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Multi-layer solar selective absorber coatings based on W/WSiAlN$_x$ /WSiAlO$_y$N$_x$/SiAlO$_x$ for high temperature applications

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ABSTRACT

A simulated and an experimental design of multilayer solar selective absorber coatings for high temperature applications is presented in this study. The optical tandem is composed of four layers deposited by magnetron sputtering on stainless steel substrates at room temperature. The first is a back-reflector tungsten layer, that is followed by two absorption layers based on WSiAlN$_x$/ WSiAlO$_y$N$_x$ structure for phase interference. The final layer is an antireflection layer of SiAlO$_x$. The design was conducted with the help of SCOUT software creating a multilayer model based on transmittance (T) and reflectance (R) spectra of individual thin layers deposited on glass substrates. The final design shows simultaneously high solar absorptance $\alpha = 96.0\%$ and low emissivity $\varepsilon = 10.5\%$ (calculated at 400 °C) together with high thermal stability at 450 °C, in air, and 600 °C in vacuum for 400 h and 300 h, respectively.

1. Introduction

Structures based on transition metal nitrides and oxynitrides are commonly used in selective solar thermal absorber stacks because of their high thermal stability, high oxidation resistance, good diffusion barrier and excellent selectivity [1–7]. Such stacks can be used in the concentrated solar power (CSP) technology, that uses parabolic-trough solar systems to improve energy absorption and employing it in steam turbines to produce electricity or in other high temperature applications [8–10]. However, any absorber tandem should be highly efficient in terms of selectivity, that is, it should have a high absorptance (α) at solar radiation region (wavelength range of 0.3–2.0 μm), and a low thermal emittance in IR region (wavelength range dependent on temperature application, but usually greater than 2.0 μm). Superior selectivity can be achieved if the multi-layer absorber tandem has a decreasing refractive index and extinction coefficient from substrate to surface, which can be easily obtained by appropriate choice of layers thicknesses and material composition. In the ideal case, at the front of the solar absorber, in the antireflection layer, *n* and *k* should be 1 and 0, respectively.

The most used transition metals are Ti [2,11–13], Cr [1,4,7], W [6,14], Nb [15], Zr [3] and Al [16] or combination between them. Most of these designs showed good thermal stability and oxidation resistance and share the same structure of general design as substrate (i.e. stainless steel) / back reflector metal (i.e. W) / metal nitride / metal oxynitride/ oxide layer as antireflection layer.

In the previous studies, a design of solar absorber tandems based on AlSiOx:W cermets with high (HA) and low (LA) metal volume fraction (W/AlSiO$_x$:W(HA)/AlSiO$_x$:W(LA)/AlSiO$_x$,) [17] and based on nitride/ oxynitride layers (W/CrAlSiN$_x$/CrAlSiO$_y$N$_x$/SiAlO$_x$) [1] were studied and fully illustrated. The final design showed simultaneously a high solar absorbance $\alpha \approx 95\%$ and low emissivity $\varepsilon = 10$–12% (calculated at 400 °C) together with high thermal stability at 450 °C and 400 °C, in air, and 580 °C and 600 °C in vacuum, respectively. The current work, also based on nitride/oxynitride structure, but the transition metal chromium was replaced with tungsten and the result was excellent. So, this work presents a new design of solar selective absorber coating for high temperature applications, with the structure (W/WSiAlN$_x$ /WSiAlO$_y$N$_x$/SiAlO$_x$).

2. Materials and methods

2.1. Coatings deposition

All films were deposited by dc magnetron sputtering on p-doped Boron Si (100) (used for Scanning Electron Microscopy (SEM) and X-Ray Photoelectron Spectroscopy (XPS) analyses), glass (used for tracing the optical properties of single layers) and polished stainless steel (AISI304) substrates (used for Energy Dispersive X-ray Spectroscopy (EDS) analyses, X-ray diffraction(XRD) and accelerated lifetime thermal

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Table 1
Experimental details of the multilayer stack coatings.

Layer	Target	Deposition time min: s	Working pressure (Pa)	Reactive gas Partial pressure (Pa)	Target current density (mA/cm^2)
Tungsten (W)	W	2:30	0.37	–	12.7
WSiAlN	W + 9Al + 9 Si[a]	0:42	0.41	N_2 0.17	6.4
WSiAl(ON)	W + 9Al + 9 Si	0:32	4.5	N_2 - O_2 (85–15%) 0.30	6.4
SiAlO	Si80Al20	1:36	0.37	O_2 0.06	6.4

[a] 9 silicon pellets with a diameter of 10 mm and 9 squares of aluminum pieces with 1 cm × 1 cm distributed uniformly on the W target erosion zone.

tests of resulting tandems). The depositions were performed using a substrate holder placed 9 cm above the target and working in static mode. Tungsten layers were deposited using a tungsten target (99.99%) with a diameter of 10 cm. Then, the same target was used to deposit $WSiAlN_x$ and $WSiAlO_yN_x$ layers, by adding 9 silicon pellets with a diameter of 10 mm and 9 squares of aluminum pieces with 1 cm × 1 cm on the target erosion zone. For $SiAlO_x$ oxide layer, a Si80 Al20 at% target was used, with oxygen as a reactive gas.

All layers were deposited in similar conditions by dc magnetron sputtering (P_{Ar} = 0.37 Pa, current density 6.4 mA/cm^2, pulsed bias of −60 V, f = 90 kHz, room temperature and base pressure 2 ×10^{-4} Pa), except in tungsten layer case, in which the current density was 12.7 mA/cm^2. Silicon and stainless steel substrates were ultra sound cleaned in acetone for 15 min, and ion etched before the deposition. During the target cleaning process, the substrates were protected by a stainless steel shield. Further details about the multi-layer deposition parameters of the stack are presented in Table 1.

2.2. Coatings' chemical composition, bonding, structure and morphology

The coatings' chemical composition of thick individual layers was assessed by means of EDS analyses. The measurements were performed on randomly selected regions of samples surface with an acceleration voltage of 7 keV. Scanning electron microscopy analysis was performed in a NanoSEM-FEI Nova 200 (FEG/SEM) equipment, to determine the coatings thickness and morphology.

For structural and oxidation resistance studies, glancing incidence angle XRD was used for single layers and for tandem before and after annealing, performed by employing a Bruker AXS Discover D8 operating with Cu Kα radiation. The measurements were performed at fixed incidence angle of α = 3°.

The chemical bonding state of thick WSiAlNx and WSiAlOyNx single layers (similar to those used in multilayer stack) was evaluated using X-Ray Photoelectron Spectroscopy (XPS) analysis. XPS was performed in a Kratos AXIS Ultra HAS X-Ray Photoelectron Spectroscopy system from Centro de Materiais da Universidade do Porto (CEMUP), using an Al Kα (1486.7 eV) X-Ray source, with a 40 eV pass energy. The C1s line at 285.0 eV was used to calibrate the binding energies. The XPS spectra were analyzed in CasaXPS software [18], and all peaks were fitted using a Shirley background and GL (30)[1] line shape. For W 4 f core level, fittings were done assuming the peak doublets with spin-orbit separation (ΔE_P) 4 $f_{5/2}$ – 4 $f_{7/2}$ = 2.18 eV and with peaks intensity ratio $I_{W4f_{5/2}}/I_{W4f_{7/2}} = 0.75$. In some cases, it was necessary to involve $W5p_{3/2}$ at higher binding energy (BE) side of 4 $f_{5/2}$ with $BE_{W5p_{3/2}} = BE_{W4f_{7/2}}+5.8$ and $I_{W5p_{5/2}}/I_{W4f_{7/2}} = 0.08$ [19].

2.3. Thermal treatment of the absorber tandem

The optical stack was subjected to annealing tests in air at 450 °C and in vacuum at 600 °C for 400 h and 300 h, respectively. According to vacuum annealing, the furnace was evacuated to the base pressure of 5.0 mPa and annealing was performed for three steps 150 h, 50 h and 100 h, respectively. After each step, the vacuum was broken, and the reflectance was measured to evaluate the absorptance and the emissivity. On the other hand, the steps for air annealing were 150 h and 250 h.

2.4. Characterization of optical properties and SCOUT simulation

The transmittance (T) and the reflectance (R) of individual thin layers of $WSiAlN_x$, $WSiAlO_yN_x$, W and $SiAlO_x$ deposited on glass substrate were measured by using a Shimadzu PC3100 spectrophotometer, in the wavelength range of 0.25 – 2.5 μm with scan step of 1 nm. The reflectance data were obtained at quasi-normal incidence (angle of incidence of 8°) using an Al mirror as reference. Results were used to calculate the optical constants (refractive index n and extinction coefficient k) and thicknesses, by using the software SCOUT [20] to simultaneously fit an optical model to the transmittance and reflectance spectra of each individual layer. SCOUT allows to perform a standard spectrum simulation employing the Fresnel equations together with appropriate models for the frequency dependent complex dielectric function ($\tilde{\varepsilon}_r = \varepsilon_1 + i\varepsilon_2$). To model $\tilde{\varepsilon}_r$ we have considered a sum of several contributions as shown in Eq. (1)

$$\tilde{\varepsilon}_r = \varepsilon_{back\ ground} + \tilde{\varepsilon}_{Drude} + \sum \tilde{\varepsilon}_{Lorentz} + \tilde{\varepsilon}_{OJL} \quad (1)$$

where $\varepsilon_{back\ ground}$, $\tilde{\varepsilon}_{Drude}$, $\tilde{\varepsilon}_{Lorentz}$ and $\tilde{\varepsilon}_{OJL}$ are real high frequency dielectric constant, Drude model (free carriers contribution), harmonic Lorentz oscillators (bound charges contribution) and OJL model (accounts for other interband transitions), respectively [21,22]. Notice that all these models use causal quantities to describe the dielectric function, including the OJL model that is specifically modified in the SCOUT software to ensure the Kramers-Kronig compatibility between the real and imaginary parts of the dielectric function. Then, the complex refractive index ($\tilde{n}$) can be calculated from the relation $\tilde{n}^2 = (n + ik)^2 = \tilde{\varepsilon}_r$.

The first step was to measure and model the reflectance (R) and transmittance (T) spectra of the glass substrate to extract its optical constants. These quantities were later used in the simulation of the spectra of each layer deposited on a similar substrate. Based on the results obtained from individual layers, the final coatings of thermal absorber were also optimized by SCOUT.

The normal solar absorptance (α_s) was determined from Eq. (2) by calculated or experimental spectral reflectance data $R(\lambda)$ and ASTM AM1.5D solar spectral irradiance, $I_s(\lambda)$, at the wavelength range of 0.3 – 2.5 μm.

$$\alpha_{sol} = \frac{\int_{0.3\mu m}^{2.5\mu m} I_s(\lambda)[1-R(\lambda)]d\lambda}{\int_{0.3\mu m}^{2.5\mu m} I_s(\lambda)d\lambda} \quad (2)$$

The infrared specular reflectance spectra were measured in the wavelength range of 2–25 μm (wavenumber range 5000 – 400 cm^{-1}) at near normal incidence (angle of incidence α ≈ 11°) with a Fourier Transform Infrared spectrometer Bruker IFS 66 V equipped with a globar source, a KBr beam-splitter and a DTGS detector. The measurements were performed in vacuum at room temperature and spectra were recorded at 4 cm^{-1} resolution with 16 scans. Before the sample measurement a background reference was performed with an

[1] GL (p): Gaussian/Lorentzian product formula where the mixing is determined by m = p/100, GL (100) is a pure Lorentzian whereas GL (0) is pure Gaussian.