is universally applied. He et al. introduced four basic methods to estimate the emissivity spectrum of a sample: The calorimetric method, the optical reflectivity method, the multispectral radiation thermometry, and radiation energy method. [46]

For the calorimetric method, the sample has to be heated up and an energy balance helps in determining the emissivity. Therefore, the heat power delivered to the sample, the temperatures of the emitting surface of the sample, and the surroundings in a vacuum are measured over time. To be sufficient accurate, this method requires a well-insulated sample on the side and back, and the parasitic heat losses must be accounted for. [65]

The reflectivity method is the experimental method to determine the spectral emissivity corresponding to the presented calculations in Section 2.1.1. Experimentally, the sample is illuminated with infrared energy and the percentage of

energy reflected from the surface is measured. Then, the emissivity is calculated from the reflectance and the use of Kirchhoff's law. [46]

The multispectral radiation thermometry conducts measurements of the radiation at three or more wavelengths as well as an emissivity model. The sample-preparation is not effortful and the temperature is not limited for this method. However, its accuracy is low and there is no common model that can be applied for all the materials. [66]

The energy method is the most widely used method to assess the emissivity of a sample. It takes the ratio of the radiation power of the sample surface over the radiation power of a black body at the same temperature. The main problem regarding its accuracy is to select a suitable black body for the measurement. [46]

3.6.2. Emissivity Measurement with FTIR

FTIR is a method for measuring infrared spectra of samples. This method is especially applied as a chemical analysis of the different molecules and their concentration in the sample. FTIR uses the fact that the peak positions in an infrared spectrum depend on the molecular structure. Furthermore, FTIR has the following characteristics. Because of the low energy of electromagnetic waves, they rarely damage the sample. Additionally, the sample can be in various states, like solid, crystal, fiber, film, liquid or gas. Infrared spectroscopy can use infrared absorption, reflection, emission, as well as photo acoustic spectroscopy. [67]

These interferometers can be designed in different ways, but the basics of interferometer operation are similar for all interferometer types. Most common today is the Michelson interferometer (see Figure 32). This interferometer consists of an

infrared source, three mirrors, a beam splitter, and a detector. The collimating mirror collects the light from the source and works parallelizing. Additionally, there is a fixed and a moving mirror. In the middle of the three mirrors is a beam splitter, which partly transmits the light towards the fixed mirror, and partly reflects the light towards the moving mirror. After that, the mirrors reflect the light back to the beam splitter, where they are recombined into one light beam that interacts with the sample and then reaches the detector. The optical design of a Michelson interferometer is shown in Figure 32. [68]

Depending on the optical path difference, the reflected waves interfere constructively or destructively and thus, generate periodic intensity. Finally, this interferogram will be Fourier transformed into an infrared spectrum. [68]

Figure 32: Structure of Michelson interferometer [68]

FTIR offers two methods, the direct and the indirect method, to measure the spectral emissivity of a sample. The direct method takes the ratio of the sample radiation and the blackbody radiation to generate the emissivity spectrum, which

corresponds to the energy method. The indirect method corresponds to the reflectivity method and the emissivity spectrum is generated from the measured transmission and reflectivity of the sample. [69]

Moreover, FTIR has several practical advantages. The biggest advantage is that the whole spectrum is detected simultaneously. In addition, FTIR has a very high increase in source throughput over the infrared frequency range. [67]

CHAPTER 4 – FINDINGS

In order to find a selective thermal emitter design, that can be applied to enhance the efficiency of a TPV system, different design combinations are analyzed. In the following, the spectral emissivity results of various thin film designs are presented. Thin films of a single material with various thicknesses, doped materials of various thicknesses as well as different volume fractions and radii of the nanoparticles and surface gratings with different dimensions are examined. Furthermore, a sample experimental measurement of the spectral emissivity of two specimens is conducted and the results are compared to the corresponding calculations.

4.1. Spectral Emissivity of Different Thin Film Structures

Initially, the spectral emissivity of a thin film of one single material deposited on a 1 μm layer of Gold is calculated. The thickness of the thin film is varied and also compared to the spectral emissivity of bulk material. Therefore, a first impression can be gained on the shifting of emissivity spectrum for different materials and various thicknesses of thin films.

Figure 33 shows the results of the spectral emissivity for Si-layers of different thicknesses t (0.1 μm , 0.4 μm , 0.8 μm and 0.4 mm). The spectral emissivity for bulk material (0.4 mm) is almost constant at a value of 0.68 between wavelengths from 0.8 μm to 2.8 μm . The thin films of Si have high emissivity peaks (approx. 0.77) between 0.5 μm and 0.8 μm , which decrease and shift slightly to a higher wavelength

with increasing layer thickness. Above a wavelength of 1 μm , small peaks up to 0.2 can be seen. These peaks also shift to the right for thicker layers. In addition, the described peaks have the same maximum value but they widen over a larger wavelength range.

Figure 33: Spectral emissivity of a thin film of Si of various thicknesses t on a 1 μm Au layer

Furthermore, selective thermal emitters made of SiO_2 -layers with thicknesses of 0.1 μm , 0.4 μm , 0.8 μm and 0.4 mm are simulated. The spectral emissivity of the thin films varies regarding the height of the peaks, which can be identified at wavelengths of approx. 8 μm , 8.6 μm , 9.4 μm and 12.3 μm . The two latter peaks split into two peaks very close to each other for thicker films. The second peak occurs at a wavelength of 9.7 μm and 12.6 μm , respectively. The emissivity of bulk SiO_2 shows an inversed peak at these wavelengths. Moreover, the emissivity of bulk SiO_2 is high between 6 μm and 8 μm as well as above 9.4 μm and shows peaks at 8.6 μm and

9.4 μm . For a thin film of 0.1 μm the last three peaks almost vanish. Comparing the spectral emissivity to the refractive index of SiO_2 shows that they clearly are dependent. The results for the SiO_2 -films of different thicknesses on a 1 μm Au-layer are illustrated in Figure 34.

Figure 34: Spectral emissivity of thin films of SiO_2 of various thicknesses t on a 1 μm Au layer

At last, the spectral emissivity of Gold, Silver, Copper, and Tungsten are calculated. The results show that the emissivity spectra of these materials do not change for different layer thicknesses or bulk material. The cause of this might be that these materials are highly reflective metals. Au, Ag, and Cu have a constant emissivity value for wavelengths longer than approx. 1 μm . Ag has the lowest emissivity value close to zero. The emissivity value of Au, and Cu lie around 0.019 and 0.026, respectively. For shorter wavelengths, all three metals show a high emissivity between 0.62 and 0.83. As mentioned in Section 3.5.2, W can be treated as a free-electron

metal for wavelengths above approx. 3 μm . This can also be seen by the emissivity value that stays almost constant at approximately 0.03 for wavelength above 4 μm . For short wavelengths below 1 μm , the emissivity is above 0.5 and then decreases. The calculated results are presented in Figure 35.

Figure 35: Spectral emissivity of a 1 μm Cu, Ag, Au and W layer

4.2. Spectral Emissivity of Different Doped-Materials

In the following, the calculated spectral emissivity of selective thermal emitters consisting of thin films made of Silicon, Silicon Carbide, and Silicon Dioxide doped with different materials are presented. To analyze the effect of different design parameters, the surface thickness, the particle radius, and the volume fraction have been varied.

4.2.1. Doped Silicon

A selective thermal emitter design of a thin film of Si doped with Au nanoparticles is analyzed. The particle size is set to be 50 nm in diameter and the volume fraction of particles in the host material is 25%. Figure 36 shows the spectral emissivity results for doped Si thin films of different thicknesses on a 1 μm Au layer.

Figure 36: Spectral emissivity of Si-thin films of various thicknesses t doped with Au nanoparticles of $r = 25 \text{ nm}$ and $vf = 25\%$

From Figure 33, it can be seen that Si films without embedded nanoparticles also show a high emissivity up to 0.8 for short wavelengths up to 1 μm . Doping of the material with Au particles increased the peaks up to almost 0.9, but also shifted and widened the peaks towards higher wavelengths. This effect gets more intense for thicker films. A very thin film of 0.1 μm shows an emissivity of almost zero above 3 μm , where Si still has emissivity peaks up to a value of 0.2. Bulk material of Si

doped with Au particles shows the same peak as the thin films for wavelength below 1 μm , but reaches a constant value of 0.55 for wavelengths above 2 μm .

Subsequently, the spectral emissivity of a 0.4 μm thick film of Si doped with Au nanoparticles of the same size on a 1 μm Au layer is simulated for different volume fractions from 5% to 30% (see Figure 37). It can be observed, that the peaks shift to higher wavelength regions and increase in their value.

Figure 37: Spectral emissivity of 0.4 μm Si-thin films doped with Au nanoparticles of $r = 25$ nm and various volume fractions vf

Moreover, the radius of Au nanoparticles is varied for a 0.4 μm thin film of doped Si. The radius is set to 1 nm, 10 nm, 25 nm, and 50 nm. For the radii of 10 nm, 25 nm, and 50 nm, distinct peaks can be identified below a wavelength of 3 μm . The change in spectral emissivity of these designs is minimal, but it increases with decreasing radius. For a radius of 1 nm, the peak values decrease except for the last peak at

2.8 μm . However, the overall spectral emissivity increases, so that no distinct peaks can be identified anymore. The results are displayed in Figure 38.

Figure 38: Spectral emissivity of 0.4 μm Si-thin films doped with Au nanoparticles of $v_f = 25\%$ and various radii r

To see how different particle materials influence the spectral emissivity, a 0.2 μm thin film of Si, Si doped with Au, SiO_2 , and W nanoparticles ($r = 25 \text{ nm}$, $v_f = 10\%$) are compared (see Figure 39). The emissivity spectrum of Si and Si doped with SiO_2 are very similar. The latter only shifts to the left for approx. 0.05 μm . The spectrum shifts to the right and the emissivity peaks enhance greatly for Au nanoparticles. Tungsten nanoparticles increase the spectrum further, also over the whole spectrum between 0.5 μm and 2 μm . These results show, that W enhances the emissivity of the material exactly in the wavelength region that is of interest for the application of this study.

Figure 39: Spectral emissivity of 0.2 μm Si-thin films doped with different nanoparticles of $r = 25 \text{ nm}$ and $vf = 10\%$

4.2.2. Doped Silicon Carbide

As Tungsten shows a great enhancement of the emissivity in the wavelength region of interest, another selective thermal emitter design of a thin film of SiC doped with W nanoparticles on a $1 \mu\text{m}$ Au layer is analyzed. The nanoparticles have a radius of 25 nm and the volume fraction of particles in the host material is 25%. At first, the influence of the thickness of doped SiC thin films is analyzed by varying the thickness from $0.1 \mu\text{m}$ to $0.5 \mu\text{m}$ and comparing it to bulk material (0.4 mm). The distinct peaks of SiC thin films can still be seen at $10.3 \mu\text{m}$ and between $12 \mu\text{m}$ and $13 \mu\text{m}$, but they decrease with a decreasing thickness. This design creates a high spectral emissivity between 0.6 and 0.9 at wavelengths below $3 \mu\text{m}$. The emissivity of the $0.1 \mu\text{m}$ thin

film almost reaches zero for wavelengths over 3 μm . Similar to doped Si thin films, the emissivity spectrum widens for larger thicknesses and additional peaks split from the low wavelength region. Bulk material (0.4 mm) has a high emissivity at 0.7 in average until 10.3 μm , which then decreases rapidly to almost zero. These results are shown in Figure 40.

Figure 40: Spectral emissivity of SiC-thin films of various thicknesses t doped with W-nanoparticles of $r = 25 \text{ nm}$ and $vf = 25\%$

Furthermore, the effect of different volume fractions is analyzed, which is varied from 5% to 30%. The thickness of the thin film is selected to be 0.1 μm because this reduces the emissivity to almost zero for wavelength above 2 μm . The particle radius is 10 nm and the doped SiC is deposited on a 1 μm Au layer. The emissivity peaks that can be seen for a volume fraction of 5% at approx. 0.4 μm and 1.3 μm increase and widen with higher fractions. For a volume fraction of 30%, the emissivity decreases

again. A volume fraction of 20% (red) shows promising results for TPV application. The results are shown in Figure 41.

Figure 41: Spectral emissivity of 0.1 μm SiC-thin films doped with W-nanoparticles of $r = 10$ nm and various volume fractions vf

As the data for the dielectric constants of Tungsten are extracted from Palik and no research on a function model is available that includes the effect of different radii, the change of this design parameter shows no effect on the calculations. However, concluding from the size effects of Au nanoparticles, this might result in even higher emissivity values in this region.

To observe the effect caused by doping materials, various thin film of SiC are plotted along with SiC doped with Au and W nanoparticles in Figure 42. All designs result in a spectral emissivity close to zero in the Reststrahlen band. Pure SiC shows emissivity values between 0.2 and 0.4 below 2 μm . For higher wavelengths, the

spectrum changes significantly with different magnitudes of the thickness. The plot illustrates clearly that doping the dielectric material with metal nanoparticles can significantly enhance the emissivity in this region.

Figure 42: Comparison of the spectral emissivity of SiC-thin films with various thicknesses and doped with different nanoparticles

4.2.3. Doped Silicon Dioxide

The third material, on which the effect of doping has been analyzed, is SiO₂. Therefore, SiO₂ films of different thicknesses doped with W nanoparticles with a radius of 25 nm and a volume fraction of 10% have been analyzed. The emissivity peaks of SiO₂ thin films (see Figure 34) can also be identified for doped SiO₂. However, they decrease with a decreasing layer thickness. The high emissivity at very short wavelengths widens from below 0.5 μm (SiO₂ thin films) up to 1.8 μm (doped

SiO₂ thin films). This wavelength region widens with the layer thickness. The calculated emissivity is plotted in Figure 43.

Figure 43: Spectral emissivity of SiO₂-thin films of various thicknesses t doped with W-nanoparticles of $r = 25$ nm and $\nu f = 25\%$

As mentioned before, the dielectric function resulting from the optical constants of Tungsten does not take care of the scattering effect caused by the size of the particles. Thus, the spectral emissivity does not change for different radii and only the effect of different volume fractions is analyzed. The results for a 0.1 μm thin film of SiO₂ doped with W for volume fractions from 5% to 30% are shown in Figure 44. For wavelengths shorter than 2 μm , the emissivity increases with increasing volume fraction. Subsequently, the spectral emissivity decreases to the same value close to zero. The 0.1 μm thin film of doped SiO₂ with a volume fraction of 30% shows

emissivity values up to 0.9 in the wavelength region from 0.8 μm to 1.3 μm , which is useful for applying this design in TPV systems.

Figure 44: Spectral emissivity of 0.1 μm SiO_2 -thin films doped with W-nanoparticles of $r = 10 \text{ nm}$ and various volume fractions

4.3. Spectral Emissivity of Different Surface Gratings

In this section, the spectral emissivity of selective thermal emitters consisting of surface gratings made of Silicon Carbide, or Silicon Dioxide combined with Tungsten is calculated. To analyze the effect of the different design parameters, the thickness of the surface grating, the period, and the filling factor have been varied. Subsequently, Tungsten is replaced by Au and Cu and the spectral emissivity is compared for the

same design structure. The basic design of the analyzed surface gratings is illustrated in Figure 45. The calculated results are presented in the following.

Figure 45: Analyzed surface grating structure of SiC or SiO₂ and Tungsten

4.3.1. Silicon Dioxide and Tungsten Surface Gratings

Initially, different surface gratings consisting of SiO₂ and W are simulated. The variation of the layer thickness shows similar effects to doped materials. The emissivity spectrum widens but also decreases with increasing thickness. The emissivity peaks characteristic for SiO₂ can still be identified, but they are almost suppressed by very thin films of 0.05 μm to 0.1 μm . The calculated results for the spectral emissivity of various thicknesses are illustrated in Figure 46.

Figure 46: Spectral emissivity of SiO₂ and W surface gratings with various thicknesses t ($L = 100$ nm, $\phi = 50\%$)

Furthermore, the period and filling ratio of a $0.1 \mu\text{m}$ thin surface grating have been varied because the emissivity is close to zero for wavelengths longer than $2 \mu\text{m}$. The calculated results for a filling ratio of 50% with various periods are shown in Figure 47 and for a period of 200 nm with different filling ratios in Figure 48.

Different periods especially show a change of the spectral emissivity below wavelengths of $0.5 \mu\text{m}$, which increases for smaller periods from values below 0.5 ($L = 0.2 \mu\text{m}$) to 0.75 ($L = 0.05 \mu\text{m}$). The spectral emissivity does not change significantly for higher wavelengths and no trend depending on the period can be determined. The highest value over 0.8 occurs for a period of $0.1 \mu\text{m}$. A similar trend can be observed for different filling ratios. The emissivity increases for a higher ratio below $0.5 \mu\text{m}$. Furthermore, it decreases for wavelengths above $1.4 \mu\text{m}$ and no trend can be identified for the wavelength region in between.

Figure 47: Spectral emissivity of 100 nm SiO₂ and W surface gratings with various periods L ($\phi = 50\%$)

Figure 48: Spectral emissivity of 100 nm SiO₂ and W surface gratings with various filling ratios ϕ ($L = 200 \text{ nm}$)

The spectral emissivity of a selective thermal emitter made of a $0.1 \mu\text{m}$ surface grating of SiO_2 and W with a period of 200 nm and a filling ratio of 50% reaches up to 0.8 between wavelengths of $0.8 \mu\text{m}$ to $1.3 \mu\text{m}$. This outcome matches the spectrum of interest for the application for TPV systems.

4.3.2. Silicon Carbide and Tungsten Surface Gratings

Subsequently, the spectral emissivity of SiC and W surface gratings has been analyzed. The spectral emissivity reaches local maxima up to 0.74 below $2 \mu\text{m}$, which decrease with an increasing grating thickness. Moreover, the spectrum widens and shifts to higher wavelengths. The calculated emissivity spectra are plotted in Figure 49.

Figure 49: Spectral emissivity of SiC and W surface gratings with various thicknesses t ($L = 200 \text{ nm}$, $\phi = 50\%$)

Figure 50: Spectral emissivity of 50 nm SiC and W surface gratings with various periods L ($\phi = 50\%$)

Figure 51: Spectral emissivity of 50 nm SiC and W surface gratings with various filling ratios ϕ ($L = 100 \text{ nm}$)

Figure 50 and Figure 51 show the spectral emissivity of a 50 nm SiC and W surface grating with varied period and filling ratio. The period has been varied from 0.05 μm to 0.2 μm with a ratio of 50% and the ratio was increased from 30% to 70% with a period of 0.1 μm . The highest emissivity value suitable for the application of this study has been reached with a period of 0.1 μm and a filling ratio of 70%, which reaches 0.9 at a wavelength of 0.9 μm .

Subsequently, the spectral emissivity of SiC surface gratings combined with different metals (Au, Cu, and W) is shown in Figure 52. Au and Cu result in almost the same spectral emissivity that reaches values around 0.7 between wavelengths of 0.2 μm and 0.5 μm . However, the emissivity is significantly lower in the interesting wavelength region than the emissivity of SiC and W surface gratings.

Figure 52: Spectral emissivity of SiC-Au, SiC-Cu and SiC-W surface gratings ($t = 50$ nm, $L = 100$ nm, $\phi = 70\%$)

4.4. Evaluation of Results

In this section, the results that showed a great enhancement of the spectral emissivity in the wavelength region between 0.4 μm and 1.8 μm are compared to the EQE-spectrum of different TPV cells. The design options most suitable for the EQE of GaSb (black) and InGaAs (grey) are SiC doped with W ($t = 0.1 \mu\text{m}$, $r = 10 \text{ nm}$, and $\nu f = 20\%$), SiO₂ doped with W ($t = 0.1 \mu\text{m}$, $r = 10 \text{ nm}$, and $\nu f = 30\%$), and a surface grating of SiO₂ and W ($t = 0.1 \mu\text{m}$, $L = 0.2 \mu\text{m}$, and $\phi = 50\%$). The different emissivity and EQE spectra are compared in Figure 53.

Figure 53: Comparison of different spectral emissivity results to the EQE of a GaSb and InGaAs

Another selective emitter design consisting of a SiC and W surface grating ($t = 50 \text{ nm}$, $L = 100 \text{ nm}$, $\phi = 70\%$) matches the EQE-spectrum of Si- and GaAs-cells. This design reaches emissivity values between 0.65 and 0.9 in the wavelength region from 0.4 μm to 1 μm . This wavelengths region corresponds to the EQE spectrum of Si

and GaAs. The comparison of the emissivity and EQE spectrum is shown in Figure 54.

Figure 54: Comparison of spectral emissivity result to the EQE of Si and GaAs

4.5. Experimental Measurements

Besides theoretical calculations, experimental measurements of different selective emitter designs are also important to study and verify their effects. Therefore, Copper plates are spray-coated with silicon-carbide nanoparticles and Silver nanoparticles. After that, the emissivity is measured with the FTIR using the reflectance method.

4.5.1. Sample Fabrication

The sample is fabricated via spray coating. Two samples are generated; one Copper plate is spray-coated with SiC nanoparticles and the other one is spray-coated with SiC and Ag nanoparticles. The SiC nanoparticles have a diameter of 45-65 nm

and the Ag nanoparticles of less than 100 nm. For spray-coating, the Cu plates a 0.1 wt.% solution consisting of SiC nanoparticles and ethanol is mixed. After the Copper plates are cleaned with standard acetone, the sample is heated up to 300 °C on a hot plate, so that the ethanol evaporates quickly after being applied to the Cu plate. The solution is filled into an airbrush-spray-gun, which is controlled by compressed air (20-30 PSI). The airbrush is pointed perpendicular to the surface of the plate for spray-coating. When the solution is applied, the ethanol evaporates and the film of SiC nanoparticles stays on the plate. The same procedure is conducted with a solution of 0.1 wt.% SiC and 0.1 wt.% Ag nanoparticles.

After the sample has been fabricated, the results are viewed with the Scanning-Electron-Microscopy (SEM) to approximate the thickness and the uniformity of the coating. The SEM can be used to examine the microstructural characteristics of solid objects. It provides images with a very high resolution in the order of 1-5 nm (10-50 Å). Heterogeneous organic and inorganic materials can be observed on a nanometer to micrometer scale. Besides its high resolution, SEM became popular due to the three-dimensional-like images that can be obtained. The SEM works with a fine electron beam focused on the specimen, that either sweeps across the surface in a raster to obtain images or stays in one position to obtain an analysis. This electron beam interacts with the sample and generates different signal types, like secondary electrons, backscattered electrons, characteristic x-rays, and other photons of various energies. The secondary and backscattered electrons vary due to changes in the surface topography and thus, can be used to obtain an image of the surface. The images appear to be three-dimensional due to the large field depth of the SEM and to the shadow

relief effect of the secondary and backscattered electron contrast. The SEM can also help analyzing the composition of the specimen by using characteristic x-rays. These x-rays originate from the electron bombardment and give qualitative identification and quantitative elemental information of the specimen. [70]

Figure 54 shows different images of the Cu plate coated with SiC nanoparticles generated by the SEM. The thickness of the coating can be estimated from the side view of the specimen shown in a). It is less than $8.6\ \mu\text{m}$ because the image was taken from an angle of 53° . Figure 54 b) and c) allow a closer look at the surface of the coating. As expected, the surface is not uniform and clusters of nanoparticles are seen. By further zooming in, it becomes apparent that one particle is less than $100\ \text{nm}$ in diameter. Figure 54 d) shows an image of the x-ray analysis of the material composition from the edge of the specimen. The yellow part indicates the Cu plate and the SiC coating (red) ends before the edge.

Figure 55: SEM images of a Cu-plate coated with SiC nanoparticles

Figure 55 a) shows an image of the surface of the Cu plate spray-coated with SiC and Ag nanoparticles. Furthermore, Figure 55 b) shows the results of the x-ray microanalysis of the surface where Si and Ag are the main appearing materials.

Figure 56: SEM images of a Cu-plate coated with SiC and Ag nanoparticles

4.5.2. FTIR Results

After the samples have been fabricated, their spectral emissivity is measured using the FTIR. The spectral emissivity is obtained by the indirect method through the measurement of the reflectance. Therefore, the Attenuated Total Reflectance (ATR) method is used. The FTIR works with the same principles as described in Section 3.6.2. However, the ATR is mounted to the FTIR to measure the reflectance. The sample is mounted onto a Ge-crystal and they need to be in close contact. Then, an IR-beam is directed to the crystal from below. The high refractive index of Ge results in an internal reflectance, which creates an evanescent wave, that interacts with the sample. This evanescent wave is then reflected and passed back to the IR beam and to the detector. [71]

The results of the FTIR measurements for both specimens are illustrated in Figure 57. Both samples show the same shape of the spectral emissivity curve, but the

SiC-Ag sample creates higher values. The peak is at the same location (between 12 μm and 13 μm) as the simulated peak for a SiC thin film. However, the coated layer is much thicker and not uniform, so that no distinct emissivity peaks can be expected.

Figure 57: Results of the FTIR-measurement for the spectral emissivity of the coated samples

Another hypothesis to explain the existence of only one emissivity peak at approx. 12.7 μm might be that only the spectral emissivity of the TM-wave has been determined. Figure 58 shows the calculated spectral emissivity of a 1 μm thin film of SiC on a 1 μm Cu layer. It can be seen, that the emissivity for the TE-wave shows two peaks, while the emissivity for the TM-wave only shows one peak between 12 μm and 13 μm .

Figure 58: Spectral emissivity of a 1 μm SiC thin film on a 1 μm Cu layer calculated for the TE- and TM wave

CHAPTER 5 – CONCLUSION

In this study different materials and selective thermal emitter designs have been analyzed regarding their emissivity spectrum. The aim was to find selective thermal emitter designs suitable for the application in TPV systems to enhance their efficiency.

Therefore, an insight into the general framework and the basic physical principles of this study, the fundamentals of thermal radiation as well as the functionality and the composition of selective thermal emitters and TPV systems in general have been given. Based on the physical principles of thermal radiation a MATLAB code has been generated, that allows the calculation of selective thermal emitter designs consisting of thin films of a single material. This code has been extended by implementing the Maxwell-Garnett-Mie theory for doped materials and the Effective-Medium theory for surface gratings. The analysis of the current state of the art on this research topic indicated a reference point for the analysis regarding materials and material combinations suitable for the TPV application. Subsequently, many different selective thermal emitter designs have been analyzed.

The results of the analysis was compared to the characteristic wavelength regions of different TPV cells, which lie in the wavelength range from 0.4 μm to 1.8 μm . Different material structures that generate high emissivity values in the wavelength range of interest, have been developed. Promising designs that meet the requirements for the application in TPV are dielectric materials doped with nanoparticles of a reflective metal and surface gratings consisting of dielectric materials and metals.

Emissivity values of up to 0.9 have been generated in the wavelength region of interest for SiC or SiO₂ doped with W nanoparticles and surface gratings consisting of SiC or SiO₂ and W.

Furthermore, simple selective thermal emitter samples are generated by spray-coating SiC and Ag nanoparticles on Cu plates. These specimens are measured with the FTIR and compared to the calculated results. The results differ from the calculated results because the fabrication technique was not sufficient accurate. However, a fabrication of various samples with a smaller magnitude and higher accuracy would have extended the resources and scope of this study.

This study gives valuable insights in different design opportunities for selective thermal emitters that can be applied for TPV systems. Four matching design structure consisting of surface gratings or doped materials have been identified. Taking into account, that the selective thermal emitter designs require less complexity to establish on the market, doped materials show very good results for the application in TPV systems and require less fabrication expenses. As this study covers a recently developed research field, every contribution is valuable. The generated MATLAB code can be used to analyze further designs. Additionally, it can be extended by implementing the optical properties of other materials.

The analysis resulted in promising selective thermal emitter designs that can be applied for TPV systems. The developed designs match the evaluated requirements and have emissivity values of more than 0.8 in the wavelength region of interest. There are references that state an influence of the radius of Au nanoparticles, which is not taken into account with the dielectric function for bulk material. This effect has not

been considered for other reflective metals, like Tungsten or Silver, because there was no information available. Furthermore, the experimental results are very inaccurate due to improvement possibilities of the fabrication resources.

Studying the size effect of different metal nanoparticles should be considered in the future work on this topic. Furthermore, not many studies can be found that consider the radius of nanoparticles. Moreover, it is of great importance to conduct experimental measurements to study other conditions of the environment that cannot be included in theoretical calculations. One factor could be the temperature that might change the material properties which again affects the emissivity spectrum.

APPENDICES

A.1: MATLAB code for *main_emissivity*

main emissivity

```
clearvars -except E1 E2 E3 E4 E5; clc; close all; format compact;
```

load parameters and constants

```
load e_data;
% first data table
lamda = e_W_data(:,1); % wavelength in micron data

% second data table\interpolation
% lamda2 = e_Si_data(:,1);
% y2 = e_Si_data(:,2);
% y3 = e_Si_data(:,3);

% e_Si_data = [];
% e_Si_data(:,1) = lamda;
% e_Si_data(:,2) = interp1(lamda2,y2,lamda);
% e_Si_data(:,3) = interp1(lamda2,y3,lamda);

% lamda2 = e_SiO2_data(:,1);
% y2 = e_SiO2_data(:,2);
% y3 = e_SiO2_data(:,3);

% e_SiO2_data = [];
% e_SiO2_data(:,1) = lamda;
% e_SiO2_data(:,2) = interp1(lamda2,y2,lamda);
% e_SiO2_data(:,3) = interp1(lamda2,y3,lamda);

%lamda = linspace(0.1,16,600); % wavelength vector in micron

n=3; % layer number
f_parameter;
```

loop

```
for i=1:length(e_Si_data)
    %1:length(lamda) % for wavelength vector
    %1:length(e_W_data) % for wavelength data

% selective emitter materials & structure
% 1st layer
t(1) = 1; % layer thicknesses in micron
m(1) = 1; % m (non-magnetic)
e(i,1) = 1; % e (free space)
% 2nd layer
```

```

t(2)      = 400;                                % layer thickness in micron
m(2)      = 1;                                % m (non-magnetic)
%e(i,2) = e_SiC(lamda(i),c,h);                % e of 2nd layer (SiC)
%[e(i,2),vf,r] = e_np(lamda(i),c,h,i);        % e of 2nd layer (nanoparticles)
%[e_te,e_tm] = e_grating(lamda(i),c,h);        % e of 2nd layer (grating)
e(i,2) = (e_W_data(i,2) + 1i * e_W_data(i,3))^2; % e of 2nd layer (W data)
e(i,2) = (e_Si_data(i,2) + 1i * e_Si_data(i,3))^2; % e of 2nd layer (Si data)

% 3rd layer
t(3)      = 1;                                % layer thickness in micron
m(3)      = 1;                                % m (non-magnetic)
%e(i,3) = e_SiC(lamda(i),c,h);                % e of 3rd layer (SiC)
%e(i,3) = e_BN(lamda(i),c,h);                % e of 3rd layer (BN)
%e(i,3) = (e_W_data(i,2) + 1i * e_W_data(i,3))^2; % e of 3rd layer (W data)
e(i,3) = (e_Si_data(i,2) + 1i * e_Si_data(i,3))^2; % e of 3rd layer (Si data)
%e(i,3) = e_Au(lamda(i),c,h);                % e of 3rd layer (Au)

% 4th layer
t(4)      = 1;                                % layer thicknesses in micron
m(4)      = 1;                                % m (non-magnetic)
e(i,4) = e_Au(lamda(i),c,h);                % e of 4th layer (Au)

% integral over incident angles
if sum(e_te) ~= 0
    [int_part_te,int_part_tm,int_part] =
        f_int_grating(i,e,e_te,e_tm,m,t,w,c,lamda); % grating integral part
    E_te(i) = (lamda(i) / 2 / pi)^2 * int_part_te; % emissivity TE
    E_tm(i) = (lamda(i) / 2 / pi)^2 * int_part_tm; % emissivity TM
    E(i) = (lamda(i) / 2 / pi)^2 * int_part; % emissivity TE & TM
else
    if n == 4
        int_part = f_int_four(i,e,m,t,w,c,lamda); % 4 layer integral part
    else
        int_part = f_int(i,e,m,t,w,c,lamda); % 3 layer integral part
    end
    E(i) = (lamda(i) / 2 / pi)^2 * int_part; % emissivity TE & TM
end
end

```

plot

```

figure;
if sum(E) ~= 0
    plot(lamda,E); % plot TE & TM
else
    hold all;
    plot(lamda,E_te); % plot TE
    plot(lamda,E_tm); % plot TM
    legend('E_{TE}','E_{TM}');
end

% format plot
title('Spectral Emissivity');
ylabel('\epsilon(\lambda)');
xlabel('Wavelength \lambda in \mu m');
xlim([lamda(1) lamda(end)]);
ylim([0 1]);

```

A.2: MATLAB code for $f_parameter$

parameter and constants

```
% incident spectrum
c      = 299792458e6;           % speed of light in micron/s
f      = c./lamda;             % frequency in Hz
h      = 4.135e-15;           % eV*s
w      = 2*pi*f;               % angular frequency in rad/s

% layer thickness allocation
t      = zeros(1,n);

% e allocation
e = zeros(length(lamda),n);    % 1st ... 3rd layer

% e_te allocation
e_te = 0;

% m allocation
m = zeros (1,n);

% kz allocation
kz = zeros(length(lamda),n);

% kz_te allocation
kz_te = zeros(length(lamda),1);

% kz_tm allocation
kz_tm = zeros(length(lamda),1);

% r_te allocation
r_te = zeros(length(lamda),n-1);

% r_tm allocation
r_tm = zeros(length(lamda),n-1);

% R_te allocation
R_te = zeros(length(lamda),n-1); %R12 | R23

% R_tm allocation
R_tm = zeros(length(lamda),n-1);

% E allocation (E(lamda))
E = zeros(length(lamda),1);
% E_te E_tm allocation (E(lamda))
E_te = zeros(length(lamda),1);
E_tm = zeros(length(lamda),1);
```

A.3: MATLAB code for e_{np}

```
function [e,vf,r] = e_np(lamda,c,h,i)

load e_data;
f      = c/lamda; % frequency in Hz
w      = h*f;     % photon energy in eV

% Material parameters
r      = 0.025; % radius of nanoparticles in micron
vf     = 0.5; % volume fraction in percent
%e_m   = e_SiC(lamda,c,h); % dielectric function of matrix
e_m    = (e_Si_data(i,2) + 1i * e_Si_data(i,3))^2;
e_np   = e_Au_np(lamda,c,h,r); % dielectric function of nanoparticles
%e_np  = (e_W_data(i,2) + 1i * e_W_data(i,3))^2;

% Size parameters
x_m    = w*r*sqrt(e_m)/c;
x_np   = w*r*sqrt(e_np)/c;

% 1st order spherical Bessel function
j_xm   = f_besselj(1,x_m);
j_xm_d = f_besselj_d(1,x_m);
j_xnp  = f_besselj(1,x_np);
j_xnp_d = f_besselj_d(1,x_np);

% 1st order spherical Hankel function
h_xm   = f_besselh(1,1,x_m);
h_xm_d = f_besselh_d(1,1,x_m,1);
h_xnp  = f_besselh(1,1,x_np);
h_xnp_d = f_besselh_d(1,1,x_np,1);

% 1st order Riccati-Bessel functions
Psi_xm = j_xm;
Psi_xm_d = j_xm_d;
Psi_xnp = j_xnp;
Psi_xnp_d = j_xnp_d;
Xi_xm   = h_xm;
Xi_xm_d = h_xm_d;
Xi_xnp  = h_xnp;
Xi_xnp_d = h_xnp_d;

% 1st electric Mie coefficient
a_1 = ((sqrt(e_np) * Psi_xnp * Psi_xm_d) - (sqrt(e_m) * Psi_xm * Psi_xnp_d))/
      ((sqrt(e_np) * Psi_xnp * Xi_xm_d) - (sqrt(e_m) * Xi_xm * Psi_xnp_d));

% Maxwell Garnett Mie
a_MGM = (3 * 1i * c^3) / (2 * w^3 * e_m^(3/2)) * a_1;

% Clausius Mossotti equation for effective dielectric function
e      = e_m * (r^3 + 2 * a_MGM * vf) / (r^3 - a_MGM * vf);

end
```

A.4: MATLAB code for $e_grating$

```
function [e_tm2,e_te2] = e_grating(lamda,c,h)

% parameter
L = 1; % grating period in micron
phi = 0.4; % filling ratio in percent
e_a = e_SiC(lamda,c,h); % grating material a
e_b = 1; % grating material b

% 0th order EMT
e_te0 = phi * e_a + (1 - phi) * e_b;
e_tm0 = 1 / (phi / e_a + (1 - phi) / e_b);

% 2nd order EMT
e_te2 = e_te0 * (1 + (pi^2)/3 * (L/lamda)^2 * phi^2 * (1-phi)^2 * (e_a-e_b)^2 / e_te0);
e_tm2 = e_tm0 * (1 + (pi^2)/3 * (L/lamda)^2 * phi^2 * (1-phi)^2 * (e_a-e_b)^2 * e_te0 * e_tm0 / (e_a * e_b));

end
```

A.5: MATLAB code for f_int

```
function [int_kx] = f_int(i,e,m,t,w,c,lamda)

kx = 0:0.0001:2*pi/lamda(i); % incident angles
fkx = zeros(length(kx),1);

for j = 1:length(kx)

% kz of 1st layer in 1/micron
kz(i,1) = sqrt((sqrt(e(i,1)) * w(i) / c)^2 - kx(j)^2);

% kz of 2nd layer in 1/micron
kz(i,2) = sqrt((sqrt(e(i,2)) * w(i) / c)^2 - kx(j)^2);

% kz of 3rd layer in 1/micron
kz(i,3) = sqrt((sqrt(e(i,3)) * w(i) / c)^2 - kx(j)^2);

% fresnel reflection coeff for 1st interface
r_tm(i,1) = (kz(i,1) / m(1) - kz(i,2) / m(2)) / ...
(kz(i,1) / m(1) + kz(i,2) / m(2));
r_te(i,1) = (kz(i,1) / e(i,1) - kz(i,2) / e(i,2)) / ...
(kz(i,1) / e(i,1) + kz(i,2) / e(i,2));

% fresnel reflection coeff for 2nd interface
r_tm(i,2) = (kz(i,2) / m(2) - kz(i,3) / m(3)) / ...
(kz(i,2) / m(2) + kz(i,3) / m(3));
r_te(i,2) = (kz(i,2) / e(i,2) - kz(i,3) / e(i,3)) / ...
(kz(i,2) / e(i,2) + kz(i,3) / e(i,3));

% generalized reflection coeff for 2nd interface
R_te(i,2) = r_te(i,2);
R_tm(i,2) = r_tm(i,2);

% generalized reflection coeff for 1st interface
R_te(i,1) = (r_te(i,1) + R_te(i,2) * exp(1i * 2 * kz(i,2) * t(2))) / ...
```



```

(1 + r_te(i,1) * R_te(i,2) * exp(1i * 2 * kz(i,2) * t(2)));
R_tm(i,1) = (r_tm(i,1) + R_tm(i,2) * exp(1i * 2 * kz(i,2) * t(2)))/...
(1 + r_tm(i,1) * R_tm(i,2) * exp(1i * 2 * kz(i,2) * t(2)));

% integral part f_kx
fkx(j) = kx(j) * ((1-(abs(R_te(i,1)))^2) + (1-(abs(R_tm(i,1)))^2));

end

% integral of f_kx over kx
int_kx = trapz(kx,fkx);

end

```

A.6: MATLAB code for *f_int_grating*

```

function [int_kx_te,int_kx_tm,int_kx] =
    f_int_grating(i,e,e_te,e_tm,m,t,w,c,lamda)

kx = linspace(0,2*pi/lamda(i),90);          % incident angles
fkx = zeros(90,1);

for j = 1:length(kx)

% kz of 1st layer in 1/micron
kz(i,1) = sqrt((sqrt(e(i,1)) * w(i) / c)^2 - kx(j)^2);

% kz of 2nd layer for TE in 1/micron
kz_te(i) = sqrt((sqrt(e_te) * w(i) / c)^2 - kx(j)^2);

% kz of 2nd layer for TM in 1/micron
kz_tm(i) = sqrt((sqrt(e_tm) * w(i) / c)^2 - kx(j)^2);

% kz of 3rd layer in 1/micron
kz(i,3) = sqrt((sqrt(e(i,3)) * w(i) / c)^2 - kx(j)^2);

% fresnel reflection coeff for 1st interface
r_tm(i,1) = (kz(i,1) / m(1) - kz_tm(i) / m(2)) / ...
(kz(i,1) / m(1) + kz_tm(i) / m(2));
r_te(i,1) = (kz(i,1) / e(i,1) - kz_te(i) / e_te) / ...
(kz(i,1) / e(i,1) + kz_te(i) / e_te);

% fresnel reflection coeff for 2nd interface
r_tm(i,2) = (kz_tm(i) / m(2) - kz(i,3) / m(3)) / ...
(kz_tm(i) / m(2) + kz(i,3) / m(3));
r_te(i,2) = (kz_tm(i) / e_te - kz(i,3) / e(i,3)) / ...
(kz_tm(i) / e_te + kz(i,3) / e(i,3));

% generalized reflection coeff for 2nd interface
R_te(i,2) = r_te(i,2);
R_tm(i,2) = r_tm(i,2);

% generalized reflection coeff for 1st interface
R_te(i,1) = (r_te(i,1) + R_te(i,2) * exp(1i * 2 * kz_te(i) * t(2)))/...
(1 + r_te(i,1) * R_te(i,2) * exp(1i * 2 * kz_te(i) * t(2)));

R_tm(i,1) = (r_tm(i,1) + R_tm(i,2) * exp(1i * 2 * kz_tm(i) * t(2)))/...
(1 + r_tm(i,1) * R_tm(i,2) * exp(1i * 2 * kz_tm(i) * t(2)));

% integral part f_kx
fkx(j) = kx(j) * (((1-(abs(R_te(i,1)))^2) + (1-(abs(R_tm(i,1)))^2)));

```

```

fkx_te(j) = kx(j) * (1-(abs(R_te(i,1)))^2);
fkx_tm(j) = kx(j) * (1-(abs(R_tm(i,1)))^2);

end

% integral of f_kx over kx
int_kx = trapz(kx,fkx);
int_kx_te = trapz(kx,fkx_te);
int_kx_tm = trapz(kx,fkx_tm);

end

```

A.7: MATLAB code for f_{int_four}

```

function [int_kx] = f_int_four(i,e,m,t,w,c,lamda)

kx = linspace(0,2*pi/lamda(i),90);          % incident angles
fkx = zeros(90,1);

for j = 1:length(kx)

kz(i,1) = sqrt((sqrt(e(i,1)) * w(i) / c)^2 - kx(j)^2); % kz of 1st layer
kz(i,2) = sqrt((sqrt(e(i,2)) * w(i) / c)^2 - kx(j)^2); % kz of 2nd layer
kz(i,3) = sqrt((sqrt(e(i,3)) * w(i) / c)^2 - kx(j)^2); % kz of 3rd layer
kz(i,4) = sqrt((sqrt(e(i,4)) * w(i) / c)^2 - kx(j)^2); % kz of 4th layer

% fresnel reflection coeff for 1st interface
r_tm(i,1) = (kz(i,1) / m(1) - kz(i,2) / m(2)) / ...
(kz(i,1) / m(1) + kz(i,2) / m(2));
r_te(i,1) = (kz(i,1) / e(i,1) - kz(i,2) / e(i,2)) / ...
(kz(i,1) / e(i,1) + kz(i,2) / e(i,2));

% fresnel reflection coeff for 2nd interface
r_tm(i,2) = (kz(i,2) / m(2) - kz(i,3) / m(3)) / ...
(kz(i,2) / m(2) + kz(i,3) / m(3));
r_te(i,2) = (kz(i,2) / e(i,2) - kz(i,3) / e(i,3)) / ...
(kz(i,2) / e(i,2) + kz(i,3) / e(i,3));

% fresnel reflection coeff for 3rd interface
r_tm(i,3) = (kz(i,3) / m(3) - kz(i,4) / m(4)) / ...
(kz(i,3) / m(3) + kz(i,4) / m(4));
r_te(i,3) = (kz(i,3) / e(i,3) - kz(i,4) / e(i,4)) / ...
(kz(i,3) / e(i,3) + kz(i,4) / e(i,4));

% generalized reflection coeff for 3rd interface
R_te(i,3) = r_te(i,3);
R_tm(i,3) = r_tm(i,3);

% generalized reflection coeff for 2nd interface
R_te(i,2) = (r_te(i,2) + R_te(i,3) * exp(1i * 2 * kz(i,3) * t(3))) / ...
(1 + r_te(i,2) * R_te(i,3) * exp(1i * 2 * kz(i,3) * t(3)));
R_tm(i,2) = (r_tm(i,2) + R_tm(i,3) * exp(1i * 2 * kz(i,3) * t(3))) / ...
(1 + r_tm(i,2) * R_tm(i,3) * exp(1i * 2 * kz(i,3) * t(3)));

% generalized reflection coeff for 1st interface
R_te(i,1) = (r_te(i,1) + R_te(i,2) * exp(1i * 2 * kz(i,2) * t(2))) / ...
(1 + r_te(i,1) * R_te(i,2) * exp(1i * 2 * kz(i,2) * t(2)));
R_tm(i,1) = (r_tm(i,1) + R_tm(i,2) * exp(1i * 2 * kz(i,2) * t(2))) / ...
(1 + r_tm(i,1) * R_tm(i,2) * exp(1i * 2 * kz(i,2) * t(2)));

```

```
% integral part fxx
fxx(j) = kx(j) * ((1-abs(R_te(i,1))^2) + (1-abs(R_tm(i,1))^2));

end

% integral of fxx over kx
int_kx = trapz(kx,fxx);

end
```

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