

Selective absorption of Carbon Nanotube thin films for solar energy applications



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ABSTRACT

A new spectrally selective coating based on carbon nanotubes (CNTs) for solar thermal applications is demonstrated. For optimized coatings solar absorptance coefficients $\alpha > 0.92$ and thermal emittance coefficients $\epsilon < 0.1$ (400 °C) were achieved. These results render CNT coatings as a low cost and high performance alternative to commercially available vacuum deposited cermet coatings for concentrated solar power (CSP) application.

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1. Introduction and motivation

For efficient conversion of solar energy to thermal energy, a high absorption of solar radiation is desired. At the same time, thermal losses by black body radiation should be minimized. To meet this requirement, spectrally selective coatings were developed. These coatings exhibit high absorption in the solar range (0.2–2.5 μm), but low absorption in the IR range ($> 2.5 \mu\text{m}$). According to Kirchhoff's law, the emissivity of an object is equal to its absorptivity. For a certain temperature applications (100 °C and 400 °C), the maximum irradiance corresponding to Planck's law is emitted at wavelengths of 7.8 μm and 4.3 μm , respectively. Considering the spectral distribution of black body radiation, the absorption edge should be close to 2.5 μm to achieve high energy efficient spectrally selective coatings.

A comprehensive overview about selective surfaces is given by Kennedy [1]. Selective surfaces are divided into 6 groups: (a) intrinsic or “mass absorbers”; (b) semiconductor–metal tandems; (c) multilayer absorbers; (d) metal–dielectric composite coatings; (e) surface texturing; (f) selective solar transmitting coatings on a blackbody like absorber [1].

Well established in the market are metal–dielectric composite coatings, such as black chrome and cermet (ceramic metal) [2]. Especially cermet coatings can be produced in a high optical quality (optical coefficients $\alpha > 0.95$ and $\epsilon_{400\text{ °C}} < 0.1$), by using comparatively cost intensive vacuum-based processes. However for high temperature applications, degradation of the coatings occurs due to thermal diffusion processes. Black chrome coatings are stable in air up to 350 °C respectively 400 °C in vacuum [1]. Using additional diffusion barriers, cermet coatings were reported to be stable up to 500 °C [3–5].

Here we present a new thin film concept based on carbon nanotubes (CNTs) exhibiting spectral selectivity and outstanding thermal stability. Although CNTs are one of the most investigated materials, showing exceptionally mechanical, electrical, thermal and optical properties [6–10] so far they have never been reported for this particular spectral selective optical property despite their high potential for being used in solar energy collecting applications [11]. Besides its promising optical and thermal properties, the new thin film concept is quite inexpensive, due to low material consumption and atmospheric pressure coating processes.

The new thin film concept consists at least of a highly reflective (low emitting) surface (copper, silver, gold, platinum, nickel, chromium, stainless steel, etc.) and a carbon nanotubes thin film on top. Furthermore the CNT thin film can be stabilized

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mechanically and thermally by using optically transparent thin films such as silicon dioxide [12]. The methods to produce spectrally selective CNT based coatings as well as their optical properties are described below.

2. Experimental details

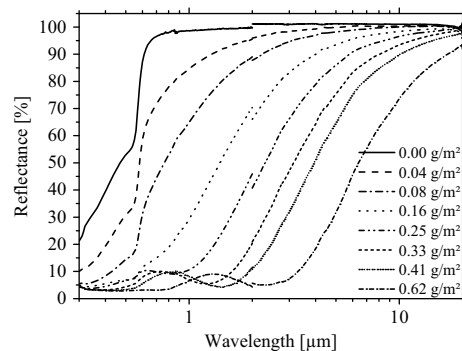
Various carbon nanotubes were applied on a number of highly reflecting substrates (stainless steel, copper, nickel, chromium) as thin films. Therefore, aqueous CNT dispersions, using anionic surfactant sodium dodecylbenzene sulfonate (SDBS), were produced and applied by spraying on a heated substrate. For a multi-wall carbon nanotubes (MWCNT) dispersion water, 0.1 m% MWCNT and 0.1 m% SDBS were dispersed by ultra-sonication (5 min, 20 kHz) and centrifugation (5 min, 3260g). For producing single-wall carbon nanotubes (SWCNT) dispersion, the chemistry (0.05 m% SWCNT, 1 m% SDBS) as well as parameter for ultra-sonication (15 min, 20 kHz) were changed instead.

The deposition was carried out using spraying techniques, such as Ultrasonic Spraying (Exacta Coat from Sono-Tek, 120 kHz) and two-substance nozzles (Schlick, Series 970). To achieve a homogeneous CNT-thin film, the substrate is heated up to 100 °C during deposition to ensure an evaporation of water, leaving only CNTs and SDBS on surface. Afterwards the SDBS and other residues (sodium carbonate, sodium sulfate) were removed by washing off in ethanol and water.

3. Characterization

The remaining CNTs form a mechanically unstable network on the surface, which can be easily damaged by touching or scratching. Those CNT-network thin films were investigated optically by total reflectance measurements using UV–VIS–NIR (0.3–2.5 μm) spectrophotometer (Perkin-Elmer, Lambda 900 with 150 mm integrated sphere) and NIR–IR (1.7–20 μm) spectrophotometer (Perkin-Elmer Spectrum 2000 with Pike integrated sphere “IntegratIR”). The reflectance spectra $R(\lambda)$ were evaluated to calculate the optical coefficients such as solar absorptance (α) and thermal emittance (ε) at certain temperatures. Following equations were been used for determination ($I_{AM1.5dir}(\lambda)$ - direct normal solar spectral irradiance, Air Mass 1.5; $I_{BB}(\lambda)$ - blackbody irradiation for a certain temperature):

$$\alpha = \frac{\int_{0.3 \mu\text{m}}^{2.5 \mu\text{m}} I_{AM1.5dir}(\lambda) \cdot (1-R(\lambda)) d\lambda}{\int_{0.3 \mu\text{m}}^{2.5 \mu\text{m}} I_{AM1.5dir}(\lambda) d\lambda} \quad (1)$$



$$\varepsilon = \frac{\int_{1.7 \mu\text{m}}^{20 \mu\text{m}} I_{BB}(\lambda) \cdot (1-R(\lambda)) d\lambda}{\int_{1.7 \mu\text{m}}^{20 \mu\text{m}} I_{BB}(\lambda) d\lambda} \quad (2)$$

4. Results

In Fig. 1 the reflectance spectra of multi-wall CNT-networks on copper coated stainless steel substrates as well as the resulting optical coefficients α and ε (@ 400 °C) varying in CNT areal loading are presented.

The copper surface itself has a very high reflectance in the NIR and IR range. Due to its opaqueness, all measured reflectance loss can be attributed to the absorption of the CNT-network on top of the copper substrate. In general a dependence of CNT areal loading regarding absorption as well as absorbed wavelength could be observed. By increasing CNT areal loading the absorption is increased as well as a shift of absorption towards higher wavelengths occurs. Thus, not only the spectral selectivity of the CNT-network can be adjusted, but also areal loading enables to shift the selectivity range spectrally with varying film thickness.

The observed spectral changes of the total absorption is caused by interband electronic transitions and π -plasmon for each carbonaceous constituent at a selected energy [13]. Due to a higher degree of impurities in MWCNTs, the absorption caused by π -plasmon is predominant. The shift of absorption towards higher wavelengths by increasing the areal loading follows the Lambert-Beer law.

The absorption by π -plasmon is the collective excitation of electrons associated with the π -band, showing a nonlinear dependency, and can be described by a Lorentzian function [13–14]. The peak maxima of this Lorentzian function correspond to the π -plasmon resonance energy and are reported to be in the range of 4.5–7 eV respectively 275–177 nm [13]. Following this function, the absorption is decreasing at lower energies respectively higher wavelength, causing the observed spectral selectivity.

For SWCNTs, the reflectance spectra are different. A lower content of carbonaceous impurities, compared to MWCNTs, is decreasing the total absorption caused by π -plasmon. However, in the near infrared two absorption peaks overlap with the reflectance spectra. These absorption peaks (S_{11} and S_{22}) are caused by the van Hove singularities in the density of state.

On the contrary, the van Hove singularities are caused by interband electronic transition and are dependent on density of states and diameter of the tubes. Depending on the chirality of the tubes, the Kataura plot shows the dependency of bandgap energy

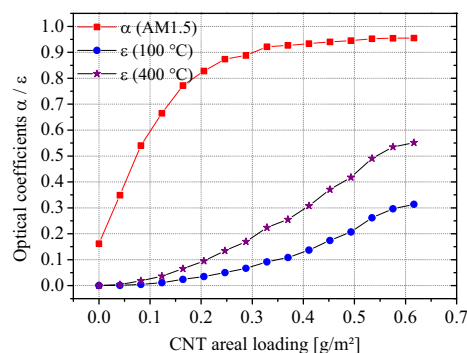


Fig. 1. Reflectance spectra and optical coefficients (solar absorptance α and thermal emittance ε) in dependence of CNT areal loading for MWCNTs on copper coated stainless steel substrates.

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