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Broadband Reflective Surfaces for Infrared Radiation

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Summary

This abstract is publicly releasable.

Aerospace materials are exposed to high levels of radiation in extreme environments, which creates heating problems due to radiative thermal load. In this project, we designed surfaces and surface coatings to reduce and reflect IR radiation for aerospace applications. Issues of radiative thermal load on aerospace materials have become increasingly critical since heating of materials negatively impacts their performance. Novel material designs through computational models can reduce the radiative load through engineered reflection. To ensure robust operation, we designed surfaces that operate over a broad region of the infrared spectrum as commonly encountered in aerospace applications. There is already an established literature for other applications on engineering the reflection spectrum. In this project, we extended and modified these established models and theories to reduce and reflect IR radiation for aerospace applications. In this project, we evaluated two alternative design variations. First, we obtained a reflective surface based on a thin-film surface filter, which is composed of several layers. In this design, the desired reflective and spectral properties were achieved through constructive and destructive interference of the reflected fields from each layer. Second, we obtained reflective surfaces based on patterned surfaces.

1. Introduction

Engineering the spectral properties of electromagnetic fields upon interaction with different surfaces has been of great interest for applications ranging from microwave and RF frequencies to optical and infrared frequencies. At microwave and RF frequencies, frequency selective surfaces have been used to tailor spectral properties of reflected electromagnetic radiation for various applications, including military applications [1]. At optical and infrared frequencies, thin-film optical filters have been heavily utilized in the literature to engineer the spectral properties of the reflection of light from surfaces for various applications, including optical communications and lens design [2].

More recently, developments in the interaction of light with metal-dielectric surfaces have led to significant advances in nanotechnology [3,4]. The interaction of optical fields with metal-dielectric surfaces have strong frequency dependence, therefore, metal-dielectric surfaces are good candidates for engineering the reflection and absorption spectrum of light. In particular, the metal-dielectric interfaces involving nanoparticles and patterned surfaces have been demonstrated to give great control of the spectrum of light upon interaction with surfaces and nanoparticles [5]. Such an achievement at the nanoscale has enabled scientists to overcome technological barriers and expand the frontiers for scientific breakthroughs [6] in near-field imaging, solar cells, data storage, light emitting devices, spectroscopy, and bio-chemical sensors. Through the development of advanced thin-film manufacturing and characterization techniques, the manipulation of surface properties of thin-layers has given scientists and engineers an effective tool to control the interaction of light with surfaces.

In this research project, we designed surfaces and surface coatings to reduce and reflect IR radiation for aerospace applications. Coating materials were chosen such that they can withstand high thermal stresses induced by the absorbed incident radiation and their spectral characteristics were tailored in broadband to manage the reduce thermal loads induced by incident broadband radiation. These coatings are essential to reduce structural and stability problems occurring due to thermal stresses. Although reduction of IR radiation over a narrow bandwidth was well-studied in the literature, obtaining surface coating that will reduce and reflect IR radiation for aerospace applications over relevant bandwidths is more challenging, which are intrinsically broadband. In this project, previously established design methods were adapted and modified to extend operating spectral bandwidth. Parallel to that, new materials with superior structural and thermal characteristics were also investigated.

In this project, coatings composed of metal/dielectric materials were modeled and detailed analyses of the geometrical parameters and material properties were conducted to understand the driving mechanisms of the resulting spectral reflection characteristics. During the project, multiple subjects were studied which required tailoring the spectral reflection in broadband spectrum. Both homogenous and inhomogeneous structures were developed, analyzed and their potential in tailoring the reflection characteristics were demonstrated. Enhancement of spectral reflectance of the selected refractory metals in

broadband spectrum and passive radiative cooling were studied. Although these applications have different and challenging spectral reflectance requirements, similar methods were utilized to achieve successful results. This demonstrates the robustness of the techniques employed in this project.

There exists a vast literature regarding to spectral reflectance with refractory metals. Refractory metals, including Tungsten, Tantalum, Molybdenum and Niobium, are known for their good thermomechanical properties. Various applications require operations in extreme environments, where refractory metals can benefit the devices to withstand against thermally and mechanically harsh conditions. Among these applications, hypersonic applications [7-9], space applications [10], and solar/thermophotovoltaics [11, 12] are the most notable ones in which extreme temperature are observed. In addition to these applications, the absorption of the incident infrared radiation, which results in a temperature increase, is undesired in large infrared telescopes [13-14] and night-vision systems [15]. Absorption of the incident radiation in these applications brings thermal load to the system, therefore, thermal and mechanical damage can be observed. This damage in system components degrade the device performance due to heat dissipation in the components. To overcome such issues, reflectors that are composed of Al or Ag are utilized with protective coatings [16-20]. However, problems like adhesion, corrosion, durability and degraded reflectance performance due to damages are some issues that are encountered in these coatings [17-18,20]. A possible solution to these issues is to use metals with higher hardness, also known as refractory metals. Although spectral behavior of W, which belongs to the family of refractory metals, is widely studied for high emissivity applications [21-22] and its oxide form for electrochromic applications [23-24], it is not widely studied for applications which demand broadband high reflectance.

For effective use in extreme environments, engineering the broadband reflection spectrum of surfaces composed of refractory metals is of great interest. A particular problem for aerospace materials in extreme environments is the exposure to high levels of infrared radiation. If absorbed, the incident radiation in aerospace materials creates high levels of heating, which can create structural and stability problems in materials. For radiative heating, broadband sources such as solar irradiance plays an important role in extreme environments. Solar radiation peaks around 500 nm, and it is strong in 300 – 3000 nm spectrum. Beyond 3000 nm, radiated power degrades and becomes relatively low [25]. For materials with high absorption in the spectral range of sources, which radiate at visible and infrared spectrums, large temperatures and thermal stresses can occur. To overcome this problem, a detailed understanding of optical coatings, composed of thin-films, which influence the interaction of visible and infrared radiation with refractory metals is essential both to control/minimize the impact of the absorbed radiation and to design surfaces. Advances in nanotechnology, which enables manipulation of electromagnetic waves at the visible and near-infrared spectrums, 2D and 3D optical filters are widely used to engineer spectral characteristics of the surfaces [26-30]. High emissivity coatings are widely studied, and results are reported in the literature [31-33]. In recent years, Ag is heavily utilized as

broadband reflector for day time radiative cooling applications [34-37], due to its intrinsic broadband reflection in visible and near-infrared spectrums. Good reflectors in the visible spectrum, such as Ag, have relatively low Young's modulus and melting point.

Metals are widely used as solar irradiance reflectors [38-39], since they are intrinsically good and broadband reflectors in the visible and near-infrared spectra. Although metals like Ag, Au, Al or Cu are good reflectors in the visible and near-infrared spectra, they have relatively low melting points and Young's modules, whereas it is opposite for refractory metals such as W, Ta, Mo and Nb [40]. Despite their attractive thermomechanical properties, spectral reflectivity of these refractory metals cause setbacks for use in extreme environments. As we will discuss later in the manuscript, the reflectivity of the refractory metals in 1500-3000 nm spectrum is above 95% in average, whereas it is around 40% -50% range in 300-1500 nm spectrum. Such low reflectivity in 300-1500 nm spectrum gives rise to increase of temperature, since a significant portion of the solar irradiance exists in the 300-1500 nm spectrum.

In this project, to generate high reflection in broadband spectrum individual periodic high-low index layers, which generate high reflection around a wavelength, were designed at different wavelengths and stacked together. Due to the low destructive interference of the reflected beams at the front surface, broadband reflection was achieved over the spectrum. Although sharp peaks at distinct wavelengths were observed over the spectra, they do not lead to reduction in reflection in broadband spectrum. Underlying mechanisms of resulting sharp peaks were explained with Fabry-Perot resonators. Effect of material properties on reflection were also studied. In addition, we adapted the concept of impedance matching that is widely used in RF and microwave applications, as impedance mismatch and developed broadband reflectors with refractory metals with less number of layers. Overall, these studies yielded structures that exhibits very high reflection in broadband spectrum, which can be used in aerospace applications, thermal management and thermophotovoltaics.

Although separate and extensive literature also exist for passive radiative cooling, similar approaches to methods that are used to enhance reflection, can be utilized for passive radiative cooling. Therefore, to be able to demonstrate the potential of proposed methods at different problems, we also studied passive radiative cooling problem.

Passive radiative cooling coatings are based on tailoring the spectral emission and absorption at different wavelength intervals. These approaches can be divided into nighttime or daytime cooling design concepts based on the targeted operation times. Radiative cooling for nighttime operations has been studied extensively in the literature and high cooling performances were reported [41-47]. This is achieved by increasing emission in the 8-13 μm spectrum, where atmosphere is transparent and radiation from terrestrial objects is maximum. The 8-13 μm spectral transparency window allows radiative heat transfer between sky and objects, and therefore, provides opportunities for effective passive radiative cooling.

Usually materials like SiO [42-43,48], Si₃N₄ [49] and SiO_{0.6}N_{0.2} [50] are utilized in passive radiative cooling applications, due to their lossy nature in atmospheric transparency window, with a broadband reflector, e.g. a metallic layer at different forms e.g. films and patterns. By the aid of nanoparticles, higher radiative cooling performances compared to bulk films are achieved. When particles like SiO₂, TiO₂ or SiC are added in films (polymers or other type of materials), selective emission that lead to radiative cooling occurs. Several examples of these type of coatings are reported in the literature with varying material configurations [51-53]. High reflection requirement is usually achieved by a metallic back reflector in these types of structures and emissive layers that contains particles are selected among non-absorbing materials in visible and near-infrared spectra.

In addition to particle based or single layer films, photonic structures composed of multilayer thin-films and patterned surfaces are also utilized for passive radiative cooling, thanks to advancements in nano/microtechnology [54-56]. Generally, designed thin-film filters composed of different layers with varying optical properties and thicknesses [35,37 57-58]. Different optimization methods are adapted to design thin-film coatings for passive radiative cooling [59-62]. Unless the sensitivity of the spectral emissivity to layer thicknesses is low, these types of structures can be heavily utilized. Finally, patterned surfaces composed of air holes [63] and triangles [64,65] are developed. Such patterned surfaces are also combined with multilayer structures [36, 66], which exhibit selective emission very close to ideal profile. Although elevated performance with these kinds of sophisticated topologies are achieved, difficulties in the fabrication steps may restrict their use in applications.

Several review papers have outlined the current progress in the field of daytime passive radiative cooling concepts are published in the literature [67-72]. In addition to design and performance evaluations, applicability of daytime passive radiative cooling in different application areas, e.g. thermal management in buildings [73-77] and thermophotovoltaics [78-80], are also reported.

Despite the extensive literature on daytime passive radiative cooling, there are still missing points regarding to effect of materials and interference between different layers of materials. Besides those, there is a lack of a design method specific to radiative cooling which considers both spectral and radiative aspects of the problem. Although spectral optimization methods that have been previously utilized for different problems have been proven to be successful for passive radiative cooling, further improvement can be achieved with more complicated design formulations. During the research period, by benefiting from the findings obtained from tailoring methods and mechanisms for broadband reflectance, we have also studied passive radiative cooling problem which also require broadband and selective spectral response. Firstly, we studied the effect of different combinations of layer materials with different absorption characteristics in atmospheric transparency window. It was shown that significant enhancement is achieved when absorption characteristics of different materials are combined in a complementary fashion. Besides this, we have also adapted the intuitive approach that we have proposed for broadband reflectance and show that those type of designs can achieve broadband reflectance in visible and near infrared spectrums and high emission in atmospheric transparency window. Finally, we developed an optimization strategy

specific to daytime passive radiative cooling, which optimizes the layer thicknesses of selected number of layers with selected materials. Main contribution of our proposed method is that it considers both spectral and radiative aspect of the problem, whereas only spectral aspects of the problem was considered in previous approaches.

2. Methods, Assumptions & Procedures

Since low reflectance leads to absorption of incident radiation, incident solar irradiance above the atmosphere is evaluated and plotted in Fig. 1(a). Incident solar irradiance above the atmosphere is approximated as radiation from a blackbody at 5850 K. During the analysis, incident radiation in 300-3000 nm spectrum, which is plotted in Fig. 1(a), and divided into two sub-intervals 300-1500 and 1500-3000 nm. Such division is done because spectral reflectance of the selected refractory metals is relatively low in the 300-1500 nm interval, as shown in Fig. 1(b), whereas it increases up to 90% levels in the 1500-3000 nm spectrum. When incident radiation is encountered with a different medium, it is reflected, transmitted and absorbed at different percentages. Percentages of these three different spectral behaviors are dependent on optical properties of the mediums and geometry of the encountered structure. Based on the spectral distribution of incident thermal radiation and reflectance of the selected refractory metals shown in Fig. 1, absorbed power percentages by these metals in film form and present solar power are given in Table 1. Our main goal is to design filters with high reflectance in a broad spectrum to reflect the incident radiation and reduce the absorption. To achieve this, spectral reflectances/absorptances are calculated both for selected refractory metals and their coated versions with multilayer thin films.

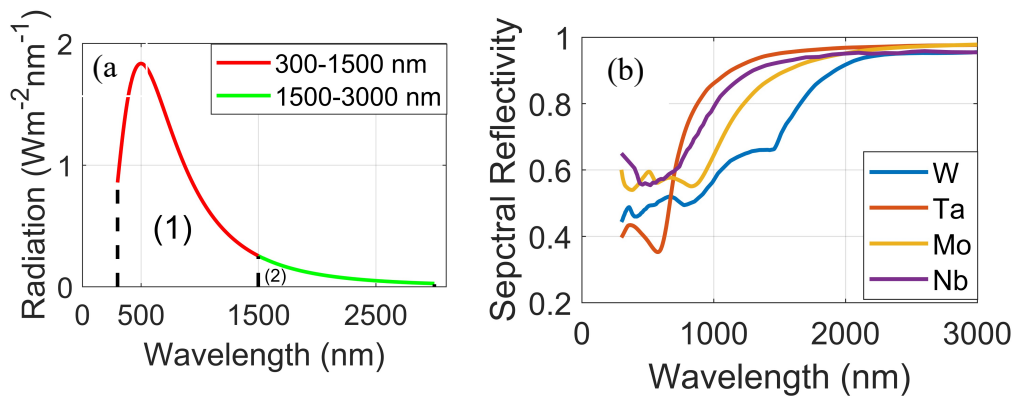


Figure 1: a) Spectral distribution of blackbody radiation of the sun that reaches to the atmosphere. b) Spectral reflectivity of W, Ta, Mo and Nb films, each 500 nm thick, with respect to wavelength on top of a silicon substrate at perpendicular angle of incidence

Table 1: Average absorptivity of 500-nm of refractory metals, W, Ta, Mo and Nb, present solar power and absorbed solar power by these at 300-1500 nm and 1500-3000 nm spectrums.

Spectrum	300-1500 nm	1500-3000 nm
Material	Absorbed Power	Absorbed Power
W	44.25 %	13.11 %
Ta	37.46 %	3.54 %
Mo	36.33 %	5.99 %
Nb	39.22 %	5.59 %
Total Solar Power	1221 W/m^2 (89.91 %)	137.67 W/m^2 (10.13 %)

To obtain spectral responses of multilayer 2D thin-film coatings, an analytical model proposed in [2] is used which is dependent on optical thickness and admittances of each layer. Used model can obtain spectral behaviors of the 2D thin-film coatings with respect to wavelength and polarization by considering refractive index, thickness and angle of incidence as inputs.

In addition to method described in [2], we have also adapted a surface impedance-based method, which was heavily utilized in RF and microwave applications. Based on this method, we developed designs on impedance plane, which allows better understanding of the changing spectral characteristics. The concept and formulation of surface impedance were demonstrated on a W layer example. Starting from intrinsic impedance of individual layers, which are solely dependent on material properties,

$$Z = \sqrt{\frac{\mu}{\epsilon}} \quad (1)$$

and including the thicknesses of the layers and their interaction with each other, surface impedance of a multilayer composed of N number of layers can be expressed as,

$$Z_i = Z_i \frac{Z_{i+1} + jZ_i \tan(\delta_i)}{Z_i + jZ_{i+1} \tan(\delta_i)} \quad (2)$$

From the surface impedance of a multilayer structure, amplitude of its reflectance coefficients and reflectance percentage are given as,

$$\Gamma_1 = \frac{Z_1 - Z_0}{Z_1 + Z_0} \quad (3)$$

and Eq. (3) can be normalized as,

$$\Gamma_{Norm} = \frac{Z_1 / Z_0 - 1}{Z_1 / Z_0 + 1} \quad (4)$$

If reflectance coefficients values obtained by Eq. (4) at different wavelengths are plotted on a complex plane, Fig. 2, it is observed that they are distributed (green dots) inside a unit circle centered at the origin (blue circle). This representation is very similar to Smith chart used in microwave and RF regimes for the purpose of impedance matching. From this representation, it is clear that zero reflectance at a wavelength is achieved only if amplitude of the reflectance coefficient is zero, appear at the origin (red star). Since this condition is only satisfied if $Z_{Surf} = Z_0$, origin of the unit circle is called as perfect impedance matching point. On the other hand, magnitude of the reflectance coefficients on any point on the unit circle is always 1 ($|\Gamma| = |re^{i\theta}|$, if $r = 1$). Therefore, any point on the unit circle is called perfect impedance mismatch point. Based on these, following is deduced: Reflectance is reduced as the reflectance coefficient approaches to the origin and it increases as reflection coefficient moves away from the origin. Such characteristics of the reflectance coefficients on the unit circle (S-plane), can be utilized to engineer the reflectance spectrum of the

multilayers. Correlation between the reflection coefficients/S-parameters and spectral reflection are demonstrated in, Fig. 2 with a simple example.

In Fig. 2(b), spectral reflectance of 500 nm thick tungsten is depicted, and corresponding reflectance coefficients are shown in Fig. 2(c). As seen from Fig. 2(b), reflectance of W is below 60 % at wavelengths shorter than 1 μm and it starts to increase at longer wavelengths and reaching up to 95 % levels. Reflection coefficients of low reflectance spectrum (blue points) are closer to the origin and start to approach left side of the unit circle for longer wavelengths (red points).

By utilizing multilayer structures, position of reflection coefficients on the -S plane can be altered, which changes the reflection magnitude. Based on this, thin-film multilayer structures for various type of problems including broadband reflectance and passive radiative cooling can be developed.

During the research period, both intuitive and physic based numerical optimization methods were developed and studied. The principal motivation of intuitive method for broadband reflection from refractory metals is to reduce the spectral absorption of refractory metals, especially 300-1500 nm spectrum, through optical coatings. It is well known that optical filters, which consists of periodic low-index/high-index filters, can increase the reflection of surfaces in at distinct spectral points. In this case, we aim to use periodic low-index/high-index filters to increase the broadband reflectance from refractory metals coated by multilayer films so that they reflect incident radiation in 300-1500 nm spectrum. While achieving this task, the optical filter should not create additional burden on the materials system, such as creating additional absorption from longer wavelengths. To achieve this goal, we use dielectric materials that do not absorb at visible and near-infrared are selected, such as TiO_2 , SiO_2 and Al_2O_3 . Similar approach is also adapted to radiative cooling, which require high reflection at shorter wavelengths and high emission in 8-13 μm . By benefiting from the lossy characteristics of TiO_2 , SiO_2 , Al_2O_3 in 8-13 μm wavelengths, high emission requirement is satisfied while achieving high reflection at shorter wavelengths simultaneously.

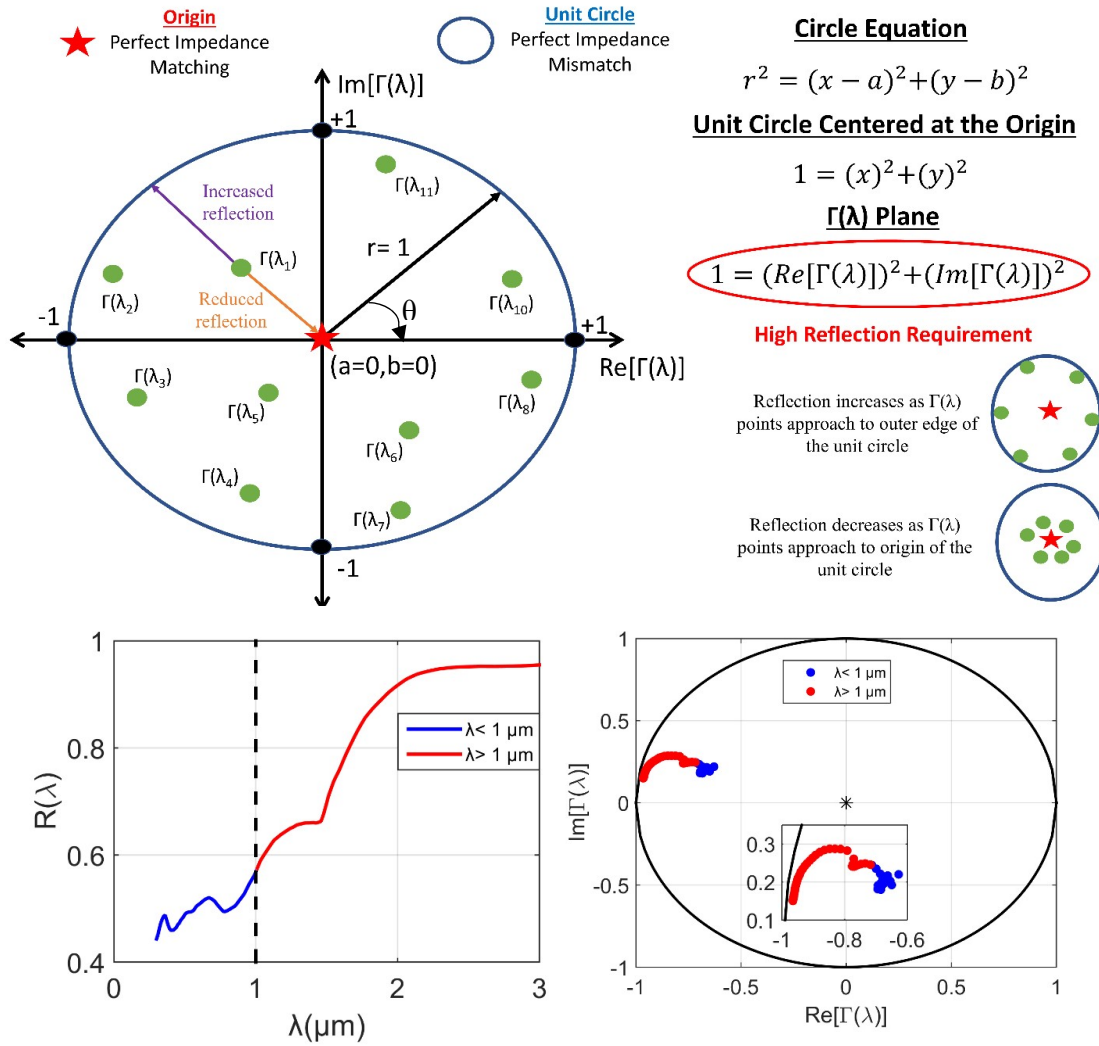


Figure 2: a) Representation of reflection coefficients/-S parameters in complex-impedance/-S plane. b) Reflectivity of W in 0.3-3 μm spectrum interval. c) Reflection coefficients of W in -S plane.

2.1. Periodic High-Low Index Segments Designed by Intuition for Broadband Reflectance

Since high reflectance is desired at the front surface for both applications, constructive interference of the reflected beams between the adjacent layers is required. To achieve such constructive interference, periodically altering high-low index layers are utilized. Since reflected beam experiences 180° phase change when encountered a high index layer and no phase change occurs in the interaction of the incident beam with low index layer all of the reflected become at the same phase at the front surface. A schematic for a periodic high-low index system is depicted in Fig. 3, which shows the reflected wave components in two separate colors depending on relative index of the adjacent medium to incident medium. Green components are the components which are reflected from a medium which has higher refractive index than the incident medium and it is the opposite for waves illustrated in orange. By adjusting the optical path in each

layer through refractive index and thickness, reflected beams have the same phase at the front surface, thus high reflection is achieved.

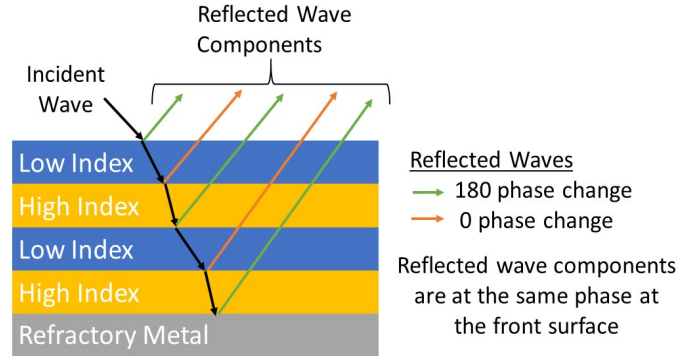


Figure 3: Schematic of the high-low index periodic structures on which reflected wave components that either experiences 180° (green) or 0° (orange) phase change are visualized.

Location of such high reflection zone in the spectrum are tuned by controlling the thicknesses of the periodic layers. By setting the optical thickness of the layers to $\pi/2$ at a specified wavelength, high reflection around that wavelength are achieved. Relationship between the optical and geometrical thickness of a layer is given in Eq. (5) where, ' δ ' is the optical thickness, ' n ' is the refractive index, ' k ' is the extinction coefficient, ' d ' is the geometrical thickness, ' θ_r ' is the angle of refraction and ' λ ' is the wavelength. From Eq. (5), thickness is solved to determine required film thicknesses to achieve high reflection zone around the selected wavelength. We used lossless materials in 300-3000 nm spectrum to obtain geometrical thicknesses, ' t ', from Eq. (5). A periodic filter is designed on top of Tungsten, to generate high reflectance around 600 nm with 9 layers of alternating TiO_2 - SiO_2 layers wavelength for which both schematic and structure is depicted in Fig. 4(a) and 4(c).

$$\delta = \frac{(n - ik) * t * \cos(\theta_r)}{\lambda} \quad (5)$$

In Fig. 4(b) reflectance of periodic TiO_2 - SiO_2 segments with central wavelengths of 600, 800 and 1000 nm are plotted against wavelength. As shown, high reflectance zones around specified wavelengths are achieved with different segments. In this filter, TiO_2 is selected as high index and SiO_2 is selected as low index materials. Although optical thicknesses are set to $\pi/2$ at the specified wavelengths, center of the high reflection zones shifted to slightly lower wavelengths because of the interference with the W at the bottom. However, bandwidths of the high reflectance zones for these individual designs are extremely low when compared to the bandwidth of the solar irradiance. Such a filter reflects only a small portion of the incident radiation and it is in need of bandwidth increase. To increase the bandwidth, several periodic segments are stacked. Each segment in this stack is composed of periodic layers. To obtain broad spectral reflection, these segments are stacked, each of which has a different central wavelength and final structure is visualized in Fig. 4(c).

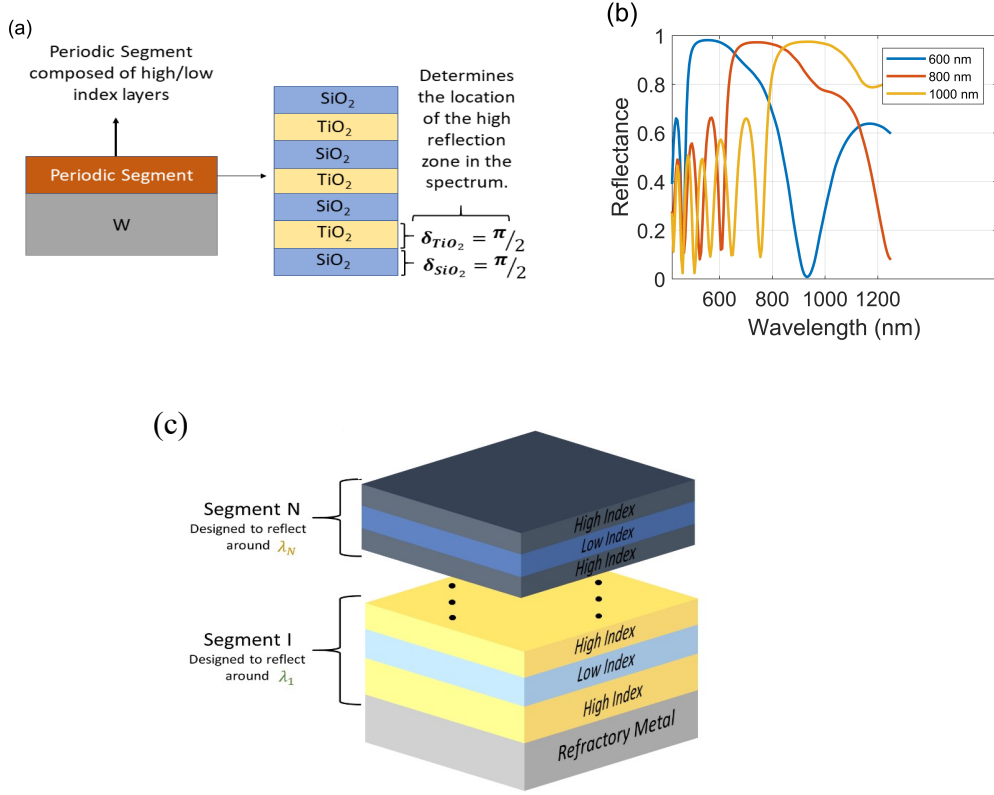


Figure 4: a) Schematic representation of an individual segment composed of high-low index layers. b) Reflection of the structure depicted in Fig. 2(a). c) Schematic representation of stacked segments designed to reflect at separate wavelengths.

With this approach, high reflection requirement in the desired spectrum interval can be achieved. By utilizing lossy materials in 8-13 μm spectrum will lead to high emission in that spectra, therefore, radiative cooling can be simultaneously achieved.

Besides the intuitive use of periodically arranged high/low index layers for both applications in similar fashions, different methodologies have been adapted for the physics based numerical solutions to these problems, based on impedance formulation.

2.2. An Impedance Mismatch Based Design formulation for Broadband Reflectance: From Homogenous to Non-homogeneous

In this part aim, is to preserve high reflectance of W at longer wavelengths while enhancing it in shorter wavelengths. Based on this, design spectrum separated as low and high reflectance spectrum and a weighting is introduced in the mathematical expression of the problem and defined as,

$$\max \alpha \int_{\lambda_1}^{\lambda_2} |\Gamma(\lambda) e^{i\theta(\lambda)}| d\lambda + (1 - \alpha) \int_{\lambda_2}^{\lambda_3} |\Gamma(\lambda) e^{i\theta(\lambda)}| d\lambda \quad (6)$$

where α is the weighting parameter, λ_1 , λ_2 and λ_3 are 0.3, 1 and 3 μm respectively. α is chosen as 0.7 to keep the reflection reduction rate small at longer wavelengths, while enhancing it at shorter wavelengths. Both homogenous and inhomogeneous structures' spectral characteristics are analyzed on the S-plane.

Based on this formulation, layer thicknesses are optimized for the selected number of layers and layer materials and resulting spectral behaviors are analyzed. In order to improve the mechanical stability of the multilayer structure, we are inspired from the morpho butterfly wing like structures, which are reported in the literature for high reflection. Those type of structures composed of layers separated by small (in transverse direction) lift-off layers and provides space for the layers to be expanded. Therefore, we designed homogeneous multilayer structures composed of TiO_2 layers separated by air gaps. Then, we study the effects of lift-off material and their dimensions, as well as the dimensions of the TiO_2 layers and periodicity of the multilayers. All the parameters and structure configuration are schematized in Fig. 5.

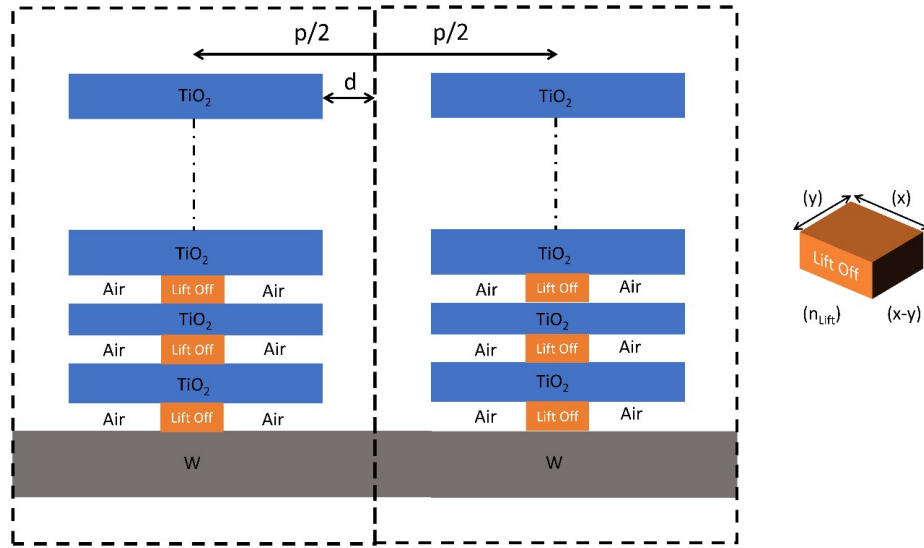


Figure 5: Scheme of the inhomogeneous multilayer structures inspired from morpho butterflies.

2.3. Passive Radiative Cooling & Cooling Power Based Design Formulation

Passive radiative cooling in terrestrial environments are achieved by simultaneously reflecting the incident thermal radiation and emitting in in 8-13 μm spectrum at which radiation spectra of surfaces around 283 – 323 K temperatures and atmospheric transparency window coincides. Spectral distribution of the solar irradiance and atmospheric transmittance are demonstrated in Fig. 6.

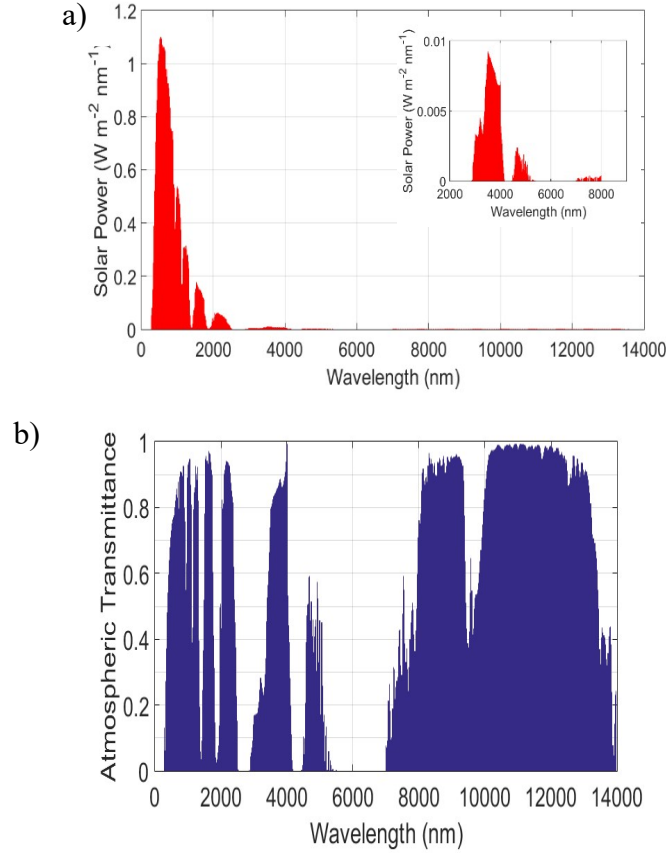


Figure 6: a) Spectral distribution of the solar irradiance AM1.5 Global tilt spectrum. b) Atmospheric transparency with respect to wavelength.

In Eq. 7 black body radiation formula to calculate the radiation from surfaces at varying temperatures with respect to wavelength is given.

$$I_{BB}(T, \lambda) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/\lambda k_B T} - 1} \quad (7)$$

where λ , h , c , k_B are wavelength, Planck's constant, the speed of light and the Boltzmann constant, respectively. Based on the blackbody radiation formula depicted in eq. (7), radiative heat components absorbed and radiated by the body as well as the cooling power of a surface is given as,

$$P_{Cool} = P_{Rad} - P_{Atm} - P_{Sun} - P_{Cond+Conv} \quad (8)$$

where, P_{Cool} is the cooling power of the surface. P_{Rad} is the power radiated away from the surface and expressed as,

$$P_{Rad} = A \int_0^{\pi/2} d\Omega \cos \theta \int_0^\infty d\lambda I_{BB}(T, \lambda) \varepsilon(\lambda, \theta) \quad (9)$$

where, ε is the emittance of the surface and $d\Omega = d\theta \sin \theta$ is the angular integral over a hemisphere. P_{Atm} is the absorbed atmospheric thermal radiation given as,

$$P_{Atm} = A \int_0^{\pi/2} d\Omega \cos \theta \int_0^{\infty} d\lambda I_{BB}(T, \lambda) \varepsilon_{Atm}(\lambda, \theta) \varepsilon(\lambda, \theta) \quad (10)$$

absorbed solar power, P_{Sun} , is given as,

$$P_{Sun} = A \int_0^{\infty} d\lambda I_{Sun}(\lambda) \varepsilon(\lambda, \theta_{Sun}) \quad (11)$$

at a fixed incident solar irradiance angle θ_{Sun} . Finally, $P_{Cond+Conv}$ term is expressed as,

$$P_{Cond+Conv} = Ah_c (T_{Amb} - T) \quad (12)$$

to include the non-radiative heat fluxes in the system. In Eq. (11), I_{Sun} is the AM1.5 Global tilt spectrum, which is given in [35]. Eq. (12) is for the contributions from conduction and convection. These equations are used to evaluate the cooling power of the structures under consideration. However, the connection between spectral profiles and the cooling power was not clearly outlined during the design methods reported in the literature.

By using equations (8) - (12) and considering the spectral distribution of solar irradiance and atmospheric transmittance (as shown in Fig. 6), the following spectral requirements to maximize the cooling power of surfaces can be determined: A daytime passive radiative cooling structure should strongly emit in the 8-13 μm spectrum, where the atmosphere is mostly transparent and highly reflects at shorter and longer wavelengths to prevent solar irradiance and atmospheric thermal radiation absorption. Generally, the requirement of low absorption in visible and near-infrared spectra is fulfilled by coating a strong metal reflector on the structure, e.g. Ag, and by using lossy materials to enhance emittance in the 8-13 μm interval.

From these equations, spectral requirements for thermal management in different applications can be derived. For instance, high reflection is required to avoid solar irradiance absorption in solar spectrum both for aerospace and radiative cooling applications. On the other hand, radiative cooling requires selective emission in atmospheric transparency window located in 8-13 μm spectrum while reflecting in the spectrums where solar irradiance is high and atmosphere is opaque. To evaluate the radiative powers, spectral reflection should be calculated.

Above it is stated that periodic high-low index designed for broadband reflectance can be utilized for passive radiative cooling by proper selection of layer materials. Such approach can be considered as an intuitive approach. However, if problem is formulated as a physics-based optimization problem, superior structures can be achieved.

Previous design methods for multilayers for radiative cooling, e.g. [35, 81], have focused on minimizing the error between a given ideal emittance curve and actual emittance spectrum. Objective function for such minimization is given in Eq. (13) in Table 2. Then, cooling power performances of the designed structures are evaluated by equations given in Eq. (8) - (12).

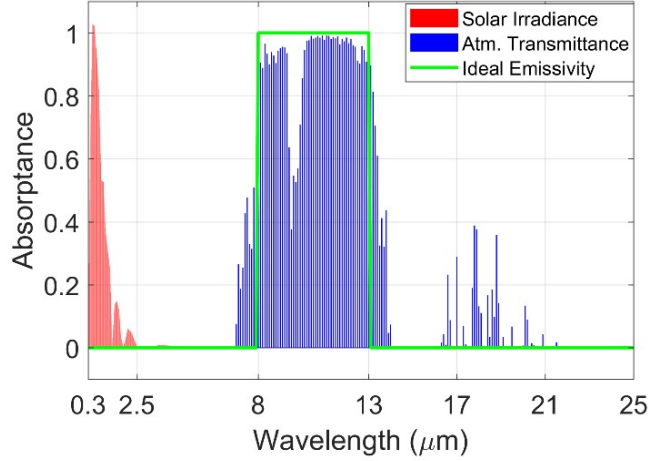


Figure 7: Ideal emittance profile used in [35] plotted with respect to solar irradiance and atmospheric transmittance.

Table 2: Mathematical expressions for spectral and cooling power-based formulations

Approach	Cost Function	Eq.
(1) Spectral	$\min \left \varepsilon_{Target}(\lambda) - \varepsilon_{Actual}(\lambda) \right $	(13)
(2) Cooling Power	$\max P_{Cool} = P_{Rad} - P_{Atm} - P_{Sun}$	(14)

The cumulative spectral error in terms of minimum mean squares based on the difference between ideal and actual emittances serves as a reference to compare the spectral performance of different designs. Although the resulting structures with non-ideal emittance profiles might outperform each other in terms of cumulative errors, they do not necessarily result in higher cooling powers. This is because of the broadband nature of the problem and the spectral distribution of solar irradiance and atmospheric transparency.

Due to the broadband nature of the problem, coatings alter the spectral behavior over the entire spectrum. Therefore, a coating increasing the emittance in the 8-13 μm spectrum may also enhance the absorbance at longer wavelengths, where the atmospheric thermal radiation is strong. Such an increase in longer wavelengths introduces significant thermal load to the system, and if not compensated by emitted power, total cooling power decreases. Therefore, during the design processes, the effect of spectral behavior on the cooling powers should be considered. This is achieved by reformulating the optimization problem based on the cooling power. In this case, the cost function is transformed from (1) to (2) as shown in Table 2. Spectral behaviors of the two 4-layer structures designed based on the objective functions given in Table 2, are demonstrated in Fig. 8.

Fig. 8 shows that, there is a considerable difference in absorptance around the 11 – 19 μm interval, whereas only slight changes exist in shorter wavelengths. Minimum mean square errors between actual and ideal emittances are 31.03 and 38.55 and cooling powers are around 55 and 70 W/m^2 respectively for spectral and CP approaches. These results indicate the superiority of the CP approach over the spectral approach. Even with the increased absorption (P_{Atm}) at wavelengths longer than 13 μm , the CP method results in structures with higher cooling powers due to reduction in P_{Sun} and increase in P_{Rad} (demonstrated in table 3). These results show the importance of weighting on the spectral behaviors based on the contribution to cooling powers. The proposed method is called cooling power (CP) approach, since it focuses on cooling power maximization by tailoring the spectral emittance, instead of pure spectral error minimization.

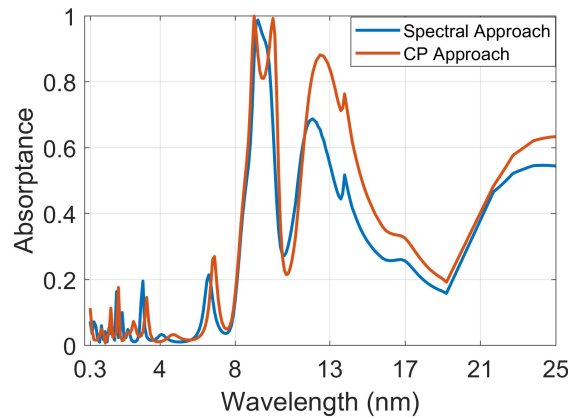


Figure 8: Spectral absorptance of 4-layer structure at perpendicular angle of incidence, designed by spectral and cooling power methods for which cost functions are depicted in Table 2

Table 3. Radiative heat components for the structures with 4 layers designed by spectral and CP approach

Radiative Heat Components	Spectral Approach	CP
P_{Rad} (W/m^2)	148.79	175.39
P_{Sun} (W/m^2)	25.52	22.68
P_{Atm} (W/m^2)	68.19	82.97
P_{Cool} (W/m^2)	55.07	69.73

Design procedure which leads to results depicted in Table 3, compared to previous approaches are described below: First the reflectance coefficients are obtained based on the impedance formulation described above and problem is modified as,

$$\max P_{\text{Cool}} = P_{\text{Rad}}(T, \varepsilon(\lambda)) - P_{\text{Atm}}(T, \varepsilon(\lambda)) - P_{\text{Sun}}(\lambda) \quad (15)$$

in which P_{Rad} and P_{Atm} depend on surface emissivity. Based on radiative heat transfer components. In Eq. (15), ' $\varepsilon(\lambda)$ ' is expressed in terms of normalized reflectance coefficients as $1-|\Gamma_l|^2$ based on surface impedance of the structure.

First, 100-nm Ag is coated on the top of Si substrate, and its surface impedance is obtained using Eq. (2). Next, SiO₂ and TiO₂ layers are added in a series, and the surface impedance of the final structure is formed by leaving the layer thicknesses as unknowns. The optical properties of these materials are obtained from the literature [82-83]. The reflectance coefficients for these materials are obtained using Eq. (3) and are mapped to the complex gamma plane using Eq. (4). Finally, residual errors are defined from the normalized gamma values, are inserted in the cost function given in Eq. (15), where the layer thicknesses are obtained. A flow diagram for the complete procedure is depicted in Fig. 9.

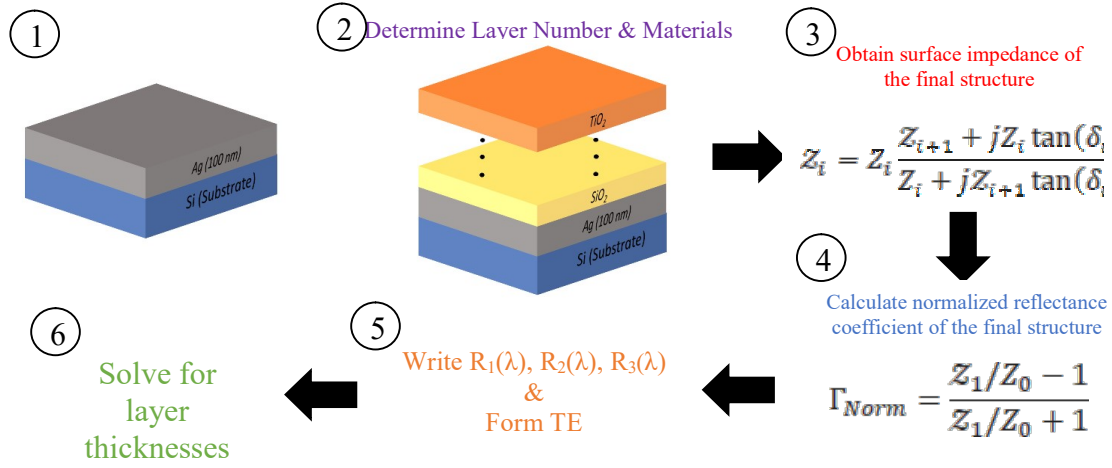


Figure 9: Design steps for cooling power-based optimization approach

Besides the cooling power and temperature reduction evaluations, resulting spectral characteristics are also quantified by defining the residual errors as,

$$R_i = \sqrt{(0 - \text{Re}(\Gamma_1(\lambda)))^2 + (0 - \text{Im}(\Gamma_1(\lambda)))^2} \quad (16)$$

which is defined in terms of norms of difference between perfect impedance matching point and final reflection coefficients.

3. Results & Discussions

In this section, results obtained by following the methods described in section 2, are reported. They are categorized under the sub-sections based on the problem definitions and applied methodologies. In subsection 3.1, results related to achieving a near unity broadband reflection with alternating high-low index layers are given. In the next subsection, wave impedance analysis methods are used to design the reflection spectrum of homogenous multilayer structures. In addition, effects of geometrical perturbations, which yield inhomogeneous structures to provide enhanced thermomechanical stability, on the reflection spectrum is analyzed. In subsection 3.3 and 3.4 similar methods are adapted to daytime passive radiative cooling problem. In subsection 3.3 results related to enhancement in cooling power are presented. In the final subsection, results of a superior thin-film design methodology which is obtained by reformulation of the problem, for passive radiative cooling are demonstrated. In this section, it is shown that wave impedance analysis can be used to evaluate the resulting reflection characteristics in broadband spectrum.

3.1. Intuitive Design with Periodically Arranged High/Low Index Layers for Enhanced Spectral Reflection with Refractory Metals

In Fig. 10(a) to 10(d), spectral response of periodic segments, which have 7 layers of TiO_2 and SiO_2 on top of W, Ta, Mo and Nb layers, which are designed to have reflectance peaks around 450, 500, 750, 900, 1000, 1200, 1500, 2000 and 2200 nm are demonstrated. Central wavelengths are determined by considering the bandwidth of the individual segments and effects on the reflectance in broadband spectrum. As shown in Fig. 4(b) each segment's reflectance decreases at distant wavelengths. We started with a segment, with central wavelength of 450 nm, which creates high reflectance zone above 95 % from 370 nm to 575 nm. We selected the next segment's central wavelength such that its reflectance is above 95% around 575 nm, therefore spectral reflectance of the resulting structure does not drop below 95% and continuity of the bandwidth of high reflectance is achieved. In this particular design, the reflectivity in each segment generates a high reflection zone with a reflectance above 95 % in a spectral interval of few hundreds of nm width. One can select a higher percentage, but it will result in a higher number of segments. Other segments are added in this manner and high reflectance in 300-3000 nm spectrum is achieved. During the determination, we also considered the effect of the segments at distant wavelengths, e.g. a segment with central wavelength of 1000 nm can create a sharp reflectance dip at 400 nm when stacked together with other segments. To decrease the number and magnitude of reflectance dips we shifted central wavelengths of the existing segments and added segments with central around the reflectance dips, by obeying the continuity of the bandwidth rule discussed above. It is shown that highly broadband reflectance is obtained in 300-3000 nm spectrum for coated W, Ta, Mo and Nb. Magnitude and location of the sharp dips are varied for structures because of the different interference of the segments with the bottom metallic

layer. Improvement percentages over 500-nm W, Ta, Mo and Nb by these filters in terms of absorbed powers are also reported in Table 4.

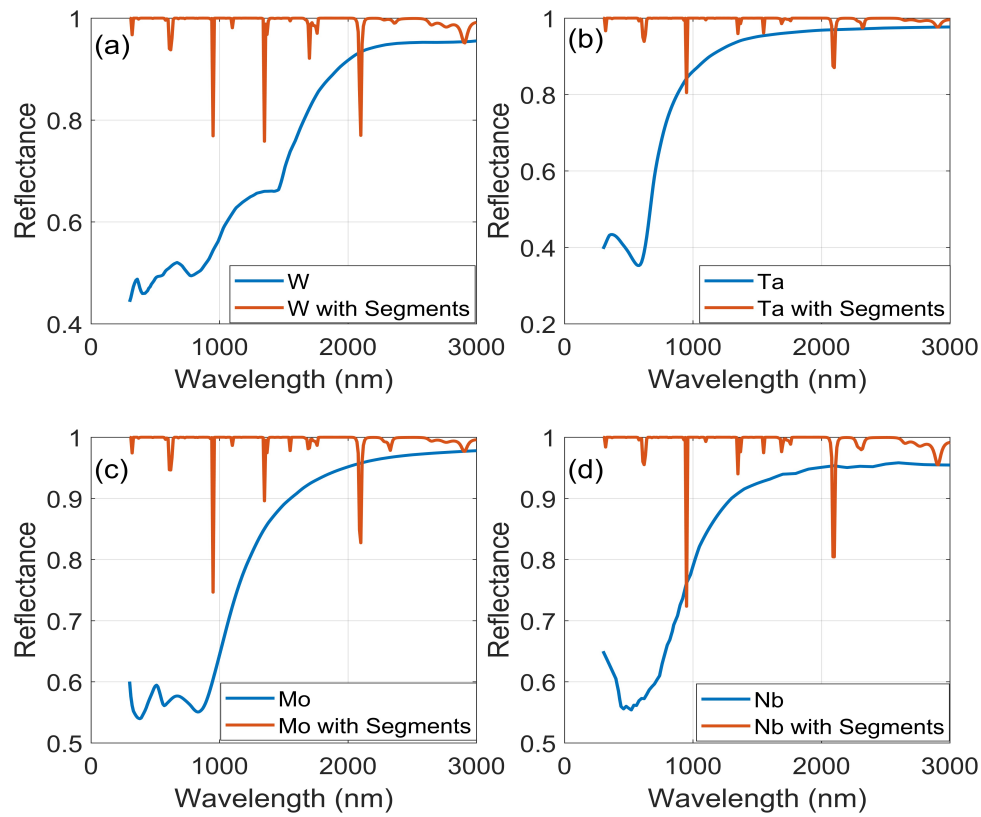


Figure 10: Spectral reflectance of multilayers composed of multiple segments designed to reflect around 450, 500, 750, 900, 1000, 1200, 1500, 2000 and 2200 nm wavelengths with different refractory metals.

Table 4. Comparison of average absorption percentages of uncoated and coated W, Ta, Mo and Nb with periodic segments for which spectral reflectances are depicted in Fig. (5).

Average Absorptions & Improvements					
Spectrum Interval		W	Ta	Mo	Nb
300-1500 nm	Uncoated	44.2 %	37.4 %	36.3 %	39.2 %
	Coated	0.5 %	0.15 %	0.10 %	0.13 %
	Absorption Reduction	98.7 %	99.5 %	99.7 %	99.6 %
1500-3000 nm	Uncoated	13.1 %	3.54 %	5.99 %	5.59 %
	Coated	1.5 %	0.59 %	0.65 %	0.06 %
	Absorption Reduction	87.8 %	83.3%	89.13 %	84.91 %

As shown in Table 4, reduction rate of absorbed powers of refractory metals are around 99 % for 300-1500 nm spectrum and 85 % for 1500-3000 nm spectrum when coated with periodic segments.

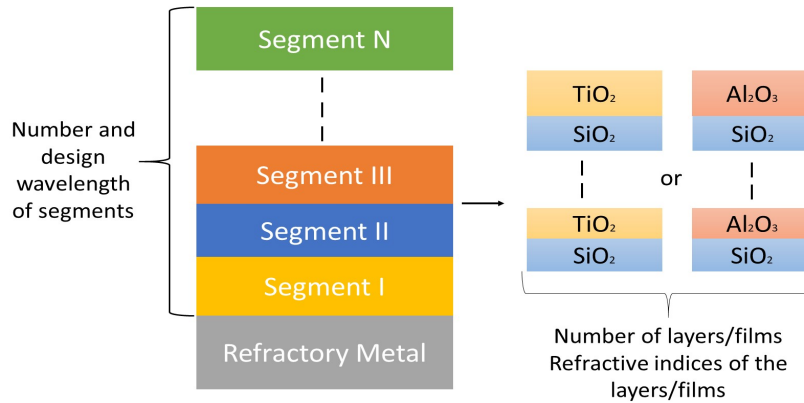


Figure 11: Representation of possible design parameters for multiple segments

Several design parameters, visually depicted in Fig. 11, including number of segments, layer numbers in the segments and materials in the segments are analyzed in this section. Effect of number of number of segments are compared by adding the above segments one by one on top of the W, Ta, Mo and Nb films and results are given in Fig. 12(a). Although average reflectivities converge to same levels for 8 segments, higher average values are obtained with Ta, Mo and Nb when compared to W at less number of segments. Reason of higher average at less number of segments with Ta, Mo and Nb is the littleness of the absorption of these metals when compared to W.

Number of layers in the segments are compared for various structures in Fig. 12(b). Not an increasing trend is observed with increasing number of layers, which indicates that number and magnitude of reflectance dips increase. From Fig. 12(b) it is shown that average reflectances are smaller for 5 and 7 layers when compared to 4 and 6 layers. Reason of such behavior is reflectance dips whose negative effects are enhanced when layer numbers are 4 and 6. Reason of such negative effects is discussed in detail in the next paragraph.

The reflectance dips in Fig. 10 resemble to the response of a Fabry Perot filter [chapt. 5 of Ref. 2]. Fabry Perot filters are composed of periodic high-low index films, each quarter wavelength thick, separated by a half wavelength thick film and designed to transmit incident wave at the selected wavelength and reflect the incident waves around that wavelength. Proposed filters consist of periodic high -low index segments which is similar to Fabry Perot filters. For demonstration, structures of Fabry Perot filters, their responses and approximate formation of those in proposed filters are depicted in Fig. 13(a), 13(b), and 13(c) respectively. Response of the Fabry Perot filters with demonstrated configuration in Fig. 13(a), for varying substrates with refractive indices of 1.4, 2 and 3 is depicted in Fig. 13(b). It is observed that bandwidth or magnitude of high

reflectance zones around the transmission gap wavelength are not altered with varying refractive index of the substrate but decreases the magnitude of the transmission at the central wavelength of 500 nm. This indicates that back reflection from bottom layers seem to be highly affecting the transmission behavior at the central wavelength.

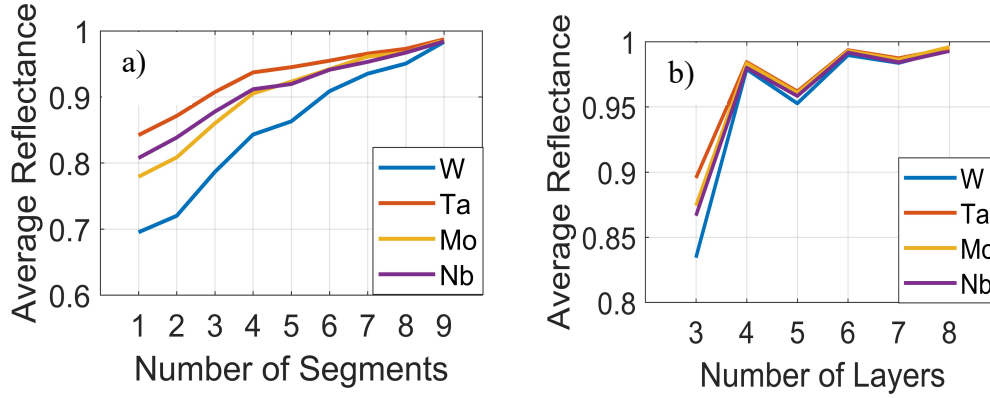


Figure 12: Average reflection with increasing number of segments. b) Average reflection for increasing number of layers per segments.

As shown, trends observed in the responses of Fabry Perot filters are very similar to responses observed in discussed broadband filters in terms of reflectance dips. To make an easier comparison, we consider a filter that is composed of periodic segments with central wavelengths of 400 nm 600 nm on top of 500 nm tungsten and Si substrate. In this filter top layer is selected as TiO_2 , so when there are odd number of layers bottom layer of each segment becomes TiO_2 . This creates TiO_2 - TiO_2 interfaces at intersection locations of two segments. When such interface occurs, this TiO_2 - TiO_2 interface acts as an almost perfect single half wavelength layer at 490 nm wavelength between two different periodic segments, because optical thicknesses of these two layers add up to π at 490 nm wavelength. Formation scheme of the half wavelength in between periodic segments is depicted in Fig. 13(c). In Fig. 14(a), spectral reflectance of Fabry Perot filter designed at 490 nm wavelength and filter with periodic segments at 400 and 600 nm, at which TiO_2 - TiO_2 interface is formed and optical thicknesses add up to π on top tungsten is compared. As depicted in Fig. 14(a), similar reflection drops at 490 nm wavelength are observed. High reflectance zones around 490 nm is present at each filter with higher reflectances around 350 nm at the filter because, filter has periodic segment designed at 400 nm whereas periodic reflector of Fabry Perot is at 490 nm. Number of layers in the segments are 5 in each filter.

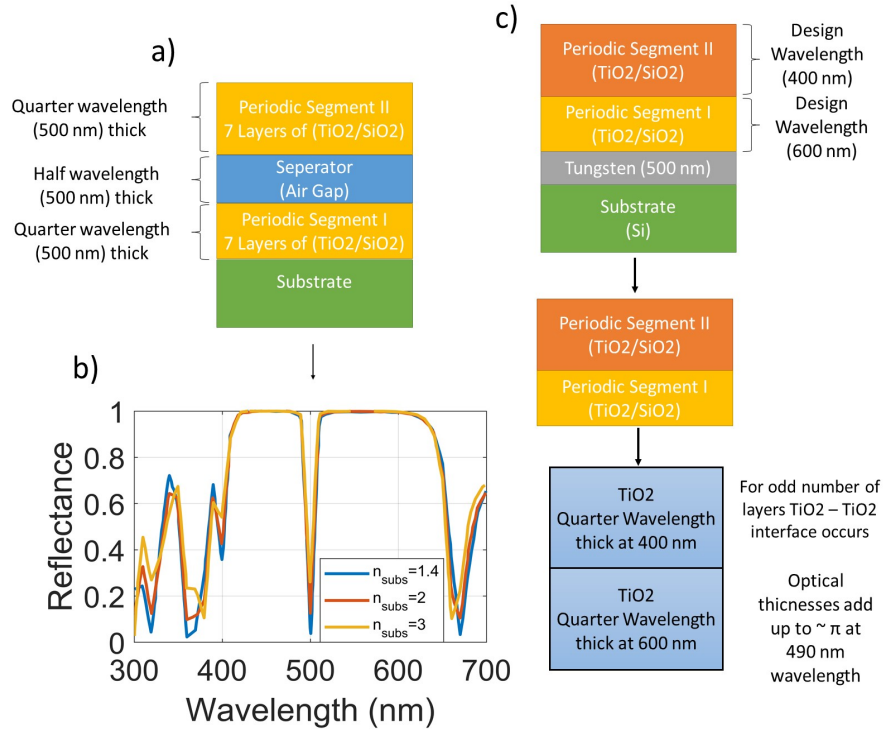


Figure 13: a) Schematic for fabry-perot filter designed at 500 nm. b) Formation of fabry-perot like structures in stacked segments. c) Effect of refractive index of the substrate on the fabry-perot mode.

As mentioned, segments of the periodic filter depicted in Fig.14(a) starts with TiO₂ and last layer of each segment becomes TiO₂ for odd number of layers. For even number layers SiO₂ become the last layer and SiO₂-TiO₂ interfaces occur instead of TiO₂-TiO₂. In Fig. 14(b), spectral reflectance of the filter in consideration with 4 and 5 layers are illustrated. As shown, when layer number is 5 reflectance drop occurs at 490 nm due to TiO₂-TiO₂ interface, whereas it is prevented when layer number is 4. This trend explains the reason why average reflectances are reduced for odd number of layers in Fig. 12(b). When the order of the layers is changed, starting with SiO₂ instead of TiO₂ and average reflectances are plotted against number of layers, an increasing trend is observed. Since segments' central wavelengths are kept identical, this result indicates that SiO₂-SiO₂ interfaces do not form approximate Fabry Perot filters as good as TiO₂-TiO₂ interfaces.

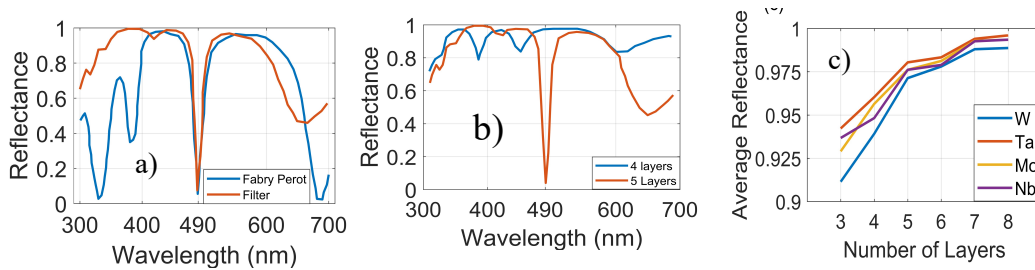


Figure 14: a) Comparison of reflectance fabry-perot designed at 490 nm and 2 segments on top of tungsten with design wavelengths of 400 and 600 nm. b) Comparison of reflectance of 2 segments on top of tungsten with design wavelengths of 400 and 600 nm with 4 and 5 layers. c) Average reflectance of the structures with increasing number of layers when top layers are SiO₂.

We also investigated the performance of thin-film filters by substituting Al_2O_3 instead of SiO_2 . Al_2O_3 has higher melting point and Young's modulus than SiO_2 which makes it a better candidate for coatings in extreme environments. Such a change degrades the optical performance of the coatings since refractive index of Al_2O_3 is less than SiO_2 . Due to the decreased refractive index ratio of the segments, shown in Fig 15(a), both magnitude and bandwidth of the reflection zone created by a single segment is reduced which is illustrated in Fig 15(b). Such reduction in reflectance of the segments rises the need for higher number of segments to cover 300-3000 nm spectrum interval. In Fig. 15(c), reflectance of segments with TiO_2 and Al_2O_3 at wavelengths 320, 370, 450, 500, 575, 660, 750, 860, 970, 1130, 1260, 1420, 1620, 1840, 2500 and 2580 nm, on top of 500-nm thick tungsten film. Average reflectance of the structure in 300-3000 nm spectrum is around 98% which is similar to previous structures. However, differently from TiO_2 - SiO_2 segments, such broadband high reflectance is achieved by 16 segments. Absorbed powers are calculated for these structures with varying bottom metallic layers of W, Ta, Mo and Nb which are tabulated on table 5. When compared to results given in table 2, this structure absorbs more power than the structure which consists of TiO_2 and SiO_2 .

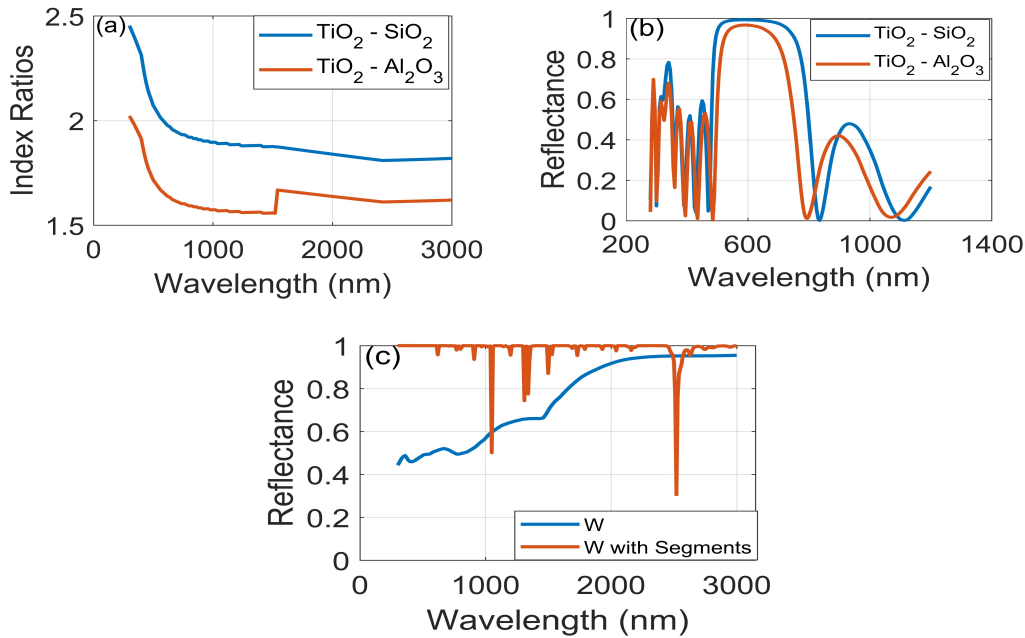


Figure 15: a) Refractive index ratios of TiO_2 - SiO_2 and TiO_2 - Al_2O_3 pairs. b) Comparison of reflectance of single segment designed to reflect around 600 nm by TiO_2 - SiO_2 and TiO_2 - Al_2O_3 pairs. c) Spectral reflectance when multiple segments are stacked together on top of W with TiO_2 - Al_2O_3 pairs.

Table 5. Reduction rates of absorbed powers by segmented structures (TiO₂-Al₂O₃) with 500-nm W, Ta, Mo and Nb for spectral intervals of 300-1500 nm and 1500-3000 nm.

Spectrum Interval	Reduction Rates of Absorbed Powers			
	W	Ta	Mo	Nb
300-1500 nm	98.53 %	98.86 %	98.29 %	98.45 %
1500-3000 nm	91.90 %	81.48 %	87.73 %	81.93 %

As shown in Table 5, similar reduction rates with TiO₂-Al₂O₃ filters when compared to TiO₂-SiO₂ filters. However, reaching to such high reduction rates require higher number of segments than previous structures do.

Finally, in Fig. 16, the average reflectance of the structures for various incidence angles are demonstrated. As shown in Fig. 16, average reflectance of the structures reduces with increasing incidence angle. The maximum average reflectance is observed at 0° since high reflectance zones are designed for this angle of incidence.

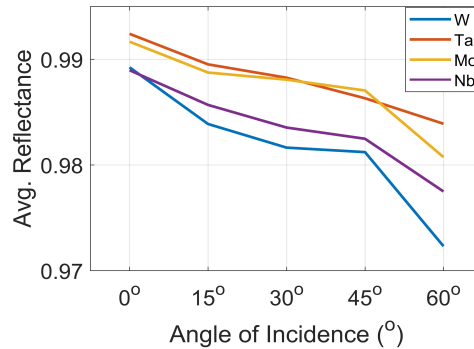


Figure 16: Average reflectance of the stacked segments on top of refractory metals for varying angle of incidence.

Although comparison for theoretical and experimental results are not reported, theoretical methodology applied in this work has been widely used for optical filter designs and experimentally verified in the literature [84-85]. The fabrication of a high number of segments with a high number of layers would be challenging, however fewer segments which include oxide layers can be fabricated by ion beam deposition which is currently used to produce very thin oxide multilayers [86]. A metal layer at the bottom can be coated via DC sputtering technique which can also be used to produce oxide layers on top of the refractory metal [84].

In real applications, effect of temperature on optical properties should also be considered. Temperature dependency of optical properties of the dielectrics in the devices brings a limit on operating temperature. In the literature it has been shown that optical properties of SiO₂ and Al₂O₃ do not vary significantly until 900 K and 1900 K levels respectively [87]. However, phase change in TiO₂, from anatase to rutile occurs at the temperatures around 900 K levels, results in changes in optical properties of TiO₂ in the visible spectrum. Therefore, structures in the manuscript can operate until 900 K temperatures according to studies reported in the literature

on these materials. For operational condition beyond 900 K, other materials may be used with changes to designs based on the outlined methodology.

By designing broadband reflectors with refractory metals instead of soft metals like Ag, Au, Cu, or Al, more durable devices are obtained. Soft metals are vulnerable to scratches and other environmental damages which can alter the optical behaviors. Even if they are coated with hard protective layers such as SiO₂ or Al₂O₃ [18,88], several problems occur due to attempt of coating materials with higher hardness on softer materials [17-18,20]. When soft metal reflectors are replaced with refractory metals, broadband reflectors with higher durabilities are obtained.

3.2. Broadband High Reflection Based on Impedance Mismatch and Morpho Butterfly Inspired Multilayers

For a fixed weight value ($\alpha=0.7$), average reflectance of the multilayer with increasing number of layers are depicted in Fig. 17(a) and spectral reflectance of the multilayer composed of 12 layers is shown in Fig. 17(b). As seen, average reflectance of the multilayer in both spectrum interval reaches to 97 % levels from 0.5 and 0.8 levels for 12 layers. Change of average also indicates that when layer number is higher than 4, there exist enough design parameter to increase the average in both spectrum interval. Amplitudes of the reflectance coefficients are also demonstrated in S-plane in Fig. 17(c). Illustrated amplitudes of the reflection coefficients of W with and without multilayer agrees with the spectral characteristics. As seen, all amplitude values shift towards outer edge of the unit circle.

Besides the broadband reflectance enhancement, multilayer structure yields sharp drops over the spectrum. To analyze the nature of the peaks, as well as the broadband reflectance characteristics, total optical path, δ_{Total} , that light travels throughout the homogeneous multilayer structure, is plotted in Fig. 17(d). It is well known that a medium highly reflects incident wave if the optical path at that wavelength is odd multiple of $\pi/2$. By relying on this, odd multiples, m , of $\pi/2$ is also marked on the plot depicted in Fig. 17(d). It is observed that there is a very good fit between $m\pi/2$ and δ_{Total} which clarifies the broadband reflectance behavior. Wavelengths of the sharp drops over the spectrum are also marked which correspond to $\lambda = 0.42, 0.56, 1.23, 1.46$ and $1.88 \mu\text{m}$ wavelengths. Here it is observed that sharp dips appear in the regions between the wavelengths where odd multiples are crossing with δ_{Total} . More explicitly, high reflectance zones over the spectrum are generated when δ_{Total} becomes close to odd multiple of $\pi/2$, and in between two odd multiples, δ_{Total} approaches to even multiples of $\pi/2$ which is associated with high transmission. Due to the increased number of odd multiple modes at shorter wavelengths, therefore the even multiples, rate of appearance of sharp dips increases and more oscillatory reflectance spectrum is observed.

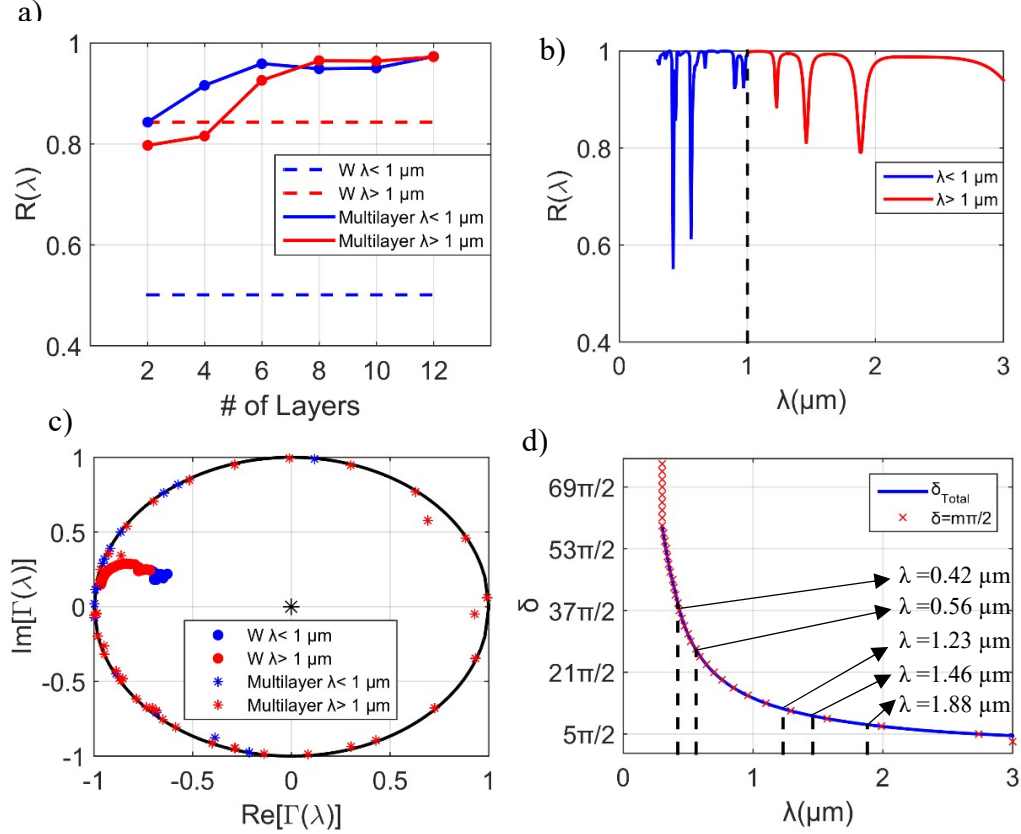


Figure 17: a) Average reflectance of multilayers for increasing number of layers. b) Spectral reflectance of multilayer with 12 layers. c) Reflection coefficients of W and multilayer structures. d) Total optical path that light travels throughout the multilayer.

As a next step, the effects of lift-off material properties and its dimensions on the reflectance spectrum are studied and corresponding results are depicted in Fig. 18(a) and 18(b). In Fig. 18(a), n_{Lift} is set to 1.41, and the reflectance spectrum for the updated multilayer with twelve layers is obtained.

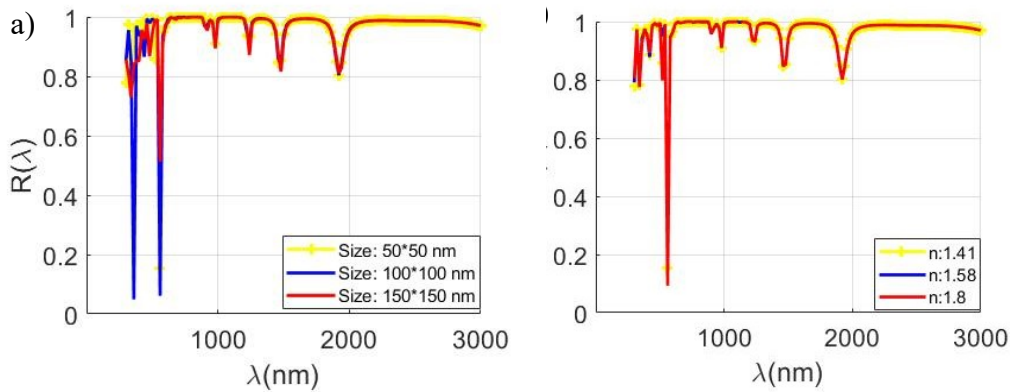


Figure 18: a) Reflectance spectrum of the structure with 12 layers in which lift-off layers ($n = 1.58$) of different sizes are added. b) Reflectance spectrum of the structure with 12 layers in which lift-off layers (100×100 nm) of different refractive indices are added.

A decrease in reflectance, especially at the shorter wavelengths is observed with increasing lift-off dimensions. This stems from the perturbation introduced in the air medium, which violates the situation considered in the design stage. With increasing volume fraction of the lift-off material, the effective index of the medium starts to deviate more from the presumed value of $n_{Air} = 1$ and alter the interference effects between the mediums. Similarly, in Fig. 18(b) in which the reflectance spectrum for varying n_{Lift} is depicted for 50*50 nm lift-off material dimensions, reflectance intensities start to decrease slightly. Similar reasoning is also valid here.

According to Fig. 5, the distance of two neighboring ridges, (d) parameter, is one of the most important variables, which affects the reflectivity of the structure. In this regard, the average reflectivity for distances of 200, 400, 600, 800, 1000 nm has been calculated, and the results can be seen in Fig. 19(a). It can be understood from this figure that increasing the distance between two adjacent ridges decreases the amount of reflectivity from 94% to less than 90%. Furthermore, to compare the effect of the shape of inhomogeneous structures on spectral characteristics, the reflectance of the proposed model for the morpho butterfly wing's nanostructure is depicted in Fig. 19(b-d). Regarding this figure, for each selected model the average reflectance is more than 90% in the given spectrum. However, increasing the gap between two adjacent ridges causes frequent oscillations, especially in shorter wavelengths, which leads to reduced average reflectance. Such oscillations stem from the additional interference effects induced by the air gaps between the periodic structures introduced by non-zero d . Contribution from such additional interference effects alters the total optical path that waves travel through the structure. However, total optical path can't be calculated by the theory developed for homogeneous layers, which is only applicable for zero d . Therefore, a $-S$ parameters retrieval method [89] is applied to calculate the $-S$ parameters of the studied multilayer structures. $-S$ parameters can be treated as transfer function of the multilayer structure, therefore provides an understanding of the optical response of the structures in consideration. Since the reflectance spectrums of the structures are of interest, only S_{11} parameters are analyzed.

S_{11} parameters are identical to reflectance coefficients given in Eq. (4) and can be represented with magnitude and phase terms. Since phase term determines the optical path that wave travels, phase of S_{11} terms, $\angle S_{11}$, are studied in the entire spectrum interval. To make an explicit evaluation, the distinct reflection dips occurring in 1-1.6 μm spectrum are analyzed. Then analysis is extended to broader spectrum.

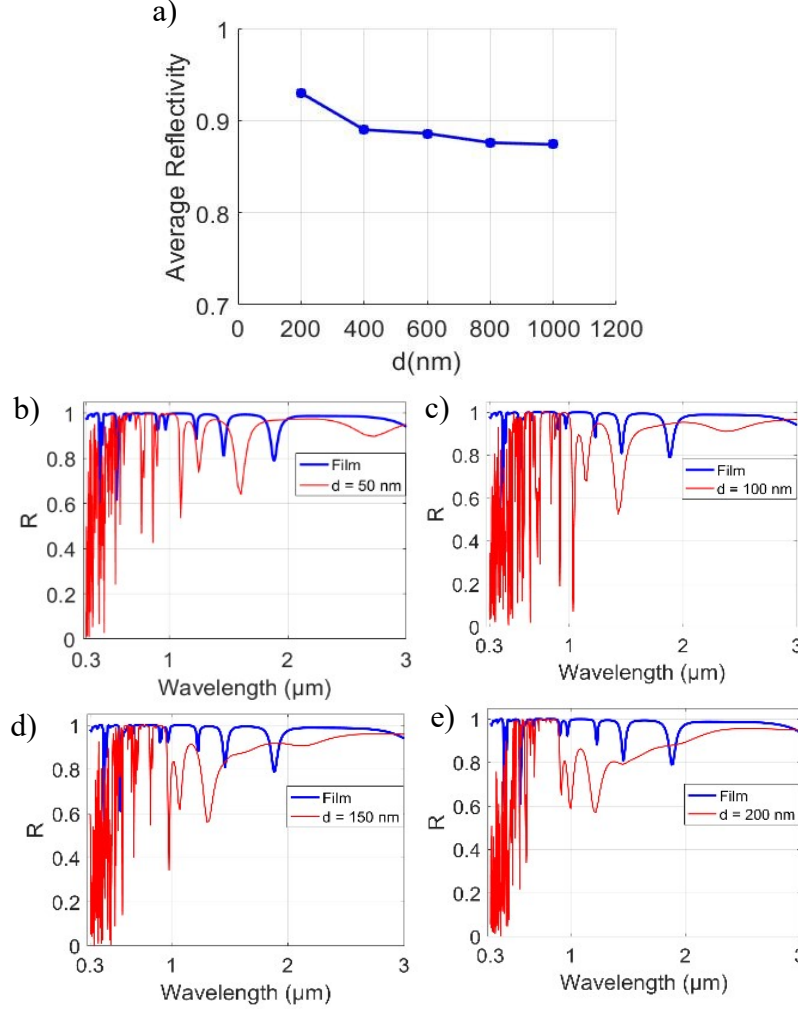


Figure 19: a) Average reflectance of structures for varying distance/periodicity. b-c-d-e) Spectral reflectance of the structures for varying distance/periodicity.

In Fig. 20(a), reflectance dips occurring in 1-1.6 μm wavelength interval for the structures with $d = 50, 100, 150$ and 200 nm are depicted. As seen, all these dips are shifted to shorter wavelengths compared to homogenous film. For the structures with $d = 50, 100, 200$ nm two dips and for the $d = 150$ nm single dip are observed. In Fig. 20(b), $\langle S_{II} \rangle$ are plotted with respect to wavelength and even multiples of π are marked with black dashed lines. As seen, the $\langle S_{II} \rangle$ curve of the structure with $d = 50$ nm crosses 4π at 1.6 μm and 2π at 1.26 μm . When considered with the reflectance spectrum depicted in Fig. 20(a), it can be seen that crossing points are very close to reflection dips. Similar trends are observed for the structure with $d = 100$ nm whose $\langle S_{II} \rangle$ crosses 0 and 2π at wavelengths 1.15 and 1.42 μm wavelengths respectively which corresponds to location of the reflectance dips. Single crossing at 2π occurs for the structure with $d = 150$ nm and resulting in single dip in reflectance spectrum. Finally, the structure with $d = 200$ nm have two crossing points 1.21 and 1.45 μm which result in a distinct and

relatively smooth dip in reflectance spectrum respectively. To analyze the characteristics at shorter wavelengths which exhibit more frequent oscillations, $\langle S_{11} \rangle$ curves in $0.3 - 3 \mu\text{m}$ spectrum are plotted with even multiples of π are marked and demonstrated in Fig. 20(c). As seen, slope of the $\langle S_{11} \rangle$ curves are nearly similar for $\lambda > 1 \mu\text{m}$, therefore number of $m\pi$ crossings ($m = 0, 2, 4, \dots, N$) are observed in the spectrum. With increasing slope of the $\langle S_{11} \rangle$ curves at $\lambda < 1 \mu\text{m}$ number of $m\pi$ crossings increase, therefore the number of oscillations.

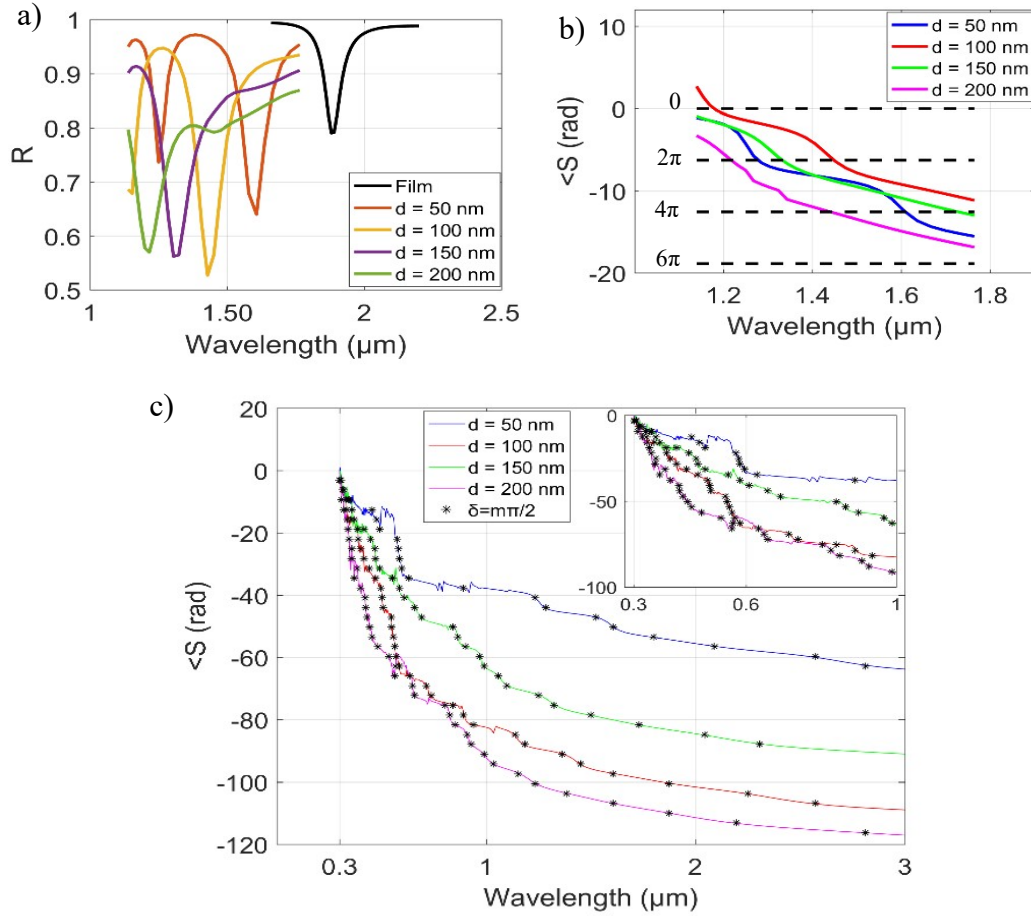


Figure 20: a) Distinct reflectance dips for the structures with different d . b) $\langle S_{11} \rangle$ curves of the structures with different d for which reflectance dips are shown in Fig. 19(a). c) $\langle S_{11} \rangle$ curves of the structures with different d in $0.3 - 3 \mu\text{m}$ interval with even multiples of π are marked.

3.3. Evaluation of Periodically Arranged Layers for Passive Radiative Cooling

In this section, analysis results for 2 types of multilayer structures composed of periodically arranged layers. Firstly, combination of 3 alternating layers with high emission in 8-13 μm spectrum interval are studied. Purpose of this analysis is to observe the effect of dispersion in layer materials to overall absorption/emittance. Therefore, spectral reflection of alternating SiO_2 , Al_2O_3 and TiO_2 layers on top of an Ag layer is calculated and analyzed. Secondly, similar to approach described for reflection with refractory metals problem, multiple periodic segments are stacked together to achieve broadband reflection in visible and near-infrared spectrums and high emission in 8-13 μm interval simultaneously. Corresponding results for these two separate analyses are briefly described in the following subsections.

3.3.a. Achieving Enhanced Emission with Material Dispersion

It is well known that optical properties, and therefore emissivity, of materials usually have strong wavelength dependence. To improve the emissivity of the coating, adding materials with stronger absorption in the 8-13 μm spectrum may yield better results. Strong absorption of Al_2O_3 makes it a good candidate for improving the emissivity of the coating. As a comparison, absorptions of SiO_2 , TiO_2 and Al_2O_3 are plotted against wavelength in Figs. 21(a-c), respectively. The results show that absorption of these materials has a strong wavelength dependence and Al_2O_3 has stronger absorption in the 8-13 μm spectrum compared to SiO_2 and TiO_2 . SiO_2 has absorption peak around 9 μm , whereas TiO_2 does not have an observable peak until 14 μm as shown in Figs. 21(a) and 21(b) respectively. When absorption graph of Al_2O_3 is considered, which is illustrated in Fig. 21(c), it does not absorb in the visible and near-infrared spectrums and by slightly increasing its absorption makes a peak around 13 μm . Non-absorbing behavior of Al_2O_3 in the visible and near-infrared spectrum makes it an appropriate material for a radiative cooling design. Also, it has higher absorption rates than SiO_2 and TiO_2 after 10 μm spectrum, which would improve overall emission in 8-13 μm spectrum.

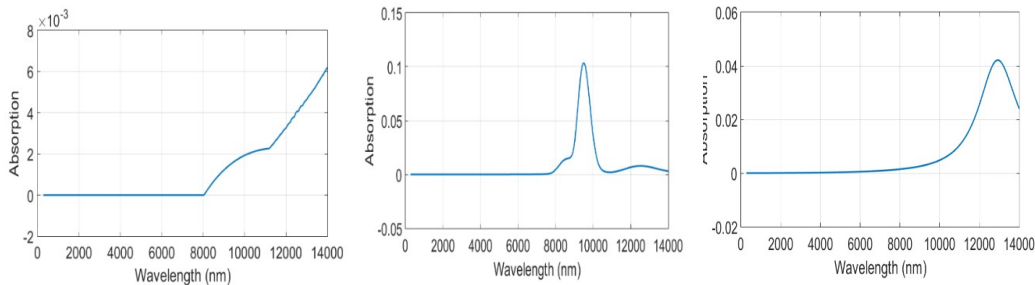


Figure 21: a) Absorption of SiO_2 with respect to wavelength, which has absorption peak around 9 μm . b) Absorption of TiO_2 (anatase) with respect to wavelength, which does not have an observable absorption peak until 15 μm . c) Absorption of Al_2O_3 with respect to wavelength, which has absorption peak around 12 μm .

Based on these, spectral reflection of 3 stacks of alternating TiO_2 , SiO_2 , Al_2O_3 . In Fig. 22(a), the designs with and without Al_2O_3 are compared. In one of the designs 9 layers of alternating TiO_2 and SiO_2 , each 200-nm thick, are used in absorption segment, whereas alternating TiO_2 , SiO_2 and Al_2O_3 are used with the similar thicknesses and number of layers in the other design. In other words, overall thickness and number of layers are identical for both designs. We also conducted a parametric study on the design with Al_2O_3 to analyze the effects of film thicknesses, number of layers and angle of incidence. As shown in Fig. 22(a), the design with Al_2O_3 yields a dramatical increase in emission. Average emissivity in the 8-13 μm spectrum increased from % 55 to % 71 for the same overall thickness and number of layers.

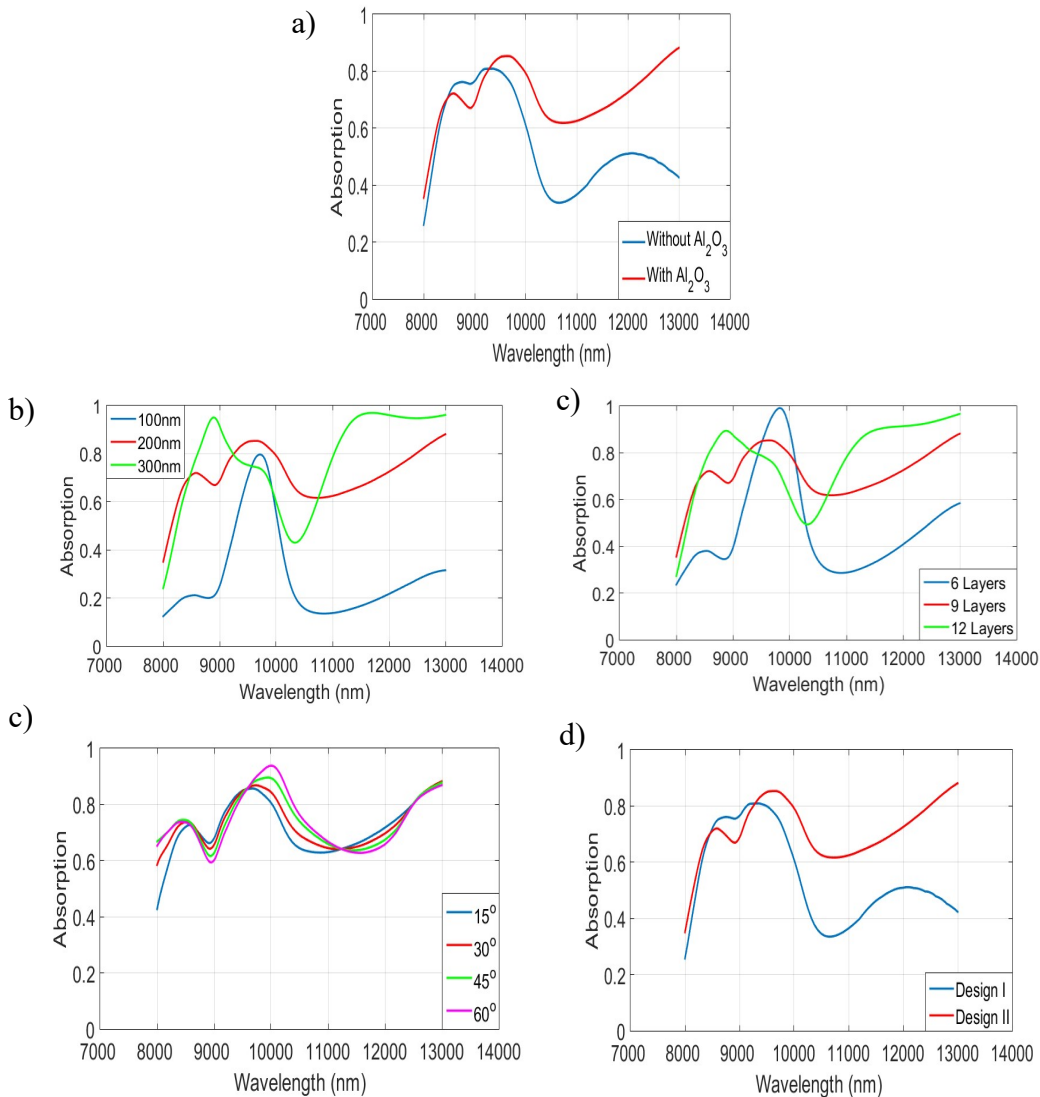


Figure 22: a) Comparison of emission curves of the two designs to show the effect of Al_2O_3 . b) Comparison of emission curves of the designs in the mid-infrared spectrum which have layers of 100, 200 and 300 nm thick, 9 layers in total, in absorption segment. c) Comparison of emission curves of the designs in the mid-infrared spectrum which have 6, 9, 12 layers, each 200 nm thick, in absorption segment. d) Comparison of emission curves in mid-infrared spectrum for incidence angles. e) Comparison of emission curves of previous design and new design with 9 layers, each 200 nm thick, in absorption segment.

For the proposed design, the effect of layer thicknesses, number of alternating triplets and angle of incidence are shown in Figs. 22(b), 22(c) and 22(d) respectively. In addition, spectral emissivity of previously implemented structure and new structure with 3 triplets are compared in Fig. 22(e). As shown in Figs. 22(b) and 22(c), as the layer thicknesses and number of layers are increased, average emissivity in the mid-infrared spectrum is increased to % 78. The source of high absorption in the mid-infrared spectrum is the combination of the optical properties of the materials and interference effects. Absorption of SiO₂, TiO₂ and Al₂O₃ in the mid-infrared spectrum is demonstrated in fig 21. The proper selection of the layer thicknesses increases the total optical path that light travels in the absorbing layers through interference effects, thus broadband absorption in the mid-infrared spectrum is achieved. No optimization technique is applied in the current design due to the large number of parameters and the resulting high computational load. However, absorption can be further improved by thickness optimization which can increase the total optical path that light travels through interference. In addition, the results suggest that the structure's emission both in visible to near-infrared and in mid-infrared spectrums are not dramatically affected at various angle of incidences. More importantly, this increase obtained without any increase emission in visible to near-infrared spectrum. As expected, emission after 10 μm spectrum increased dramatically due to strong absorption of Al₂O₃ around that spectrum. That increase in emission results in increase of cooling power to 62 W/m². With these results it is shown that by selecting appropriate materials which have different absorption peaks in 8-13 μm spectrum, absorption in that spectrum can be increased dramatically without any thickness increase or even further increase can be obtained by increasing the layer thicknesses or adding more layers without losing from the reflection percentage in the visible and near-infrared spectrums.

3.3.b. Periodically Arranged High/Low Index Layers for Radiative Cooling

As discussed in 3.1, periodic high-low index layers are proven to be very effective in achieving high reflection over a broadband spectrum. Similar design methodology is also adapted to radiative cooling design. By using TiO₂ and SiO₂, which are absorbers in the 8-13 μm spectrum, in the proposed design, emission requirement of radiative cooling can also be achieved. 8 segments are used to generate high reflection zones around 300, 600, 750, 900, 1200, 1500, 2000 and 2300-nm wavelengths. Parameter analysis is also carried out for this case. Fabrication of a high number of periodic segments would be challenging, however fewer segments can be produced by ion beam deposition which is currently used to fabricate extremely thin oxide multilayers [86]. As technology progresses and new fabrication techniques emerge, higher number of segments can be fabricated. Structure's average reflectance in 280 nm to 2.5 μm and average emission in 8-13 μm is calculated for different angle of incidences and number of layers in the segments and related results are illustrated in Fig. 23.

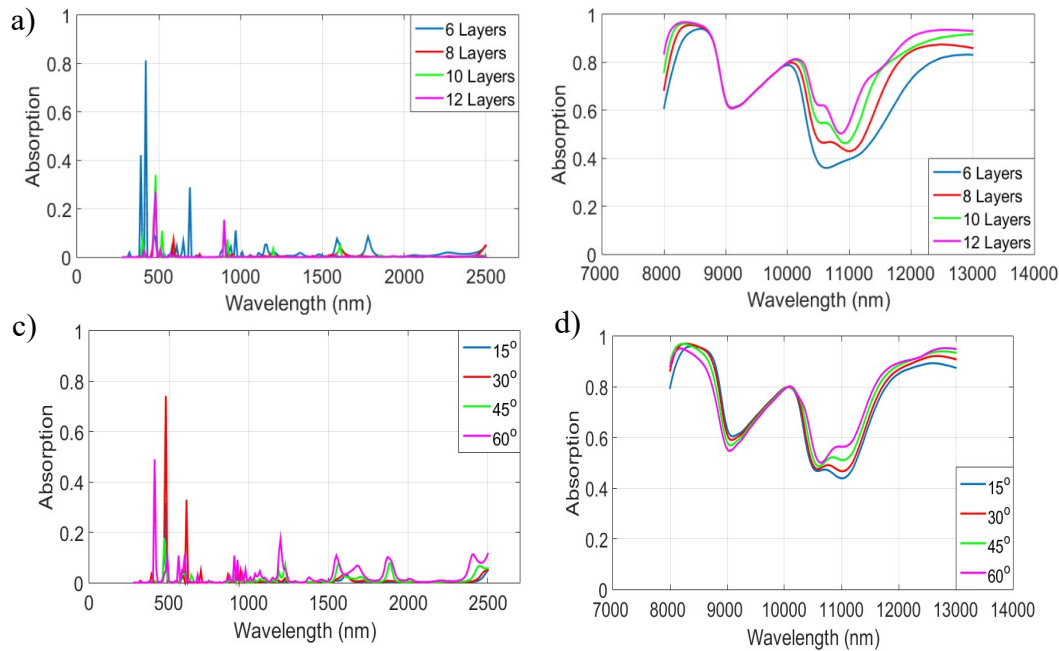


Figure 23: a) Absorption graphs of quarter wavelength stacks in 280–2500 nm spectrum with 6, 8, 10 and 12 layers. b) Absorption graphs of quarter wavelength stacks in 8-13 μm spectrum with 6, 8, 10 and 12 layers. c) Absorption graphs of quarter wavelength stacks, each have 8 layers, in 280-2500 nm spectrum at 15° , 30° , 45° and 60° incidence angles. d) Absorption graphs of quarter wavelength stacks each have 8 layers, in 8-13 μm spectrum at 15° , 30° , 45° and 60° incidence angles.

Table 6. Average reflectance and emission in corresponding spectrums with respect to layer numbers and angle of incidences

Number of Layers in the Segments	Reflectance in 280 nm – 2.5 μm	Emission in 8-13 μm	Angle of incidences	Reflectance in 280 nm – 2.5 μm	Emission in 8-13 μm
6	% 98.51	% 68.53	15°	% 99.39	% 74.60
8	% 99.57	% 73.4	30°	% 99.32	% 75.94
10	% 99.74	% 77.23	45°	% 98.97	% 76.98
12	% 99.9	% 79.74	60°	% 97.49	% 77.46

The coatings, of which the absorptions are plotted against wavelength for various conditions in Fig. 23, are used to generate high reflection until 2.5 μm spectrum where high solar energy is present. In every scenario, reflection percentage is above %97 until 2.5 μm and increases dramatically after that wavelength. In Table 6, it is shown that as number of layers increased from 6 to 8, 10 and 12 average reflectances increase to % 98.51, %99.57, %99.74 and %99.9 respectively. Also, absorption percentages increase to %68.53, %73.4, %77.23 and %79.74. High performance improvements are obtained both in reflection and emission in the desired spectrums. Barrier due to presence of an absorbing layer is overcome and by using absorbers in 8-13 μm spectrum high absorption in that spectrum is also obtained without using an extra absorption segment. When effect of angle of incidence angle is examined in Fig. 23(c)-23(d) different behavior is

observed. It is shown that as angle of incidence increased, average reflectance in the visible and near-infrared spectrums decreased, but average emission in mid-infrared spectrum is increased. In the previous designs, structure's average reflectivity in the visible and near-infrared spectrums varies slightly but it is about % 2 in this case. Change of average reflectance is expected because layer thicknesses are determined for perpendicular angle of incidence. So, testing the structure with different angle of incidence, which is not designed for, causes performance variations. Still, average reflectance remains at very high values and emission increase in the mid-infrared spectrum causes less loss of cooling power.

A periodic design for perpendicular angle of incidence which has 8 layers of TiO_2 and SiO_2 is implemented and absorption/emission graph of it at 40° angle of incidence (it is incidence angle of the sun in Istanbul on 23rd March at 12 pm) is shown in Fig. 24(a). Structure has average reflectance of % 99.2 in the visible and near-infrared spectrums and % 77 emission in the 8-13 μm spectrum interval. When radiative power equations are calculated from 280 nm to 13 μm spectrum radiative cooling power becomes 85.5 W/m^2 . This result is achieved despite high absorption in the 2.5-8 μm spectrum, which is reflected by Ag in the previous designs. As discussed, considerable heating load is present in the 2500-8000 nm spectrum and reflecting this would result in higher cooling power. Reflection in that spectrum can be increased by adding more periodic segments or adding an Ag layer at the bottom of the periodic design which is a simpler way. In Fig. 24(b), absorption/emission graph of periodic design with an Ag layer at the bottom is shown. It can be seen that absorption after 2.5 μm wavelength decreased dramatically. Ag layer does not introduce absorption in the visible spectrum in this case, because incident irradiance is highly reflected by periodic layers which are above Ag, thus extremely low amount of energy reaches to the Ag layer to be absorbed. Also, adding Ag layer increases the absorption in the 8-13 μm interval to % 84. In this case, radiative cooling power becomes 103 W/m^2 .

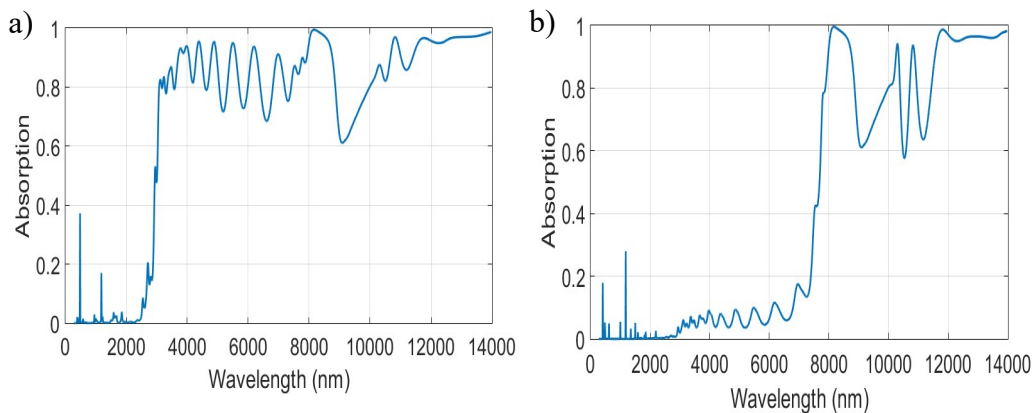


Figure 24: a) Emission graph of periodic design consist of 8 layers of TiO_2 and SiO_2 , which has average reflectance of % 99.2 in 280 nm to 2.5 μm spectrum and emission of % 77 in 8-13 μm spectrum interval. b) Emission graph of the similar periodic design whose emission is shown in Fig. 9a, with an Ag layer added at the bottom. Average reflectance in 280 nm to 2.5 μm spectrum is % 99.25 and emission is % 84 in 8-13 μm spectrum interval. Also, structure has significantly high reflection in 2.5-8 μm spectrum when compared with the design which does not have Ag at the bottom.

3.4. Cooling Power Based Design Method for Passive Radiative Cooling

As described in the previous section, radiative cooling performance is highly dependent on both spectral and radiative dynamics. Due to this, both spectral aspect and impact of spectral aspect on radiative dynamics should be included in the design stage. To address this, methodology proposed in section 2.3 is developed and corresponding results are given in this section.

Following the procedure given in section 2.3, layer thicknesses are solved for layer numbers of 1 to 7, and cooling power of these structures is displayed in Fig. 25(b). As seen, an increasing trend in cooling power ($T_{\text{Surf}} = 300 \text{ K}$ and $T_{\text{Amb}} = 297 \text{ K}$) is observed with increasing number of layers. Cooling power reaches 100 W/m^2 with 7 layers on the top of Ag layer. The spectral distribution of the absorptance/emittance is also shown in Fig. 25(c) and 25(d), where selective emission occurs in the $8\text{--}13 \text{ }\mu\text{m}$ spectrum and high reflection is seen elsewhere. Average reflectances in the $0.3\text{--}8 \text{ }\mu\text{m}$ and $13\text{--}25 \text{ }\mu\text{m}$ spectra are 97% and 50% respectively, and the emittance in the $8\text{--}13 \text{ }\mu\text{m}$ spectrum is 80%.

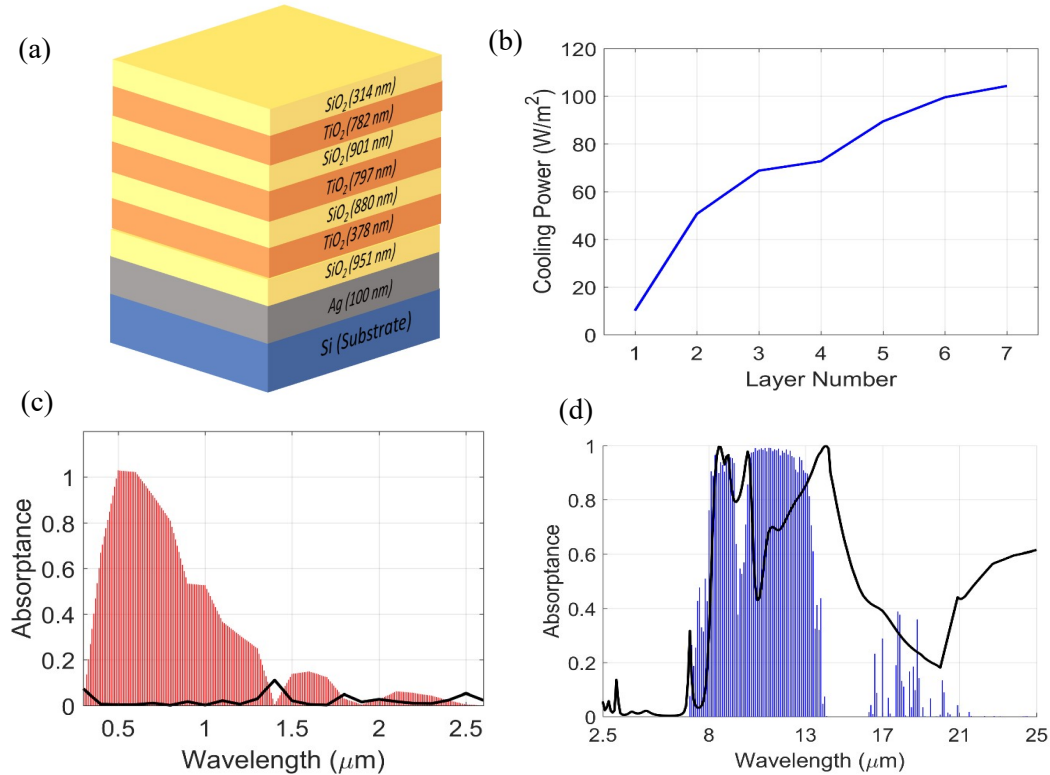


Figure 25: a) Final structure with 7 layers. b) Cooling power at 300 K and $T_{\text{Amb}} = 297 \text{ K}$. c) Absorptance of the structure depicted in (a) in spectrum interval $0.3\text{--}2.5 \text{ }\mu\text{m}$ plotted on solar irradiance in this interval at perpendicular angle of incidence. d) Absorptance of the structure depicted in (a) in spectrum interval $2.5\text{--}25 \text{ }\mu\text{m}$ at perpendicular angle of incidence, plotted on atmospheric transmittance in this interval.

Normalized gamma values of the final structure with 7 layers are demonstrated in Fig. 26 and are compared to gamma values of Ag. As seen in Fig. 26(a), gamma values of the Ag layer in the $0.3\text{--}8 \text{ }\mu\text{m}$ spectrum are clustered on the left side of the circle.

When seven layers are coated on the top of Ag, we see that $\Gamma(\lambda=1.5)$, $\Gamma(\lambda=4.5)$ and $\Gamma(\lambda=7)$ values change but remain very close to the outer bounds of the unit circle. Therefore, the high reflectance at these wavelengths is still preserved. However, $\Gamma(\lambda=0.3)$ also approaches to the outer edge of the unit circle, thus its reflectance is increased, as shown in Fig. 25(c) and distinct absorptance peak due to Ag layer is suppressed. This suppression has significant impact on P_{Sun} component since radiation intensity around 0.3-0.4 μm spectrum is high as shown in Fig. 25(a). Gamma values are significantly altered in the 8-13 μm spectrum interval and approach to the center of the unit circle. Finally, at longer wavelengths ($\lambda \geq 13 \mu\text{m}$), gamma values deviate from the unit circle, thereby resulting in decreased reflectance and increased absorption of the atmospheric thermal radiation. These changes occur mainly because of the lossy nature of SiO_2 and TiO_2 in these spectrum ranges. By optimizing the thicknesses, spectral selectivity (high and low emission in 8-13 μm and 13 – 25 μm intervals respectively), is achieved, as seen in Fig. 25(d). High emittance in 8-13 μm spectrum is achieved except a sharp dip around 11.5 μm which is attributed to phonon polariton resonance of SiO_2 around 10 μm . Note that there is a small reduction in emission intensity around 9 μm is observed which is overlapping with the dip of the atmospheric transmittance in 8-13 μm interval. This behavior is similar to results reported in [81], in which modified ideal emittance curve in 8-13 μm (unity emission in 8-13 μm spectrum except around 9-10 μm wavelengths) is utilized. Authors of [81] report improved cooling powers due to modified ideal emittance curve by which the negative contribution of the dip in atmospheric transmittance window is suppressed. Our results indicate that CP based approach automatically achieves that modified spectral profile, by which cooling power is further improved. In Table 7, residual errors and radiative heat components (P_{Rad} , P_{Sun} , P_{Atm}) for Ag and structure with 7 layers given in Fig. 25(a) are displayed.

Table 7: Mathematical expressions for spectral and cooling power-based formulations.

	Spectrum Interval	Ag	Coated
$\ R_1(\lambda)\ $ $\ R_2(\lambda)\ $ $\ R_3(\lambda)\ $	λ (0.3-8 μm)	8.7	8.8
	λ (8-13 μm)	7.02	3.4
	λ (13-25 μm)	10.29	7.64
Radiative Heat Loads	P_{Rad} (W/m^2)	27.3	207.31
	P_{Sun} (W/m^2)	26.29	6.75
	P_{Atm} (W/m^2)	23.84	96.24
	P_{Cool} (W/m^2)	-22.83	104.32

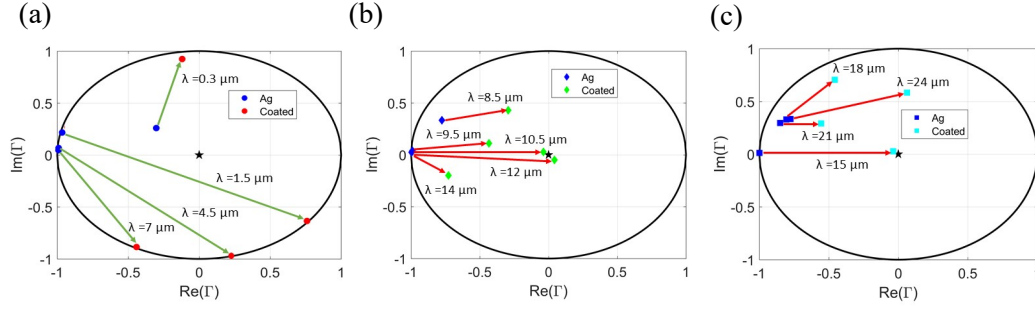


Figure 26: a) Spectral distribution of reflectance coefficients of the structure depicted in Fig. 5(a), in 0.3-8 μm spectrum, on complex gamma plane. b) Spectral distribution of reflectance coefficients of the structure depicted in Fig. 5(a), in 13-25 μm spectrum, on complex gamma plane. c) Spectral distribution of reflectance coefficients of the structure depicted in Fig. 5(a), in 8-13 μm spectrum, on complex gamma plane.

Cooling powers of the structures designed by the spectral approach and cooling power approach with number of layers changing from 1 to 7 are compared in Fig. 27. Demonstrated cooling power results are discussed with the reported values of residual errors in Table 7.

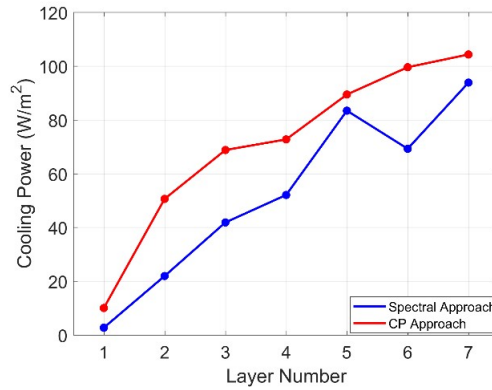


Figure 27: Cooling power comparison of the structures designed by spectral and cooling power approach with layer numbers of 1 to 7.

As shown, cooling powers of the structures are higher when designed by the cooling power approach. Also, an increasing trend is observed with increasing number of layers with this approach. In the spectral approach case, when the layer number is increased from 5 to 6, cooling power is decreased from $\sim 80 \text{ W/m}^2$ to $\sim 70 \text{ W/m}^2$. To analyze this behavior, we compared the spectral behavior of these two structures. In Fig. 28, spectral behavior of 5 and 6 layered structures designed by the spectral approach at perpendicular angle of incidence is shown. As seen from Fig. 28, the spectral behavior is not significantly altered with in the 8-13 μm band, but significant changes are observed in 0.3-8 μm and 13-25 μm spectrum intervals. In Table 8, minimum mean square error values are given for the structures. As seen, MMSE value for the 6 layered structure is lower compared to the 5 layered structure. However, the 6 layered structure exhibits higher cooling power, which is explained by considering the average emittances and radiative heat components in Table 9. The average emittances in separate intervals indicate that reduced MMSE is the result of the reduced emittance in the 13-25 μm

spectrum. Reduction in $\overline{\varepsilon_3(\lambda)}$ results in a decrease in P_{Atm} ($\sim 6 \text{ W/m}^2$), leads also a considerable rise in $\varepsilon_1(\lambda)$ and solar absorption. Thus, the total cooling power P_{Cool} is reduced to 69.25 W/m^2 from 83.42 W/m^2 . This comparison and tabulated results in Table 9 reveal the advantage of the cooling power approach over the spectral approach. In the spectral approach, the effects of spectral behavior on the cooling power are ignored during the design process. The results indicate that a quantitatively better solution, shown in Table 8, in terms of spectral behavior does not necessarily result in higher cooling powers as depicted in Table 9. When the effects of spectral behavior on cooling powers are considered in the design process, much better designs are obtained.

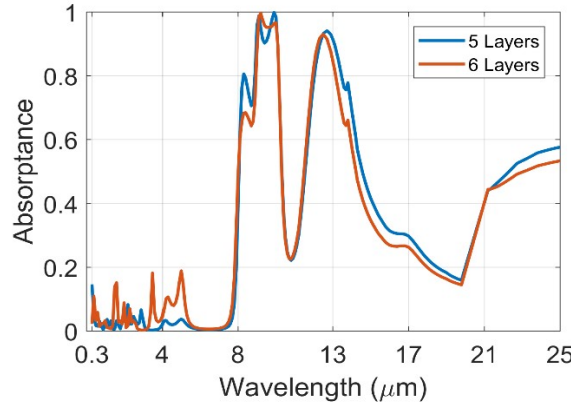


Figure 28: Comparison of spectral emittance of the structures with 5 and 6 layers designed by spectral approach at perpendicular angle of incidence.

Table 8. Comparison of MMSE of the structures with 5 and 6 layers designed by spectral approach.

$$MMSE = \sum (\varepsilon_{Ideal}(\lambda) - \varepsilon_{Actual}(\lambda))^2$$

5 Layers	33.73
6 Layers	29.60

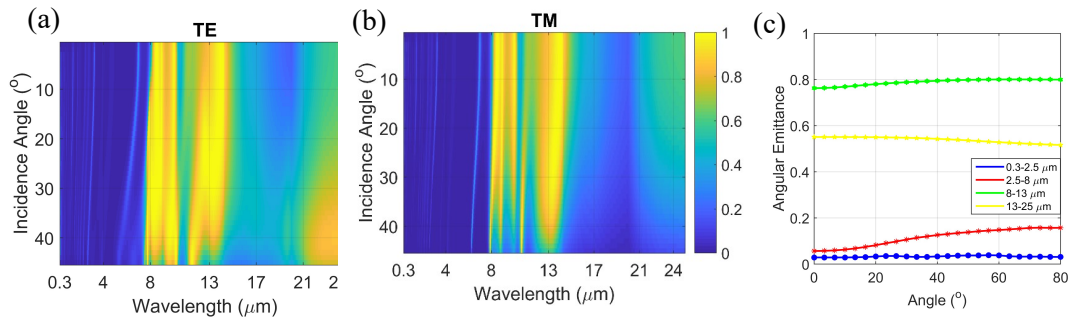


Figure 29: a) TE polarized emittance of the 8 layered structure depicted in Fig. 25(a) with respect to wavelength and incidence angle. b) TM polarized emittance of the 8 layered structure depicted in Fig. 25(a) with respect to wavelength and incidence angle. c) Angular emittance of the structure with 7 layers.

Table 9. Average emittances and radiative heat components for the structures with 5 and 6 layers designed by spectral approach

	Spectrum Interval	5 Layers	6 Layers
$\overline{\varepsilon_1(\lambda)}$	λ (0.3-8 μm)	2.78 %	5.34 %
$\overline{\varepsilon_2(\lambda)}$	λ (8-13 μm)	70.74 %	69.86 %
$\overline{\varepsilon_3(\lambda)}$	λ (13-25 μm)	42.82 %	38.89 %
Radiative Heat Components	P_{Rad} (W/m^2)	177.95	170.49
	P_{Sun} (W/m^2)	16.29	28.69
	P_{Atm} (W/m^2)	78.23	72.54
	P_{Cool} (W/m^2)	83.42	69.25

In Fig. 29(a) and 29(b), angular spectral emittances with respect to wavelength for TE and TM polarizations are displayed. As seen from these results, the selective behavior of a filter is preserved in both polarizations for wide range of angles. Also, angular emittance of the structure with seven layers, whose spectral emittance in perpendicular angle is depicted in Fig. 25(d), is shown in Fig. 29(c). Results indicate that angular dependency of the emittance of the structure is low in broadband. As seen, very low emittance values in 0.3-2.5 and 2.5-8 μm intervals are observed, whereas it is increased in longer wavelengths, especially in 8-13 μm interval. Equilibrium temperatures of the structures are also evaluated based on the spectral behavior and the radiative components and are demonstrated in Fig. 30(a) for $h_c = 5 \text{ Wm}^2\text{K}^{-1}$.

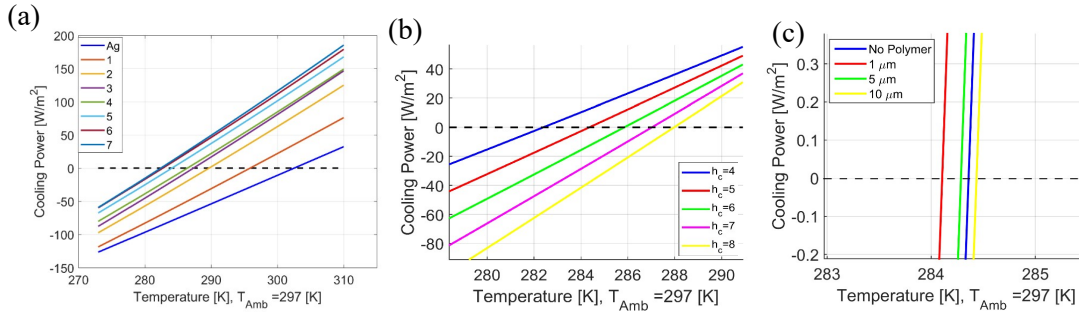


Figure 30: a) Temperature vs. cooling power curves of Ag and structures with varying number of layers, 1 to 7 with $h_c=5$. b) Temperature vs. cooling power curves for the structure with 7 layers for varying h_c values. c) Temperature vs. cooling power curves for the structure with 7 layers with and without a polymer coating of varying thicknesses with constant h_c of 5.

The equilibrium temperatures of the structures for varying number of layers are obtained by setting the cooling power equation to zero as,

$$P_{Cool} = P_{Rad}(T_{Eq}) - P_{Atm}(T_{Amb}) - P_{Sun} - P_{Cond+Conv} = 0 \quad (17)$$

The change in cooling power with respect to temperatures are demonstrated in Fig. 30(c), from which equilibrium temperatures are deduced. Parasitic heat load coefficient, h_c , of $5 \text{ Wm}^{-2}\text{K}^{-1}$ is assumed to address conductive and convective contributions and T_{Amb} is set as 297 K. The equilibrium temperature of Ag at these conditions is around 302 K. For 7 layers, the equilibrium temperature is around 282 K, which is 15 K below the ambient temperature. When h_c is set to 0, structure can achieve a steady state temperature 40 K below the ambient temperature. Previously reported values for this case are around 24 K and 19 K in [81] and [35] respectively.

In Fig. 30(b), equilibrium temperatures for h_c values ranging from 4 to 8 are also shown. The equilibrium temperature of the structure with 7 layers is increased from 280 K to 288 K when h_c is increased from 4 to 8. Results show that below ambient air temperature is still achieved when the heat exchange with the surrounding is increased. Finally, to observe the optical impact of the convection suppression through an insulator, the effect of a polymer layer on top of the designed coating's spectral emittance is analyzed.

Constant refractive index of 1.4 is assumed for the insulator polymer layer and its effect on the cooling temperature reductions are shown in Fig. 30(c). The polymer coating does not have a significant impact on the temperature of the structure for a constant h_c of 5, due to its transparency.

4. Conclusions

In conclusion, tailoring of electromagnetic spectrum for broadband reflectance was investigated in this project. By studying the interaction of electromagnetic fields with different surfaces, several design strategies were developed. Both homogenous and inhomogeneous multilayer structures were proposed. Designed broadband reflectors prevented the absorption of the undesired heat, which was the source of instability and thermomechanical failure. By choosing thermomechanically superior dielectrics that do not absorb IR radiation and stacking them together in film form such that interference of the reflected beams throughout the multilayer results in constructive interference at the front surface in broadband spectrum. Such phenomenon was achieved both intuitively and physics based numerical optimization.

By utilizing periodic high-low index segments and tuning the layer thicknesses such that there were quarter wavelength thick, relatively narrowband high reflection zones were achieved. To extend this well-known approach to broadband, individual periodic high-low index segments were designed to reflect around a central wavelength then they were stacked together to achieve broadband response. Results showed that such method was very effective. Resulting mechanisms, e.g. reflection dips, were analyzed and underlying mechanisms were studied and reported. Major drawback of this method is the required high number of layers, which may yield to instabilities in high temperature applications. To reduce the number of layers and end up thermomechanically more stable reflectors a design strategy based on impedance mismatch was proposed to design structures inspired from morpho butterflies. Those types of bio-inspired structures were shown to be effective to achieve reflection and more applicable to high temperature applications due to airgaps between the layers. Airgaps were extremely beneficial since they provide space for layers to thermally expand. Also, higher refractive index ratios due to air/TiO₂ arrangements lead to higher reflection percentages.

Developed impedance mismatch approach allowed us to design homogeneous broadband reflectors with performances comparable to that of intuitive designs, with significantly reduced number of layers. Similar reflection dips over the spectra were also observed and explained by total optical path that light travels. As a next step, to transform the structures to morpho butterfly configurations, periodicity was introduced. Effect of periodicity on broadband reflectance was also studied and resulting mechanisms were analyzed. No significant reduction in reflectance was observed in broadband spectrum.

Besides the broadband reflectance problem, developed methods were also adapted to passive radiative cooling problem to demonstrate the potential extension of the developed methods to other problems, which require spectral engineering in broadband spectrum. Selective emission required for passive radiative cooling was achieved by utilizing intuitive approach proposed for broadband reflectance problem. By benefiting from the lossy nature of the coating materials in atmospheric transparency window, broadband reflectance in solar and

near infrared spectrums were achieved while simultaneously satisfying the high emission requirement in 8-13 μm spectrum interval.

In addition, impedance-based formulation was also used to design a multilayer structure for passive radiative cooling. Also, mathematical formulation of the radiative cooling problem was modified such that it considers both spectral and radiative aspects of the problem. Introduced modification resulted in superior cooling powers compared to previously reported multilayer structures in the literature.

5. References

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6. List of Symbols, Abbreviations and Acronyms

Z : Intrinsic impedance

ϵ : Permittivity

μ : Permeability

Z : Surface impedance

N : Layer number

j : $\sqrt{-1}$

δ : Optical thickness

Z_0 : Intrinsic impedance of free space

Z_1 : Surface impedance of the top layer

Γ : Reflection coefficient

Γ_{Norm} : Normalized reflection coefficient with respect to Z_0

RF: Radio frequency

r : Amplitude of the reflection coefficient

θ : Phase of the reflection coefficient

n : Refractive index

k : Extinction coefficient

t : Geometrical thickness

ν_r : Angle of refraction

λ : Free space wavelength

α : Weighting factor

d : Distance between pillars

p : Periodicity

I_{BB} : Blackbody radiation intensity

T : Temperature

h : Planck's constant

k_b : Boltzmann's constant

c : Speed of light

P_{Cool} : Cooling power of a surface

P_{Rad} : Radiated power by a surface
 P_{Atm} : Absorbed atmospheric thermal radiation by a surface
 P_{Sun} : Absorbed solar irradiance by a surface
 $P_{\text{Cond+Conv}}$: Heat exchange due to conduction and convection
 I_{Sun} : Solar irradiance
 T_{Amb} : Ambient temperature
 h_c : Non-radiative heat exchange coefficient
CP: Cooling power
R: Residual error
Re: Real part of a complex number
Im: Imaginary part of a complex number
 n_{Subs} : Refractive index of the substrate
 δ_{Total} : Total optical path that wave travels
 n_{Lift} : Refractive index of the lift-off material
 S_{11} : Reflection coefficient in -S parameter representation
 $\angle S_{11}$: Phase of the S_{11} .
MMSE: Minimum mean square error

7. Publications from this Project

- MA Kecebas, P Menguc, A. Kosar, and K Sendur, “Passive radiative cooling design with broadband optical thin-film filters,” *Journal of Quantitative Spectroscopy & Radiative Transfer* 198, 179–186 (2017).
- MA Kecebas and K Sendur, “Enhancing the spectral reflectance of refractory metals by multilayer optical thin-film coatings,” *Journal of Optical Society of America B* 35, 1845-1853 (2018).
- MA Kecebas, P Menguc, A. Kosar, and K Sendur, “Spectrally selective filter design for passive radiative cooling,” *Journal of Optical Society of America B* 37, 1173-1182 (2020).
- M Janipour and K Sendur, “Temperature and pressure effects on the spectral reflection of layered polar dielectrics,” *Mater. Res. Express* 5, 116207 (2018)
- M Janipour and K Sendur, “Broadband infrared reflective surfaces using doped and stacked polar dielectric layers,” *AIP Advances* 8, 025213 (2018).
- M Janipour and K Sendur, “Enhancing Spectral Reflection through Controlled Phase Distribution Using Doped Polar-Dielectric Metasurfaces,” *Materials* 13, 2007 (2020).
- M Janipour and K Sendur, “Broadband infrared reflection through heavily doped and stacked polar-dielectrics,” *Optics & Photonics International Congress (OPIC 2018)*, Japan.
- MA Kecebas, P Menguc, A. Kosar, and K Sendur, “Passive Radiative Cooling System Design with Periodic High-Low Index Segments,” *NanoRad 2017: 3rd International Workshop on Nano-Micro Thermal Radiation*, KAIST, Daejeon, Republic of Korea.
- MA Kecebas and K Sendur, “Enhancing Passive Radiative Cooling Performance with Impedance Matching,” *MRS Fall Meeting 2017*, Boston, USA.
- MA Kecebas and K Sendur, “A Broadband Impedance Mismatch Technique for Reflectance Enhancement with Thin-Film Coatings”, *MRS Fall Meeting 2019*, Boston, USA

8. Invited Talks

- Prof. Kürşat Şendur visited AFRL Dayton and presented "Broadband Plasmonic Surfaces and Cool Plasmonic Transducers".
- Prof. Kürşat Şendur visited NASA Langley Research Center and presented "Tailoring the Spectral Reflectivity and Emissivity via Thin-Film Coatings and Nanostructured Surfaces".

9. AFOSR Program Review Attendance and Presentation

- 2016 Aerospace Materials for Extreme Environments Program Review at the Basic Research Innovation and Collaboration Center (BRICC) at Arlington, Virginia.
- 2017 Aerospace Materials for Extreme Environments Program Review at the Kirtland's Air Force Base at Albuquerque, New Mexico.
- 2018 Aerospace Materials for Extreme Environments Program Review at the Doolittle Institute, Niceville, Florida.
- 2019 Aerospace Materials for Extreme Environments Program Review at the Alexandria, Virginia.
- 2020 Aerospace Materials for Extreme Environments Program Review: Virtual Meeting