Multilayer passive radiative selective cooling coating based on $Al/SiO_2/SiN_x/SiO_2/TiO_2/SiO_2$ prepared by dc magnetron sputtering

N. F. Cunha[a,1], A. AL-Rjoub[a], L. Rebouta[a], L. G. Vieira[b], S. Lanceros-Mendez[b,c,d],
a Centre of Physics, University of Minho, Campus de Azurém, 4800-058 Guimarães, Portugal
b Centre of Physics, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal
c BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain
d IKERBASQUE, Basque Foundation for Science, 48013 Bilbao, Spain

Abstract

A multilayer passive radiative selective cooling coating based on $Al/SiO_2/SiN_x/SiO_2/TiO_2/SiO_2$ prepared by dc magnetron sputtering is presented. The design was first theoretically optimized using the optical constants, refractive index and extinction coefficient of thin single layers. The spectral optical constants in the wavelength range from 0.3 to 27 µm were calculated from the transmittance and reflectance data of thin single layers deposited on silicon and glass substrates. The samples were characterized by Scanning Electron Microscopy, X-ray diffraction, Fourier-transform Infrared Spectroscopy and UV–VIS–NIR spectroscopy. It is shown that the TiO_2 layer presents a partially rutile phase polycrystalline structure and a higher refractive index than amorphous SiO_2 and SiN_x layers in the spectral range from 0.3 to 2.5 µm. The cooling device was deposited on copper substrates and a thin low-density polyethylene foil with high transmittance in the 8 to 13 µm spectral range was used as convection cover material. The device is characterized by both low reflectance (high emittance) in the sky atmospheric window (wavelength range from 8 to 13 µm) and high hemispherical reflectance elsewhere, allowing for temperature drops of average 7.4 °C at night-time in winter, which corresponds to a net cooling power of ~43 W m^{-2}. Further, a temperature drop of 2.5 ºC was obtained during winter daytime.

Keywords: Passive cooling, Optical constants, Selective coating.

1. Introduction

[1] Corresponding author – e-mail address: nelssomfernandez@hotmail.com (N. F. Cunha)

The increasing energy consumption used for air conditioning and building cooling demand more efficient and environmental friendlier approaches [1, 2, 3]. One way of achieving this is by the radiative cooling of building surfaces using optimized coatings or paint. This approach allows to tailor the radiative properties of the surfaces by decreasing or increasing the absorption, emission, or reflection of radiant energy [1, 2, 4]. In terms of incoming infrared radiation from the atmosphere on a surface facing the sky, the intensity is very low in the atmospheric window (wavelengths from 8 to 13 μm). Thus, efficient passive radiative cooling surfaces should show very low reflectance and no transmittance (high absorbance) in that atmospheric window, resulting in a high thermal emittance. Furthermore, the hemispherical reflectance elsewhere must be high in order to maximize heat radiative losses and to minimize the heating by radiative absorption [5, 6]. In this way, the radiative heat can be transferred from the surface to the atmosphere, leading to radiative cooling of the surface [7].

Passive radiative cooling can be performed with a proper selection of materials, such as polymers pigmented paints or multilayer coatings. Several materials already used, include plastic foils containing polyethylene, ZnS [5], PbS [8], ZnSe, TiO_2 white painting, ZrO_2, ZnO [9, 10], SiO_2 and SiC [11, 12] and $BaSO_4$ mixed with TiO_2 [13], among others. These materials often show limitations and poor performance under direct solar radiation.

For daytime cooling, the solar radiation reduces the performance of such systems as it is necessary a very high solar radiation reflectivity (above 94% [14]) to achieve an equilibrium temperature below the ambient temperature.

Thus, multilayer coatings as convective shields have been optimized to be functional in both day and night-times. The use of a multilayer with repetitive high index-low index periodic layers allows increasing the average solar radiation reflectance and obtaining a high mid infrared absorption, which results in significant cooling powers. Multilayers with oxides usually require a back metallic reflector [14, 15, 16] and different structures have been developed with several layers based on SiO_2/S_3N_4 [6, 7], SiO_2/HfO_2 [14], SiO_2/TiO_2 [15, 18], VO_2/TiO_2 [17] and SiO_2/Al_2O_3 [16] coated on good metal reflectors such, as Al or Ag. The multilayers of birefringent polymer pairs do not need the metallic layer, as they act as dielectric mirrors, reflecting better than metals in the wavelength range in which the solar radiation is more intense [18].

The present work reports on a magnetron sputtered $Al/SiO_2/SiN_x/SiO_2/ TiO_2/SiO_2$ multilayer design for passive radiative cooling. Materials were selected to improve the optical properties, the structure and the selectivity of the device. The multilayer system was covered by a thin polyethylene foil in order to decrease the radiator convection losses. As polyethylene degrades by solar ultraviolet radiation, it hinders long-term applications, being therefore used as a proof of concept.

2. Materials and Methods

2.1 Theoretical background for selective radiative cooling

The cooling power of a selective radiative cooling system of area A (radiator + polymeric cover) can be defined by [5, 6, 8, 15]:

$$P_{cooling} = P_{rad}(T_{rad}) - P_{atm} - P_{sun} - P_{rad/cov} - P_{cond+conv}(T_{rad}, T_{cov}, T_{amb}) \quad (1)$$

where, P_{rad}, P_{atm}, P_{sun}, $P_{rad/cov}$ and $P_{con+conv}$ are, respectively, the thermal radiation power emitted by the surface, the absorbed atmospheric radiation power, the absorbed solar radiation power, the radiation flux between the polymeric cover and the radiator and the power losses due to convection and conduction. T_{rad} is the surface radiator temperature, T_{cov} is the cover temperature and T_{amb} is the ambient temperature. P_{rad} and P_{atm} are given by [19]:

$$P_{rad}(T_s) = A\left\{\int_0^{\pi/2} 2\pi d\theta \sin(\theta)\cos(\theta) \int_0^{\infty} d\lambda\, I_{BB}(T_{rad},\lambda)\, \varepsilon_r(\lambda,\theta) \frac{T_{cov}(\lambda,\theta)}{1-R_r(\lambda,\theta)R_{cov}(\lambda,\theta)}\right\} \quad (2),$$

$$P_{atm} = A\left\{\int_0^{\pi/2} 2\pi d\theta \sin(\theta)\cos(\theta) \int_0^{\infty} d\lambda\, I_{BB}(T_{amb},\lambda)\varepsilon_{atm}(\lambda,\theta)\varepsilon_r(\lambda,\theta) \frac{T_{cov}(\lambda,\theta)}{1-R_r(\lambda,\theta)R_{cov}(\lambda,\theta)}\right\} (3)$$

where I_{BB} (T, λ) is the temperature dependent spectral blackbody emissive power, $\varepsilon_r(\lambda,\theta)$ is the radiator emissivity and $\varepsilon_{atm}(\lambda,\theta)$ is the emissivity of the atmosphere, calculated from the atmospheric transmittance $t(\lambda)$ in the Zenith direction as $\varepsilon_{atm}(\lambda,\theta) = 1 - t(\lambda)^{1/\cos\theta}$. The atmospheric transmittance was obtained from the Planetarium Spectrum Generator (PSG) software from NASA [20]. $T_{cov}(\lambda,\theta)$ and $R_{cov}(\lambda,\theta)$ represent the spectral transmittance and reflectance of the cover, and the denominators in the equations take into account the multiple reflections between the cover and the radiator. The absorbed incident solar power is given by:

$$P_{sun} = A\int_0^{\infty} d\lambda\, \varepsilon_r(\lambda,\theta_{sun})\, I_{solar}(\lambda) \frac{T_{cov}(\lambda,\theta)}{1-R_r(\lambda,\theta)R_{cov}(\lambda,\theta)} \quad (4)$$

where I_{solar} (λ) is the solar spectral irradiance at the incidence angle θ_{sun} corresponding to Portugal, as evaluated from the PSG software [20].

The radiation fluxes between the polymeric cover and the radiator are calculated from [19]:

$$P_{rad/cov} = A\left\{\int_0^{\pi/2} 2\pi d\theta \sin(\theta)\cos(\theta) \int_0^{\infty} d\lambda \frac{\varepsilon_r(\lambda,\theta)\varepsilon_{cov}(\lambda,\theta)}{1-R_r(\lambda,\theta)R_{cov}(\lambda,\theta)}\left(I_{BB}(T_{rad},\lambda) - I_{BB}(T_{cov},\lambda)\right)\right\} \quad (5)$$

The power losses by convection and conduction are given by:

$$P_{cond+conv}(T_{rad}, T_{cov}, T_{amb}) = A\, h_{rc}(T_{cov} - T_{rad}) + A\, h_{ca}(T_{amb} - T_{cov}) + A\, h_{ra}(T_{amb} - T_{rad}) \quad (6)$$

where h_{rc}, h_{ca}, and h_{ra} are the nonradiative heat transfer coefficients, which account for the radiator to cover conduction/convection, cover to air conduction/convection and heat flow through the back insulation from radiator to air, respectively. The polyethylene cover works as a convection shield and its temperature is assumed to be the ambient temperature. The coefficient h_{ra}~0.83 $Wm^{-2}K^{-1}$ was evaluated assuming that the effective thermal conductivity of polystyrene foam is 0.033 $Wm^{-1}K$ [25, 26] and a foam thickness of 4 cm. The coefficient h_{rc} was calculated considering that the sum of all terms in equation 1 should be zero, when the device is in equilibrium. Thus, the coefficient h_{rc} is in the range 4 - 6 $Wm^{-2}K^{-1}$. This model was used to calculate the net cooling power, $P_{cooling}$, of the developed device by equations 1 to 6.

At the steady state temperature, T_{rad}, the sum of all terms in equation 1 should be zero, and the obtained T_{rad} is dependent not just on the emitted, P_{rad}, and absorbed power, P_{sun} and P_{atm}, but also on the non-radiative power exchanges due to conduction and convection. The terms of equation 1 were evaluated for the measured T_{rad}, whose sum equals zero. However, the available cooling power of the coating + cover system was calculated from P_{rad}-P_{sun}-P_{atm}, when the radiator is maintained at ambient temperature. Then, this model was also used to calculate the available cooling power, considering T_{rad}=T_{amb}. In this way, it can be figured out what to expect in summer, since the measurements were carried out in winter. It is to notice that the cooling power reduces when the radiator has a temperature lower than the ambient, because P_{rad} is reduced.

2.2 Optical design

The SCOUT software (version 2.99, WTheiss Hardware and Software) was used to tune the optical properties and deposition rates of the single layers of the final design, using the experimental transmittance (T) and reflectance (R) in the visible and infrared (IR) wavelength range, 0.3 – 27 μm, of the materials deposited on glass and Si substrates. SCOUT allows to perform a standard spectrum simulation employing the appropriate models for the frequency dependent complex dielectric function ($\tilde{\varepsilon}_r = \varepsilon_1 + i\varepsilon_2$). To model $\tilde{\varepsilon}_r$ several contributions have been considered for the SiN_x and SiO_2 layers:

$$\tilde{\varepsilon}_r = \varepsilon_{back\ ground} + \tilde{\varepsilon}_{Brendel} \quad (6)$$

and for TiO2 layers:

$$\tilde{\varepsilon}_r = \varepsilon_{back\ ground} + \tilde{\varepsilon}_{Brendel} + \tilde{\varepsilon}_{OJL} \quad (7)$$

where $\varepsilon_{background}$, $\tilde{\varepsilon}_{Brendel}$ and $\tilde{\varepsilon}_{OJL}$ are the real part of the high frequency dielectric constant, Brendel oscillator model (constructed by a convolution of a Gaussian function with the dielectric function of the damped harmonic oscillator model), and OJL model (accounting for other interband transitions), respectively [24, 25]. The complex refractive index ($\tilde{n}$) was calculated from $\tilde{n}^2 = (n + ik)^2 = \tilde{\varepsilon}_r$ where (n) is the refractive index and (k) is the extinction coefficient. The first step was measuring and modelling the reflectance (R) and transmittance (T) spectra of single layers deposited on glass and silicon substrates to extract their optical constants as a function of wavelength and thicknesses, which allow obtaining the deposition rates. Finally, and based on the information from those individual layers, the multilayer device was optimized by SCOUT.

2.3 Experimental details

Individual layers of SiN_x, SiO_2, and TiO_2 were deposited by dc magnetron sputtering on glass and silicon substrates, at room temperature and at a base pressure of the chamber of 2×10^{-4} Pa. Other relevant deposition parameters are presented in Table 1. The multilayer selective-cooling device was manufactured by depositing an aluminium (Al) back reflector layer and five additional layers with the deposition rates obtained from the optimisation of the above-mentioned individual layers. In the case of the TiO_2 films, experiments were performed in order to maximize the refractive index, which is obtained with the rutile phase. Working pressures in the range 0.26 to 0.37 Pa (corresponding to Ar flux rates of 35 and 50 sccm, respectively), oxygen partial pressure in the range 0.034 to 0.049 Pa (O_2 flux rates of 3.5 sccm and 5 sccm, respectively) and bias polarization in the range -60 to -100 V were evaluated. The rutile phase was obtained using the lowest partial pressures of oxygen and argon and with a bias of -100 V applied to the substrate holder. All substrates were ultrasound cleaned in acetone for 15 min, and ion etched before deposition. During the target cleaning process, the substrates were protected by a stainless-steel shield.

The transmittance and reflectance of the samples were measured using a Shimadzu PC3101 UV–VIS–NIR scanning spectrophotometer in the wavelength range of 0.25 - 2.5 µm and using a Fourier Transform Infrared spectrometer Bruker IFS 66V equipped with a Globar source, a KBr beam-splitter and a deuterated triglycine sulfate detector with KBr window, in the wavelength range 2 to 27 µm. The measurements were performed in vacuum, at room temperature, at 4 cm^{-1} resolution with 32 scans. Reflectance data were recorded at quasi-normal incidence and corrected according to Al and Au reference mirrors placed at the same position as the sample for the wavelengths 0.25 to 2.5 µm and 2 to 27 µm, respectively.

The phase structure of the TiO_2 samples was characterized by grazing incidence X-Ray diffraction (XRD) with a fixed incidence angle α= 3° and 2θ angles between 20° and 70° using a Bruker AXS Discover D8 with a Cu Kα radiation. The samples thickness and morphology were studied by a NanoSEM-FEI Nova 200 (FEG/SEM) Scanning Electron Microscopy (SEM) with an operating voltage of 10 kV.

Finally, the testing cells shown in Fig. 1 were prepared using thick polystyrene foam boxes with 40 mm thick walls, where the sample was placed at the base. A 5 cm × 5 cm sample was used for the tests, as shown in Fig. 1a. The sample was also covered by a 17.5 µm polyethylene foil (Fig. 1b) in order to minimize the convection and conduction losses and the boxes were equipped with thermocouples to measure the temperatures. The distance between the top polyethylene thin foil and the sample surface was 3 mm. The devices were placed on the rooftop of our institute building (in Guimarães, Portugal) for several days in the period from 17th of December to 15th of January. Calculations were performed using data from the PSG website at (9/1/2019 -10/1/2019). The sample was tilted 20° from the roof horizontal surface facing north to minimize the absorption of solar radiation during the day.

3- Results and discussion

3.1 Optical properties of the single layers

The optical design of the multilayer has the objective of simultaneously maximize the reflectivity of the solar radiation and to maximize the absorption in the transparent infrared atmospheric window. Fig. 2a shows the transmittance and the reflectance spectra of SiN_x, SiO_2, and TiO_2 single layers deposited on glass, in the wavelength range of 300 to 2500 nm, showing that all layers are transparent. Using these spectra, the thicknesses and the optical constants (refractive index and extinction coefficient) as a function of wavelength were obtained by SCOUT software. In figure Fig. 2b, the refractive index of TiO_2 rutile, SiN_x and SiO_2 is presented, being the TiO_2 refractive index higher than the ones of SiN_x and SiO_2. In this wavelength range, all materials show an extinction coefficient close to zero. The thicknesses of the SiN_x, SiO_2, and TiO_2 layers are 157 nm, 1.6 µm and 83 nm, respectively. The reflectance of the same layers deposited on silicon, in the wavelength range of 2.5 - 27 µm, is shown in Fig. 2c, and the corresponding extinction coefficients are shown in Fig. 2d. It is also important to note that the extinction coefficient in the IR region reveals the existence of some absorption modes in the sky transparent window region 8 to13 µm (grey box in Fig. 2d) for SiO_2 and SiN_x. It is to notice that this fact contributes to increasing the absorption in that wavelength range, which according to the Kirchhoff's law of thermal radiation, corresponds to an increase of the emissivity in the same wavelength range. These materials are thus good candidates for designing the multilayer selective radiative cooling as the differences between their refractive indices can be also used to improve the reflectivity of the Al layer in the UV-VIS region. Hence, this allows building a multilayer cooling device that can enable to achieve temperatures lower than ambient temperature during the day or night times. TiO_2 is transparent in the 8 to 13 µm range, which means that it does not help in increasing the emissivity in the atmospheric window, but allows to improve the reflectivity in the UV-Vis-NIR range. The rutile phase structure of TiO_2 has a higher refractive index than the anatase phase [25] and thus it is more adequate to improve the reflectance of solar radiation.

3.2 Structural characterization of the SiN_x, SiO_2 and TiO_2 single layers

Single layers of SiN_x, SiO_2 and TiO_2 deposited on Si substrates were used to study their morphology and structure. In Fig 3 the cross-section SEM micrographs of those layers are presented, where it is observed that SiO_2 (Fig. 3a) and SiN_x (Fig. 3b) layers show a featureless morphology, characteristic of amorphous layers. However, the cross section SEM image of the TiO_2 layer (Fig. 3c) shows some features, which is in agreement with the results of XRD analysis

(Fig. 3c), whose diffractogram shows the presence of diffraction peaks addressed to the (110), (101) and (211) main planes of the rutile phase [26][27][28].

3.3 Design of the multilayer

The design of the multilayer device was optimized using the information obtained from the transmittance, reflectance and the optical constants of the thin single layers of Al, SiO_2, SiN_x and TiO_2 by SCOUT software. The optical design was performed optimizing simultaneously the reflectivity of the solar radiation and the absorption in the transparent infrared atmospheric window. As a result, the design of a multilayer for passive radiative cooling coating was obtained with a structure based on Al/SiO_2/SiN_x/SiO_2/TiO_2/SiO_2, prepared by dc magnetron sputtering. The simulated thicknesses are shown in Fig 4a, while the measured thicknesses of the deposited multilayer are indicated in the cross-section SEM image shown in Fig. 4b. A good agreement was obtained in the range of acceptable experimental error. Figure 4 shows that SiN_x and SiO_2 layers are amorphous and because of the similarity of the mass of the atoms, it is difficult to distinguish between them, while Al and TiO_2 show some features, characteristic of polycrystalline materials.

The experimental reflectance of the multilayer deposited in the 5 cm × 5cm polished copper substrate in the wavelength range 0.3 to 27 µm is shown in Fig. 5 (black line). The design shows relatively high reflectance outside the sky transparent window, in particular in the range 0.3 to 2.5 µm, being above 88% in average, resulting from the aluminium (mirror) layer and the combination of the low and the high refractive index of SiO_2 and TiO_2, respectively. In the region of sky transparent window, the device shows a reflectance of 49%, which contributes to the high emissivity of the device in this wavelength range (51%). The polyethylene foil is very important to isolate the cooling device from humidity and wind, and thus, for low absorption by convective heating from ambient. At the same time, the polyethylene should be highly transparent as shown in Fig. 5 (red line), so that most of the radiation can pass through the foil in the sky window region. In the same figure the reflectance of the polyethylene foil (in blue) is also presented.

3.4 Cooling device performance

The weather conditions of the day of device testing (9/1/2019 -10/1/2019), which was the date defined for the calculations using the PSG software, were the following: clear sky (without clouds), 15.5 ºC high and 7 ºC low temperature, average wind speed ~3 m/s and 67% of humidity. The device showed a good cooling efficiency with an average temperature drop of 7.4 °C with respect to the ambient temperature, as shown in Fig. 6. Based on the model described in section 2.1, the performance of the cooling device was evaluated. Solar irradiation and the atmospheric transmittance spectrum for the mentioned date was obtained from the PSG website. The absorbed solar radiation was calculated at noon (solar time) on 10 January 2019 when the solar irradiance was 972 W/m^2. Considering the sample tilting (20 º facing North), the cover surface irradiance was 214 W/m^2 and using eq. 4, the absorbed power, P_{sun}, was 28 W/m^2, as presented in table 2. Without the sample tilting, the absorbed power at noon (solar time) would have been 110 W/m^2. Fig. 7ashows the solar radiation intensity in that day (in blue), together with the corresponding intensity of the absorbed radiation by the device when horizontal (in red) and when tilted (in yellow).

P_{atm} is the absorbed atmospheric radiation power, and the IR intensity was calculated using the ambient temperature, which for 7 ºC (night period) corresponds to 293 Wm^{-2}. Due to the transmittance of the atmosphere, only 181 Wm^{-2} reaches the cover surface. Finally, considering the radiator + cover system and the corresponding optical properties (equation 3), 36 Wm^{-2} are absorbed, as presented in table 2. In Fig. 7b and Fig. 7c the intensity of the atmospheric radiation that reaches the cooling device (in blue) at day and night times [20], respectively, are presented, together with the corresponding intensity absorbed by the device (in red).

P_{rad} is the thermal radiation power emitted by the surface and it was calculated using equation 2. Fig.7d and Fig. 7e show the intensities of the absorbed power from atmosphere (P_{atm}) and emitted radiation (P_{rad}) as a function of the wavelength in the range of 5- 27 µm.

The values of the remaining terms of equation 1 for day (at noon, solar time, and with the sample tilted 20º, facing North) and night times corresponding to the selected date are presented in Table 2.

The lowest temperature difference between the ambient and the coating surface temperature during daytime and the average temperature difference during nighttime are also presented in table 2. The temperature difference was 7.4 ºC during the night, and dropped to a minimum of 2.5 ºC during the daytime. This was possible with the sample tilted 20º, facing North, in order to decrease solar radiation absorption. The calculations of the terms in equation 1 for the 24 h period were also performed and the results are shown in Fig. 8. It is observed that the non-radiative heat fluxes due to conduction and convection are significant, and the insulation needs to be improved. This effect also limits the performance of the cooling device.

The available cooling power, considering T_r=T_{amb}, was calculated using the equations 1-6 and the results are presented in table 3. The ambient temperatures used in the calculations are also indicated in table 3. For daytime, the absorbed solar radiation was calculated at noon (solar time). The calculations show that this device shows a maximum cooling power of 43 Wm^{-2} during the night and does not have a cooling capacity during daytime. This effect is due to the absorption of solar radiation, as the coating has a reflectivity of solar radiation of 88%, which is not enough for this application, in which a solar radiation reflectance of 94% is needed to achieve a meaningful daytime radiative cooling.

4. Conclusions

This work presents a multilayer design for passive selective radiative cooling based on $Al/SiO_2/SiN_x/SiO_2/TiO_2/SiO_2$ and prepared by dc magnetron sputtering. The design was theoretically optimized by SCOUT software using the spectral optical constants n and k of thin single layers deposited on silicon and glass substrates. The optical constants of these single layers were obtained from the transmittance and reflectance modelling. The TiO_2 layer shows a polycrystalline rutile phase and a higher refractive index than SiO_2 and SiN_x, whereas the later layers are amorphous. The six layers of the final cooling device were deposited on 5 cm × 5 cm Cu substrates. Their morphology was studied by SEM and shows a total thickness of ~ 1.3 µm. The device shows simultaneously low reflectance (high emittance) in the atmospheric window and high hemispherical reflectance elsewhere resulting in a net cooling power of 43 W m^{-2}, calculated considering the same temperature for radiator and ambient, and a drop in the temperature of about 7.4 °C at nighttime in winter. During the winter daytime, the coating surface temperature dropped to a minimum of 2.5 ºC (with the sample tilted 20º facing North). This effect is due to the absorption of solar radiation as the coating shows a reflectivity of the solar radiation of 88%, value that is not enough to achieve a meaningful daytime radiative cooling. The non-radiative heat fluxes due to conduction and convection are significant (34 W/m^2 during nighttime), which indicates that the thermal insulation needs to be improved.

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Tables

Table 1: Experimental parameters of SiN_x, SiO_2, and TiO_2 individual layers.

Material	Target	Deposition rate (nm/min)	Reactive gas partial pressure (Pa)	Working pressure (Pa)	Current density (mA/cm$^{2)}$	Bias (V)
Al	Al	32.1	-	0.36	6.4	-60
SiO_2	Si	27.0	O_2 (0.048)	0.37	4.5	-60
SiN_x	Si	16.8	N_2 (0.06)	0.37	6.4	-60
TiO_2	Ti	2.9	O_2 (0.034)	0.26	6.4	-100

Table 1: Terms of equation 1, Prad, Psun, Patm, Prad/cov, Pcond/conv calculated for the selected day using data from PSG website and measured temperatures.

Winter	**$P_{cooling}$ ($W.m^{-2}$)**	**P_{rad} ($W.m^{-2}$)**	**P_{sun} ($W.m^{-2}$)**	**P_{atm} ($W.m^{-2}$)**	**$P_{rad/cov}$ ($W.m^{-2}$)**	$P_{cond+ conv}$ **($W.m^{-2}$)**	**Ts (ºC)**	**T_{amb} (ºC)**
Day	0	84.7	27.9	39.1	0.2	17.5	11.2	13.7
Night	0	70.3	0	35.6	0.6	34.1	-0.4	7

Table 2 - Available cooling power of the coating + cover system, not tilted, calculated from P_{rad}-P_{sun}-P_{atm}, when the radiator is maintained at ambient temperature, T_{rad}=T_{amb}, and the temperature used for calculations.

Winter	**$P_{cooling}$ ($W.m^{-2}$)**	**P_{rad} ($W.m^{-2}$)**	**P_{sun} ($W.m^{-2}$)**	**P_{atm} ($W.m^{-2}$)**	**T_{rad}=T_{amb} (ºC)**
Day (noon, solar time)	-61	88	110	39	13.7
Night	43	79	0	36	7
Summer*					
Day (noon, solar time)	-69	107	121	55	27
Night	43	90	0	47	15

Figure captions

Fig. 1: Top view of (a) the multilayer cooling device used to test the efficiency of the coatings and b) the side view of the cooling device.

Fig. 2: (a) Reflectance and transmittance spectra of the indicated layers deposited on glass, (b) refractive index (n) simulated by SCOUT, (c) reflectance spectra in the infrared (IR) range of the indicated layers deposited on silicon and (d) extinction coefficient (k) simulated by SCOUT of single layers as a function of wavelength.

Fig. 3: SEM cross section image of (a) SiO_2, (b) SiN_x and (c) TiO_2 layers, including the XRD diffractogram of the latter.

Fig. 4: (a) Simulated multilayer layers of the cooling device and (b) cross- sectional SEM image of the experimental design layers.

Fig. 5: Experimental reflectance of the multilayer (black line) deposited in the 5 cm × 5cm polished copper substrate and the transmittance of the polyethylene foil (red line) in the wavelength range of 0.3- 27 µm.

Fig. 6: Surface temperature of the cooling device (T_{design}) and ambient temperature ($T_{ambient}$) during day and night times.

Fig. 7: For the selected day: a) solar radiation intensity in the day time (blue) and respective intensity of the absorbed radiation by the device, P_{sun} (red); b) and c) intensities of the atmospheric radiation at day and night times that reaches the device surface (blue), respectively and respective intensity of the absorbed radiation by the device, P_{atm} (red); d) and e) intensities of and emitted radiation (P_{rad}) at day and night times (blue), respectively, and the respective intensities of absorbed atmospheric radiation by the device, (P_{atm}) (red).

Fig. 8: Values of P_{rad}, P_{atm}, P_{sun}, $P_{rad/cov}$ and $P_{cond+ conv}$ calculated for the 24 h period of the selected day and with the sample tilted 20º facing North, using the measured temperatures.