CHEMICAL ENGINEERING TRANSACTIONS
VOL. 84, 2021

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Paolo Ciambelli, Luca Di Palma

ISBN 978-88-95608-82-2; **ISSN** 2283-9216

DOI: 10.3303/CET2184006

Solar Selective Absorbing Coatings Obtained by Physical Vapor Deposition: Overview of Different Strategies for Increasing Performance and Efficiency of Photothermal Conversion

Cong Wang[a], Yuping Ning[a], Ping Song[a], Yongxin Wu[a], Yafei Xue[a], Yu Liu[a], Angelique Bousquet[b], Eric Tomasella[b]*

[a] School of Microelectronics, Beihang University, 37 Xueyuan Rd, 100191, Beijing, CHINA
[b] Université Clermont Auvergne, CNRS, SIGMA Clermont, ICCF, F-63000 CLERMONT-FERRAND, France
Eric.tomasella@uca.fr

Everyone is aware that the 21st century will be marked by major climate changes that result in an increase of the average temperature of our planet. Therefore, we must think different and review our global approach especially in the field of energy by using natural and renewable sources. Such approach involves developing new materials that could meet scientific and technological challenges. Although the use of solar energy for electricity production using photovoltaic cells is well known today, the use of other technologies such as Concentrating Solar Power (CSP) is under development and could produce 25% of global electricity by 2050. Here is an overview of a collaborative works carried out both at the ICCF in France and the School of Microelectronics, at Beihang University in China. Advanced research results helped do draw, at the end, some perspectives on types of promising coatings suitable for the targeted technology.

1.Introduction

We all know that even if the industrial revolution of the 19th century allowed a strong technological development in many sectors of activity, this could be done only with huge use of fossil energy. The direct consequence of such behaviour has caused a climate disruption with the emission of greenhouse gases. Concretely, this was accompanied, in the 20th century, by an increase of 0.6°C in the average temperature of the planet. In the 21st century, the industrial development of urban areas and global population increase (2 billion just in one generation) will undoubtedly increase energy needs. From the Third Assessment Report of the Intergovernmental Panel on Climate Change, (IPCC 3, 2001) it could be possible to reach at the end of this century a temperature rises from 1.5 to 5°C. If Man does not become aware of this, serious climate crisis already engaged such as desertification, floods, animal species disappearance…, could be amplified. Also, the acceleration of melting glaciers and the decrease of the surface of icebergs are evident.

Many initiatives have been taken by the states to outline the actions to be implemented. An example is the Kyoto Protocol, which was ratified in December 1997, and where the countries involved decided an average reduce of their greenhouse gas emissions by at least 5% over the period 2008-2012 compared with 1990 levels. They collectively achieved this objective with a reduction of more than 20%. More recently, at the Paris climate conference (COP21) in December 2015, 195 countries adopted the first universal, legally binding global climate deal. Governments agreed a long-term goal for keeping the increase in global temperature below 2°C above pre-industrial levels and aim to limit the increase to 1.5°C. In addition, governments agreed to strengthen societies' ability to deal with the impacts of climate change and provide continued and enhanced international support for adaptation to developing countries (COP21 2015).

Most energy is consumed for heating, cooling, transport, and power. An obvious solution to address global warming is to replace the use of fossil fuels by the way of renewable energies development. For example: solar energy, hydropower, wind, and biomass energies are serious candidates. From the data of REN21, and

Paper Received: 2 August 2020; Revised: 15 January 2021; Accepted: 24 February 2021
Please cite this article as: Wang C., Ning Y., Song P., Wu Y., Xue Y., Liu Y., Bousquet A., Tomasella E., 2021, Solar Selective Absorbing Coatings Obtined by Physical Vapor Déposition : Overview of Different Strategies for Increasing Performance and Efficiency of Photothermal Conversion, Chemical Engineering Transactions, 84, 31-36 DOI:10.3303/CET2184006

from an economic point of view, renewable energy is powering the world. 162 countries have specific targets and 135 countries have regulatory policies (REN21). Actually, at least 9 countries have over 20% solar PV and wind in their electricity mix. Concerning the technology and market development, renewables made up 64% of global net capacity additions in 2018. Wind and Solar PV are now cost competitive with fossil fuel power plants. However, renewable energy is stagnating in the heating, cooling and transport sectors and not progressing fast enough in the power sector. That is why new scientific and technological advances must be made to catch up the delay. As indicated by El Bassam, by the fact that every day 400 trillion kWh energy from the sun touches earth surface, it makes solar photovoltaic and thermal as majors system for generating electricity and heat by the mean of liquid or any other medium (El Bassam et al. 2013).
If PV technology is better known, solar thermal energy is of a growing interest in the scientific community because the used equipment can store the heat energy for a long period and hence produces electricity night and day during sunny days but also during cloudy ones. After this introduction, the overview will be composed in 3 parts. The first one will be a description of the concentrating solar power (CSP) with the optical and physical concepts. The second part will concern the description of specific case of double layer cermet structure potentiality to finish with a conclusion and some perspectives.

2. CSP technologies and spectral selectivity

Typically, the mechanism to produce electricity from solar energy in CSP systems is the following: sun rays are focused by mirrors on an absorber which heat fluids to convert this energy on electricity by the way of a power conversion device. Four categories of CSP technologies can be mentioned (Figure 1). Depending on the radiations focus and receiving energy technologies, we can distinguish : parabolic trough collector, solar tower, parabolic dish concentrator and linear Fresnel reflector (Romero et al. 2014, Ummadisingu et al. 2011, Dan et al. 2017).

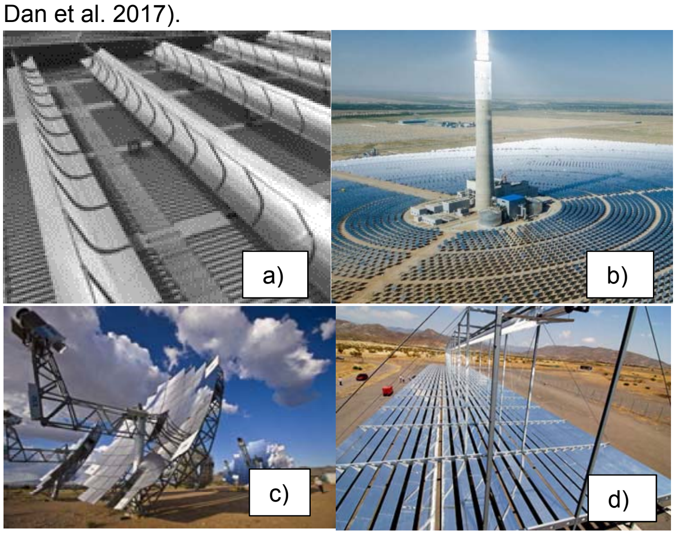

Figure 1: Schematic of four CSP systems a) parabolic trough collector (Newcastle, Australia) b) solar tower (Qinghai Province, China) c) parabolic dish concentrator (Albuquerque, USA) and d) linear Fresnel reflector (Almeria, Spain)

If we focus our interest on the cross section of the receiver tube used in the parabolic trough collector (Figure 2), we can observe an absorber deposited onto a steel tube. Transfer fluids are heated by the absorbed rays to reach a temperature close to 400°C (Ning et al. 2016).

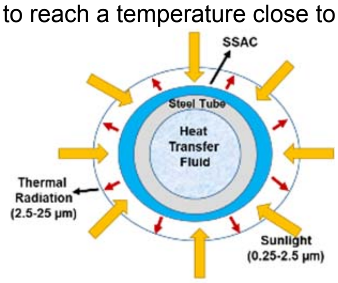

Figure 2. Cross section of the receiver tube used in the parabolic trough collector. SSAC: spectrally selective absorbing coating.

As described by Weinstein (Weinstein et al. 2015), the challenge for an absorber is sunlight absorption with minimal thermal losses. The ideal absorber therefore has high solar absorptance but low emittance at its operating temperature. The absorptance (α) of the sample is defined as the ratio of the surface absorbed radiation to the incident solar one, while the emittance (ε) is the ratio of the radiation emitted by an object at a given temperature to the radiation emitted by a perfect blackbody at the same temperature. Therefore, the absorptance (α_{sol}) and emittance (ε_{therm}) can be given as Equation 1 and 2.

$$\alpha_{sol}(\theta) = \frac{\int_{0.25\mu m}^{2.5\mu m}[1-R_\lambda]G(\lambda)d\lambda}{\int_{0.25\mu m}^{2.5\mu m}G(\lambda)d\lambda} \quad (1), \qquad \varepsilon_{therm}(T) = \frac{\int_{2.0\mu m}^{25\mu m}[1-R_\lambda]P_b(\lambda,T)d\lambda}{\int_{2.0\mu m}^{25\mu m}R_\lambda(\lambda,T)d\lambda} \quad (2)$$

where θ is the incident angle of sunlight, G(λ) is the solar spectral radiation density at an atmospheric mass of 1.5 (AM 1.5), and the reflection spectrum (Rλ) in 0.2-2.5 μm is measured by a standard UV-VIS-NIR spectrophotometer. P_b (λ,T) can be calculated by Plank's blackbody radiation, which is the spectral radiance of a black body under temperature (T). The reflection spectrum (R_λ) in 2.5-25 μm can be obtained using FTIR spectrophotometer (Nofuentes et al. 2014).
The third parameter, which is important to determine, is the photothermal conversion efficiency evolution of the coating by using Equation 3 (Chester et al. 2011)

$$\eta = \mathrm{B}\alpha_{sol} - \frac{\varepsilon\,\sigma\,T^4}{\mathrm{C}\,I_{sol}} \qquad (3)$$

where σ is the Stefan Boltzmann's constant, C is the concentration ratio, I_{sol} is solar irradiation, and T is the temperature of the coating. The constant B, which is typically selected to be 0.91, reflects absorption by the vacuum encapsulation system necessary to prevent convective heat losses.
Figure 3 clearly shows the relationship of four important spectra, i.e., ideal solar selective absorbing spectrum, blackbody radiation one, the actual solar selective absorbing spectrum and the solar radiance one (AM 1.5) (Zhang et al. 2017). The ideal absorber should possess a minimized reflectance in the entire solar spectrum ($\alpha \geq 0.95$) and simultaneously a very low emittance ($\varepsilon \leq 0.05$). This absorber must obviously be stable as long as possible when it's operating at a temperature close to 400°C. On this concept, one can consider the case of spectrally selective absorbing coating (SSAC).

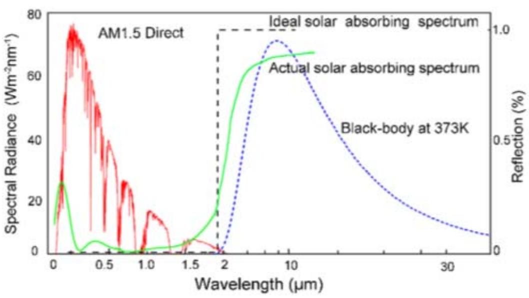

Figure 3. The relationship of four important spectrums.

Based on the absorption mechanisms and design principles, these SSACs can be categorized into six different types, as shown in Figure 4. It includes: a) Intrinsic absorber, b) Semiconductor absorber, c) Multilayer interference stacks d) Cermet absorber, e) Textured surface and f) photonic crystal (Weinstein et al. 2015, Xu et al. 2020).

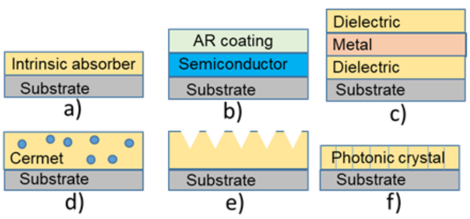

Figure 4: Schematic diagram of six typical solar absorber coatings.

3. Specific case of the double layer cermet structure

The goal of the different studies cited in this review is to obtain selective absorbing coating with high thermal stability and good optical properties. Some strategies are also developed. The typical coating structure from surface to substrate consists of an anti-reflection layer composed of a transparent ceramic material that enhances solar transmission, a low metal volume fraction (LMVF) cermet solar absorption layer, a high metal volume fraction (HMVF) cermet solar absorption layer, which forms interference absorption bilayer and an IR-reflective metallic layer that decreases the IR emission.

Using double cermet coatings offers a double advantage: possibility to decrease the diffusion and aggregation but also the oxidation of metal particles like it can be the case of single cermet layer. It is important to underline that all coatings mentioned in this chapter are obtained by Physical Vapor Deposition. The process has a low environmental impact due to controlled vacuum system (no liquid chemical wastes) and can be used to deposit complex compounds with controlled microstructure and composition.

Hence, Xue prepared high metal volume fraction AlNi–Al_2O_3 layer (HMVF), low metal volume fraction AlNi–Al_2O_3 layer (LMVF) and Al_2O_3 anti-reflection layer from bottom to top on Cu substrate as solar absorbing coating by DC and RF magnetron sputtering. Cu worked as an IR-reflective metallic layer with good infrared reflectance (Xue et al. 2013). Figure 5a shows the reflectance spectra of the whole layered coating (Cu)/AlNi–Al_2O_3 (HMVF)/ AlNi–Al_2O_3 (LMVF)/Al_2O_3 by changing the metal volume fraction of the LMVF and HMVF layer, (thickness of each layer is kept constant). They have chosen a binary alloy: AlNi in the Al_2O_3 matrix, for its potential of high thermal stability. They have shown that to balance the absorptance and emissivity, the optimized metal volume fractions of the HMVF and LMVF layers of 68% and 38%, respectively must be chosen. The coating deposited on Cu substrate was aged at 500 °C for 12 h. No significant change in the optical properties was found (Figure 5b).

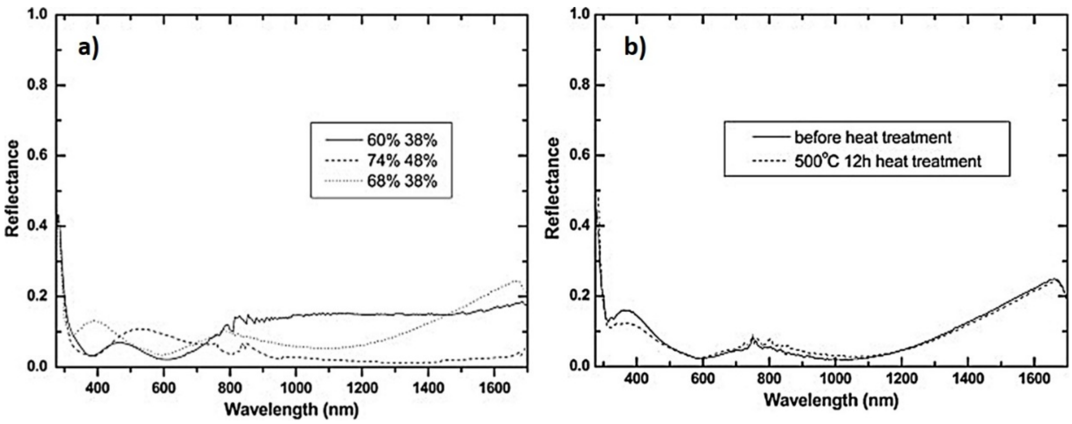

Figure 5: a)The reflectance spectra of the coating with different matching the metal volume fraction of the LMVF and HMVF layers. b) The reflectance spectra of the AlNi–Al_2O_3 cermet coating deposited on Cu substrate before and after ageing at 500 °C for 12 h.

Other design uses transition metal nitrides and oxynitrides films because of their interesting properties such as high hardness, good wear and excellent optical properties.

Liu (Liu et al 2014) described a very interesting SSAC with the following film structure: SS–(Fe_3O_4)/Mo/TiZrN/TiZrON/SiON. SS–(Fe_3O_4) is the substrate with surface oxidation (Fe_3O_4) of stainless steel (SS) piece. The Mo layer acted as infrared reflective layer, SiON layer as the antireflective coating. The TiZrN and TiZrON layers acted as double absorbing coatings. Moreover, the TiZrN layer is the diffusion barrier between SS substrate and absorbing layer. The TiZrON layer incorporating TiZrN one played a significant role in destructing interferences, which enhances absorbance. This design permitted to reach high absorptance of 0.95 and low emittance of 0.08. XRD analysis indicated that the prepared TiZrN layer consisted of TiN and Zr_2N phases, while SiON and TiZrON layers were amorphous. After heat-treatment at 500 °C for 300h in vacuum, the absorptance and emittance values of the coating became 0.92 and 0.10, respectively. These low optical properties variations as seen in Figure 6 confirm the potential of SSAC for photothermal conversion in CSP applications.

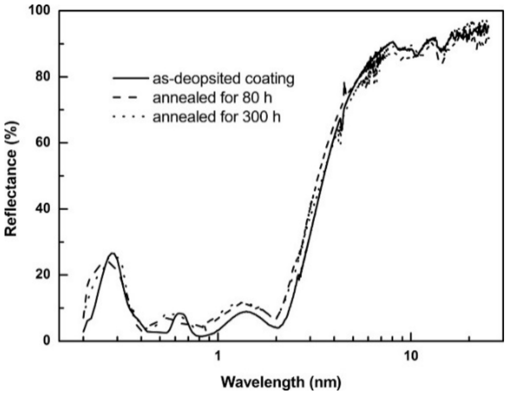

Figure 6. The reflective spectra of SS–(Fe_3O_4)/Mo/TiZrN/TiZrON/SiON before and after heat treatment in the range of 0.2–25 µm at 500 °C.

Another structure was explored in collaboration with our Chinese colleagues from the school of microelectronics at Beihang University. As reported by Wu (Wu et al, 2015) This study concern both Al/NbTiN/NbTiON/SiO_2 and Al/NbTiSiN/NbTiSiON/SiO_2 multilayers deposited on stainless steel (SS). Optical constants variation reveals that stability of the optical properties of the NbTiSiN and NbTiSiON are better than that of NbTiN and NbTiON layers. Indeed, as shown in Figure 7a and 7b, the main remarks that could be done are: there has been a significant change in reflectance spectrum of the Al/NbTiN/NbTiON/SiO_2 coating after ageing at 400 °C in air for 2 h, the absorptance decreases from 0.934 to 0.901, the emittance increases from 0.13 to 0.14, and the selective absorber efficiency decreases from 93.2% to 89.8%. When the Al/NbTiN/NbTiON/SiO_2 coating is aged at 500 °C in air for 2 h, the absorptance decreases to 0.538, and the efficiency drops to 53.5%. However, the Al/NbTiSiN/NbTiSiON/SiO_2 coating exhibits better optical performances than Al/NbTiN/ NbTiON/SiO_2 one. Indeed, after ageing at 500 °C in air for 2 h, the absorptance and emittance are 0.922 and 0.13 and the efficiency is 91.9%. These behaviors were explained by the fact that NbTiSiN and NbTiSiON layers have higher oxidation resistance than NbTiN and NbTiON layers.

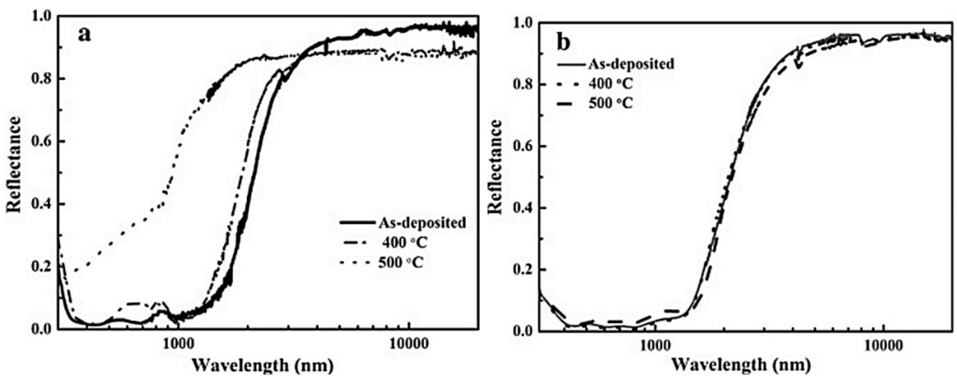

Figure 7. The reflectance spectra of: (a) Al/NbTiN/NbTiON/SiO_2 and (b) NbTiSiN/NbTiSiON/SiO_2 coatings deposited on SS substrates after ageing at different temperatures in air.

4. Conclusions and perspectives

As it can be seen in this short overview, many studies can be undertaken to increase the photothermal efficiency of SSAC in the case of CSP. We have to keep in mind that these coatings have to deliver great and stable performance for a long period (at least 20 years) to be commercialized even if they are in contact with different severe conditions during their lifetime (sunlight, wind, organic pollution, abrasion but also very cold temperature during the night are some examples…). The materials used for the coatings must be chemically and structurally stable. Standard testing procedures for SSAC are also asked (in air or in vacuum? at what temperature? On stainless steel, copper, silicon, glass?). So many parameters are not exactly defined to compare the reactivity between references found in the literature. Nanomaterials are indisputably a key approach to increase the photothermal conversion efficiency, but one can also cite very promising perspectives as shown in the paper of Song (Song et al. 2020), where (NiCuCrFeSi)N coatings deposited by

PVD can be employed to control the cutoff wavelength by merely tuning the nitrogen content of the as-deposited films. To obtain high solar absorption and low infrared emission, solar selective absorbing metasurface by designing some unique structures on the surface (Figure 8 a) and b)) are used.

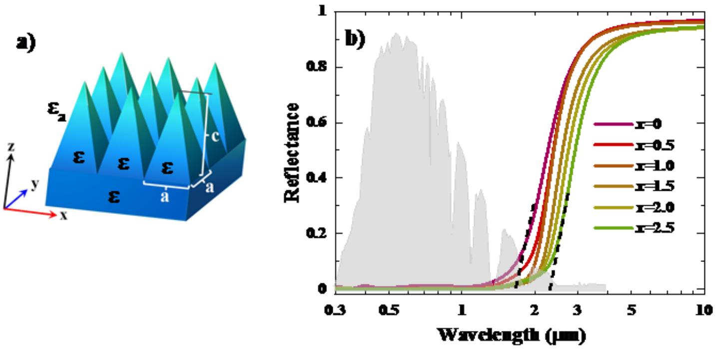

Figure 8: Design of solar selective absorbing metasurface. a) Illustration of the pyramid structure with nine unit cells. a is the side length (0.25 µm), c represents the height of the pyramid structure (0.5 µm), □ is the permittivity of the pyramid, and □$_a$ is the air permittivity. b) Simulated reflectance of (NCCFS)N films various nitrogen gas flow rates (x) with the pyramid structure. The incident light is normal to the xy plane. Black dash lines indicate the locations of the cutoff wavelength. The gray shadow area is the AM1.5 solar irradiance spectrum.

As the nitrogen content increases, (NCCFS)N metasurfaces have enhanced solar absorptions (α = 0.95–0.99), which is attributed to the redshift of the cutoff wavelength. The emittance of metasurfaces can be as low as 0.06. This result may provide a theoretical basis for the experimental realization of the solar selective absorbing metasurface and a new vision of high-entropy alloys in the field of high-efficiency photothermal conversion. Data bases on the optical, chemical and mechanical behaviours of SSACs at room temperature but also at high temperature are necessary for the scientific community if we want use CSP for numerous applications as electricity generation, heating or desalination. As it has been described by Vitte (Vitte et al. 2012), the dynamic simulation also plays a relevant role. It allows to assess a priori the effectiveness of controls and procedures to manage the very fast transients on the solar line or to estimate in advance the future performance of the units involved in CSP according to their age and operating conditions. Finally, the reader could have access to the numerical and technical comparisons between the direct thermal energy storage (TES) technologies with economic considerations in beneficial design and control to lead the process up to the sustainable power production for the concentrating solar power (CSP) plants by the way of the paper written by Ravaghi-Ardebili (Ravaghi-Ardebili et al. 2013).

References

Chester D, Bermel P, Joannopoulos JD, Soljacic M, Celanovic I. 2011, Design and global optimization of high-efficiency solar thermal systems with tungsten cermets. Optical Express;19, A245-257.

COP21, 2015, https://ec.europa.eu/commission/priorities/energy-union-and-climate/climate-action-decarbonising-economy/cop21-un-climate-change-conference-paris_en accessed 24.11.2020

Dan Atasi, Harish C. Barshilia, Kamanio Chattopadhyay, Bikramjit Basu, 2017, Solar energy absorption mediated by surface plasma polaritons in spectrally selective dielectric-metal-dielectric coatings: A critical review, Renewable and Sustainable Energy Reviews 79, 1050–1077

El Bassam, N., Maegaard, P., Schlichting, M.L., El Bassam, N., Maegaard, P., Schlichting, M.L., 2013. Distributed Renewable Energies for Off-Grid Communities 91-109.

IPCC 3, 2001, https://www.ipcc.ch/site/assets/uploads/2018/03/WGI_TAR_full_report.pdf, accessed 24.11.2020

Liu Yu, Zhifeng Wang, Dongqiang Lei, Cong Wang, 2014, A new solar spectral selective absorbing coating of SS–(Fe_3O_4)/Mo/ TiZrN/TiZrON/SiON for high temperature application, Solar Energy Materials & Solar Cells 127, 143–146

Ning Yuping, Wenwen Wang, Ying Sun, Yongxin Wu, Yingfang Liu, Hongliang Man, Muhammad Imran Malik, Cong Wang, Shuxi Zhao, Eric Tomasella, Angélique Bousquet, 2016, Effects of substrates, film thickness and temperature on thermal emittance of Mo/substrate deposited by magnetron sputtering, Vacuum 128, 73-79.

Nofuentes G, García-Domingo B, Munoz JV, Chenlo F., 2014, Analysis of the dependence of the spectral factor of some PV technologies on the solar spectrum distribution. Applied Energy, 113, 302-309

REN21, https://www.ren21.net/reports/ren21-reports/ accessed 10.11.2020