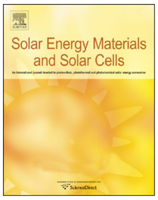
Solar Energy Materials & Solar Cells 117 (2013) 315–323

Contents lists available at SciVerse ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat



Optical modeling of multilayered coatings based on SiC(N)H materials for their potential use as high-temperature solar selective absorbers

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ARTICLE INFO

Article history:
Received 29 December 2012
Received in revised form
14 May 2013
Accepted 17 June 2013

Keywords:
Plasma enhanced chemical vapor deposition
SiC thin films
High temperature solar selective coatings
Optical modeling and characterization
Concentrated solar power

ABSTRACT

SiCH thin films grown from Ar/tetramethylsilane plasmas (PECVD) were evaluated as absorber layers in selective coatings for high-temperature solar receivers. SiCH coatings are used in thermomechanical applications because of their good thermal stability. A SiCH film with an absorption index $k(430\text{ nm}) = 0.11$ was taken as a reference for optical simulations of refractory metal–SiCH multilayer stacks and cermets. The transfer matrix method and Maxwell–Garnett effective medium approximation were used to calculate the spectral reflectance and transmittance of the selective absorbers. Their solar absorptance and thermal emittance were also deduced. A seven-layer stack with alternating metal and SiCH layers was found to present a simulated solar absorptance of 0.92 and thermal emittance of 0.08 at 500 °C.

1. Introduction

In concentrated solar power (CSP) plants, a clean and infinitely renewable energy source, the sun, is harnessed to produce electricity. CSP systems concentrate solar radiation on receivers, generally a metal, cooled by a heat transfer fluid (HTF). While other renewable energies such as photovoltaics and wind directly produce electricity, CSP first produces heat, which is much easier and cheaper to store and transport on a large scale (hundreds of MWth). The generated heat permits the production of electricity through a steam (or gas) turbine. As metallic receivers partly reflect solar light while strongly emitting infrared radiation when heated under solar flux, a spectrally selective coating can be deposited on the solar receiver. Such a coating possesses the following characteristics: (i) low reflectance in visible and near infrared (NIR) regions, to absorb efficiently the incident solar radiation; (ii) high IR reflectance, to prevent radiative emission and subsequent thermal losses; and (iii) a drastic reflectance modification at a cut-off wavelength ≈2 μm, resulting from a compromise between overlapping solar irradiance (to be absorbed) and radiative emission of the heated receiver (to be avoided). To achieve such spectral selectivity, these coatings associate several materials in multilayer stacks: (i) an IR reflective metallic layer with low emissivity (Cu, Mo, Ni); (ii) a solar radiation (VIS–NIR) absorbing material; and (iii) an antireflective top-coating to trap solar radiation (AlN [1–2], Al_2O_3 [3], Si_3N_4 [4], SiO_2 [5], SiON [6], TiO_2/SiO_2 [7]). Absorber materials are usually cermets (metal–ceramic composites) consisting of metallic inclusions in a dielectric matrix, e.g., Mo–Al_2O_3 [8,9], Pt–Al_2O_3 [10], W–AlN [2], Mo–SiO_2 [11], and W–Al_2O_3 [12]. To adapt their refractive indices to the underlying layer and further increase their absorptivity, one can either use graded cermets (metallic particle concentration gradient) [12–13] or LMVF/HMVF double layer cermets (low/high metal volume fraction) [8,11].

Commercialized solar selective coatings comprise double-layer cermet absorbers [11] and display high solar absorptance ($\alpha_S > 95\%$) and low thermal emittance ($\varepsilon_{400\ ^\circ\mathrm{C}} < 10\%$) [14–16]. These coatings mostly address the needs of parabolic trough linear receivers working with synthetic oil as heat transfer fluid, which operate below 400 °C. Some of these coatings are adapted to a molten salt HTF and withstand temperatures as high as 580 °C ($\varepsilon_{580\ ^\circ\mathrm{C}} < 15\%$) [16]. As the efficiency of heat engines (heat-work conversion) increases with temperature, R&D efforts are turned towards systems operating at higher temperatures, using other types of solar collectors and heat transfer fluids. For instance, a new generation of CSP plants couples direct steam generation (DSG) or a molten salt HTF with low cost linear Fresnel reflectors to reach temperatures higher than 500 °C. Power tower CSP can also be coupled with a DSG unit or work with molten salts to reach temperatures above 500 °C.

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http://dx.doi.org/10.1016/j.solmat.2013.06.030

Therefore, the U.S. Department of Energy (DOE) and the French Environment and Energy Management Agency (ADEME) have recently emphasized [17–18] the need to develop new solar selective coatings for CSP receivers that can withstand high temperatures, ideally under air, while maintaining high absorptivity and minimizing emissivity [19]. Aimed selective properties are typically $\alpha_S > 90\%$ and $\varepsilon(700\ ^\circ\mathrm{C}) < 40\%$ (claimed goals for NREL in U.S. Department of Energy SunShot Initiative [17]). Recently, transition metal oxides, nitrides, and oxynitrides, such as (Ti,Al)(O,N) [1,4,5,20,21], Nb(Ti,Al)(O,N) [6,22], and Mo/HfO$_x$ multilayer stack [23] selective coatings, have proved to present suitable thermal stability at high temperature. Transition and refractory metal carbides and silicides have also been considered [7]. These selective coatings were synthesized by plasma PVD deposition techniques, mostly reactive magnetron sputtering with DC and/or RF plasma excitation [5,6,21,22,24]. Plasma-enhanced CVD (PECVD) has also been attempted [5]. Other processes include e-beam evaporation [25], IBAD/e-beam co-deposition [7] and spin-coating [26].

Si:DLC (diamond-like carbon) and SiCH films grown by PECVD are widely used in mechanical and tribological applications [27–32] as well as in photovoltaics [33–37] for their high hardness and good thermal stability up to 650 °C under air [34]. Thermal annealing of SiCH films at higher temperatures has beneficial effects because it leads to stress reduction [28,36,38] and lower optical gaps (higher solar absorption) [35,39] through H evacuation [39,40]. The films thus appear to be good candidates for CSP receiver solar selective absorption at medium and high ($T > 400\ ^\circ\mathrm{C}$) temperatures. In fact, titanium- and chromium-containing CH and SiCH coatings were used as mid-temperature solar selective absorber coatings [41–43], and TiSi-based optical stacks have been considered for high-temperature solar selective absorbers by the U.S. National Renewable Energy Laboratory (NREL) [7].

In this work, optical properties of SiCH and SiCNH thin films were investigated to determine their potential in high-temperature solar selective applications. Such films were previously found to be chemically and mechanically stable at 550 °C in vacuum [44].

SiCH is envisaged as a ceramic matrix in solar absorbing cermets and as an absorber layer in solar selective multilayer stacks. To increase solar absorption, low refractive index SiCNH films are also considered to be antireflective top coatings in these stacks. For this purpose, SiCH and SiCNH thin films were grown by microwave PECVD from Ar/TMS (tetramethylsilane $Si(CH_3)_4$) and Ar/TMS/NH_3 mixtures, respectively. Their complex refractive indices (n, k) were measured by ellipsometry and served as input data for the transfer matrix calculation of the spectral reflectance, transmittance and absorptance of single SiCH layers and multilayer stacks including these layers. Their solar absorptance and thermal emittance were derived from reflectance and transmittance calculations. The optical response of SiCH-based cermets with high melting point refractory metal inclusions (W, Mo) was also studied. In this case, effective refractive indices were calculated using the classical Maxwell–Garnett effective medium approximation [45–47].

2. Experimental details

2.1. Material synthesis

SiCH and SiCNH thin films were synthesized by plasma enhanced chemical vapor deposition (PECVD) using four microwave (2.45 GHz) coaxial sources from Boreal Plasmas (Pont de Claix, France). For SiCH, the reactive plasma was generated from tetramethylsilane diluted in argon (Ar—3%TMS mixture). SiCNH was synthesized from a mixture of TMS (6 sccm) and NH_3 (26 sccm) precursors diluted in argon (33 sccm). The deposition temperature T_S was set to 350 °C with a heated substrate holder. For SiCH, the substrate holder was also biased using a low frequency generator (50 kHz), which caused a negative self-bias V_{DC} to be established on the sample. The $|V_{DC}|$ was set to 50 V. Coatings were grown on silicon (1 0 0) substrates.

2.2. Material characterization

Complex refractive indices (n, k) of the synthesized SiCH and SiCNH layers were measured by spectroscopic ellipsometry in the 430–850 nm range with a Jobin Yvon MM-16 polarimetric ellipsometer at an incident angle of 76°. Jobin Yvon DeltaPsi2 software was used to simulate the response of a model sample (Si substrate +SiCH or SiCNH layer). The New Amorphous dispersion formula was chosen for SiCH and SiCNH layers. This formula was derived from the Forouhi–Bloomer amorphous dispersion formula [48,49] and is well-adapted to the case of absorbing dielectrics. As a comparison, the Tauc–Lorentz dispersion formula [50] was also tested and provided similar results. The simulated optical response was then fitted to experimental results in the Marquardt least squares formulation [51] to establish pertinent parameters of the new amorphous model. Using these parameters, spectral refractive and absorption indices (n and k) of SiCH and SiCNH materials were deduced.

3. Optical theory

Complex refractive indices $N = n + i \times k$ served as input data for the optical modeling of spectral reflectance, transmittance and absorptance of metal–SiCH multilayers and composites with and without a SiCNH antireflective top layer. These values, in turn, permitted the estimation of their solar absorptance and thermal emittance, as described below.

3.1. Complex refractive indices

3.1.1. Substrate

In this study, SiCH and SiCNH films were deposited on Si substrates. For future solar absorbing applications, such materials will be deposited on stainless steel (SS) substrates. As SS complex refractive indices were not known at this point, an iron substrate was considered for calculation. Indeed, iron is the main component of stainless steel (for instance, SS 316 contains 65% of Fe) and its optical properties adequately represent the optical behavior of SS. (n, k) data for Fe was taken from the literature [52,53].

3.1.2. SiCH and SiCNH layers

For SiCH and SiCNH, (n, k) values were extrapolated in the solar to IR range (350 nm–20 μm) using the new amorphous dispersion formula parameters [48,49] which were experimentally established in the 430–850 nm range from ellipsometry measurements on our PECVD-grown SiCH and SiCNH coatings.

3.1.3. Metallic layers and metal–SiCH cermets

As high-temperature applications are envisaged, refractory metals, which are extremely resistant to heat and wear, such as tungsten and molybdenum, were considered in simulations. These metals served as IR reflective layers in multilayer selective coatings or as metallic inclusions in metal–ceramic composites (cermets) based on SiCH matrices. Complex refractive index data for W and Mo were found in the literature [52].