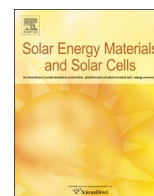




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# Advanced characterization and optical simulation for the design of solar selective coatings based on carbon: transition metal carbide nanocomposites

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## ABSTRACT

Solar selective coatings based on carbon transition metal carbide nanocomposite absorber layers were designed. Pulsed filtered cathodic arc was used for depositing amorphous carbon:metal carbide (a-C:MeC, Me = V, Mo) thin films. Composition and structure of the samples were characterized by ion beam analysis, X-ray diffraction, Raman spectroscopy, and transmission electron microscopy. The optical properties were determined by ellipsometry and spectrophotometry. Three effective medium approximations (EMA), namely Maxwell-Garnett, Bruggeman, and Bergman, were applied to simulate the optical behaviour of the nanocomposite thin films. Excellent agreement was achieved between simulated and measured reflectance spectra in the entire wavelength range by using the Bergman approach, where in-depth knowledge of the nanocomposite thin film microstructure is included. The reflectance is shown to be a function of the metal carbide volume fraction and its degree of percolation, but not dependent on whether the nanocomposite microstructure is homogeneous or a self-organized multilayer. Solar selective coatings based on an optimized a-C:MeC absorber layer were designed exhibiting a maximum solar absorptance of 96% and a low thermal emittance of ~5% and 15% at 25 and 600 °C, respectively. The results of this study can be considered as a predictive design tool for nanomaterial-based optical coatings in general.

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## 1. Introduction

Concentrating solar power (CSP) is a commercially available technology in the field of renewable energies. It is based on the conversion of concentrated solar energy into thermal and subsequently electrical energy. Nowadays, the two most prominent commercial CSP technologies are parabolic trough collectors and central receiver tower plants. Main components of CSP technology are solar light concentrators (reflectors), solar receivers (absorbers), heat transport and storage systems and electrical power generators [1]. Solar selective coatings with high absorptance ( $\alpha$ ) in the solar spectral range (0.3 – 2.5  $\mu\text{m}$ ) and low thermal emittance ( $\varepsilon_r$ ) in the infrared region (2.5 – 30  $\mu\text{m}$ ) are required for solar receivers [2]. Physical vapor deposited (PVD) solar selective coatings have been widely employed in parabolic trough systems,

where temperatures below 400 °C and vacuum environments are applied [3]. However, these solutions cannot be directly implemented in central receiver tower plants that operate at higher temperatures in air. Nowadays, commercial paints such as Pyromark<sup>®</sup> are the most commonly employed absorber coatings in tower plant central receivers. Their disadvantages are a poor solar selectivity ( $\varepsilon = 86\%$  at room temperature) and a fast degradation during operation. The latter one requires permanent maintenance and repairs typically every two years [4]. In a recent review [3], an extensive variety of PVD coatings was evaluated. Correspondingly, the coatings degrade easily at high temperatures (> 400 °C) in air due to oxidation and/or diffusion of the metal substrate into the coatings. These examples underline the necessity to develop novel types of solar selective coatings that are characterized by high-temperature stability in oxidizing environments.

State of the art designs of solar selective coatings include multilayers comprised of an antireflective layer (AR), an absorber layer, and an infrared reflection (IR) layer. Antireflective layers such as a  $\text{Si}_3\text{N}_4$  or  $\text{Al}_2\text{O}_3$  located on the top of the coating improve

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the solar absorption and stabilize the coating at high temperatures [5]. The infrared reflective layer placed under the absorber layer reduces the thermal emittance at high temperatures and acts as a thermal barrier to avoid material diffusion between the absorber material and the substrate [6].

Solar absorber layers based on nanocomposite materials were investigated in numerous studies [7,8]. Among them, a-C:MeC nanocomposites are suitable candidates for high-temperature solar absorber applications [9]. Pure a-C thin films are good candidates for solar absorber materials [10] but they are not air stable at temperatures above 300 °C. In combination with group 4, 5, and 6 transition metals, carbon forms a number of exceptionally stable interstitial carbides. These carbides are characterized by high melting points (in the range of 2600–2800 °C [11]), high thermal and electrical conductivity, and high reflectivity in the entire UV-Vis-IR spectral range [12]. The presence of these carbides stabilizes the nanocomposite microstructure at high temperatures [13,14]. Different microstructures of the a-C:MeC nanocomposites have been reported i) carbide phases dispersed in the carbon matrix in the form of nanoparticles, with different morphologies (globular or elongated [15,16]) and crystal structures (amorphous [17] or crystalline [18]) and ii) a self-forming multilayer structure with periodic concentration fluctuations of metal in a-C [19]. These systems can exhibit improved mechanical properties (lower intrinsic compressive stress, improved adherence to the substrate or better wear resistance [20]) compared to pure a-C films.

Combining the advantageous optical and thermo-mechanical properties of the individual components can result in adjustable solar selective properties for a-C:MeC nanocomposites with high-temperature resistance. Harding et al. reported that sputter deposited metal carbides (Cr, Fe, Mo, Ni, Ta and W) on copper substrates show good selective properties ( $\alpha > 80\%$  and  $\epsilon_{600\text{ °C}} \sim 7\%$ ) [21,22]. Gampp developed a multilayer coating based on hydrogenated a-C co-deposited with Cr or W by sputtering (a-C:H/Cr and a-C:H/W [23–25]). Yin et al. [26] deposited a-C:H/SS-a-C:H (SS: stainless steel) using cathodic arc technique. However, in all these examples the optical properties dropped drastically for temperatures higher than 600 °C due to different types of degradation mechanisms: i) undesired interaction between coatings and the metallic bottom layer and ii) degradation due to the intrinsic instability of the coating material itself. More recently, Schüller et al. developed a multilayer coating based on titanium and amorphous hydrogenated carbon (a-C:H/Ti) films [27] adding silicon to increase the durability in air.

The proper determination of the optical constants of the nanocomposites represents a major difficulty for the optimization of a-C:MeC solar absorber coatings up to now. This is particularly caused by the limited knowledge on the dependences of optical properties in the solar range on nanocomposite film composition, microstructure and phase morphology. In heterogeneous materials with nanoparticles much smaller than the light wavelength (such as a-C:MeC thin films), the optical properties can be described by so-called effective dielectric functions or effective medium approximations (EMA) [28]. They give a non-trivial average of the dielectric functions of the individual components of the nanocomposite in the form of an effective dielectric function ( $\epsilon_{eff}$ ) for the composite material.

Several EMAs have been established, Maxwell-Garnett (MG) [29] and Bruggeman (BRU) being the most widely used ones [30]. In both, the final effective dielectric function depends on the volume fraction of the particle material and on the optical constants of the individual constituents. Characteristic properties of the microstructure or the shape of the embedded particles are not incorporated. In contrast, Bergman (BER) representation [31] applies several corrections related to the shape of the nanoparticles and the degree of percolation of the embedded nanoparticles,

which improve the accuracy of the simulated effective dielectric function. This approximation is especially useful in cases where the microstructure plays a significant role in the optical properties of the heterogeneous material.

By now the design of absorber coatings relies very often on an empirical *ad-hoc* approach. A smart coating development, however, would require a reliable simulation of the optimized coating stack as the first and the experimental confirmation as the second step. The former would have to identify and incorporate those structure elements that are relevant for the optical response. Therefore, the first objective of this study is to apply such approach to model the optical properties of a-C:VC and a-C:MoC nanocomposite films as a solar absorber layer. The second objective is to design a complete solar selective AR layer / a-C:MeC absorber layer / IR reflector stack by using this model and to find out the theoretical limit of the absorbance at RT and at temperatures relevant for high-temperature absorber applications.

In this study, a-C:VC and a-C:MoC nanocomposite thin films with different metal carbide contents and different microstructures have been deposited by pulsed filtered cathodic vacuum arc (PFCVA). Among the different physical vapor deposition (PVD) techniques, FCVA has the highest plasma ionization ratio. This results in denser thin films with higher hardness and better adhesion [32], and allows the control of the composition ratio of absorbing carbon and reflecting/refractory carbide. The element composition of the nanocomposites was determined using Rutherford Backscattering Spectrometry (RBS) and Nuclear Reaction Analysis (NRA). Their structure was characterized by Raman spectroscopy, X-ray diffraction (XRD), and high-resolution transmission electron microscopy (HRTEM). Reflectance spectra were obtained by UV-Vis-NIR spectrophotometry, and the optical constants were measured by spectroscopic ellipsometry (SE). The optical properties were simulated comparing three different EMAs, namely Maxwell Garnett, Bruggeman and Bergman using the commercial software CODE [33]. The Bergman EMA was found to be the most suitable one for this type of materials. The dielectric functions obtained by the simulation were further used for a detailed examination of the absorbance of a-C:MeC (Me = V, Mo) layers. Based on this approach an optimized, complete stack with an outstanding solar absorbance ( $\alpha$ ) of 96% and an emittance ( $\epsilon_T$ ) of 5/15% at 25/600 °C was predicted. This is significantly better than the values reported for this class of materials so far, which were an  $\alpha=91.0\%$  with  $\epsilon_{100\text{ °C}} = 11\%$  for an a-C:Ti/SiO<sub>2</sub> stack on Cu substrate [27,34].

## 2. Experimental details

### 2.1. Thin film growth

Thin films were simultaneously grown on single crystalline Si (100) and on polished Inconel<sup>®</sup> 625 substrates in the same deposition batches. The former ones were used for Rutherford Backscattering Spectroscopy (RBS), Raman and XRD characterization while the latter were employed for high-resolution transmission electron microscopy (HRTEM) and optical characterization. Before deposition, the substrates were cleaned in an ultrasonic bath in distilled water, acetone and ethanol.

The depositions were carried out using a PFCVA system equipped with two arc sources, PFCVA-450 from Plasma Technology Limited [35] (Fig. 1). The system includes electromagnetic filters in the curved ducts to reduce the incorporation of macro-particles in the growing films. The generated arc plasmas are guided into the vacuum chamber by an electromagnetic field applied to the curved ducts. External solenoid coils are wrapped around the ducts and produce an axial magnetic field. The coils are

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