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Thermal solar absorber made of diamond-like carbon thin films

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Abstract. Solar photo-thermal collectors were prepared from pure diamond-like carbon (DLC) thin films on aluminum substrates. By only changing the deposition conditions (different bias voltage) of the DC PECVD process, coatings were fabricated consisting of five sublayers with the necessary optical parameters. As expected, absorption better than 0.9 was achieved already for submicrometer absorber thickness. Accelerated thermal ageing tests performed at 200°C and 300°C in air showed that the reflectance changes only slightly. Long operating life can, therefore, be expected of such absorbers.

1. Introduction

Solar absorbers are the most important part of solar collectors. An ideal solar absorber should be spectrally selective, i.e. it should absorb the solar radiation in the whole solar spectrum (350 ÷ 2500 nm) and should have a minimal thermal emission at ~ 8 μm for low temperature solar collectors [1, 2]. Existing absorbers in solar collectors for photo-thermal conversion are usually produced by different chemical and electrochemical processes [3]. A typical example is the so-called “black chrome” [4], which has become one of the most widely used solar absorber material.

More recently, the interest has risen in physical vapor deposited coatings (mostly by sputtering) [5]. These processes avoid wastes and are highly reproducible. Such coatings consist of different materials, e.g. aluminum oxide, titanium or chromium oxynitride [6]. Among them, metal containing hydrogenated carbon is very promising [7]. These coatings are in fact nanostructured materials containing clusters with dimensions on the nanometer length scale. By changing the metal content (usually chromium [8]) during deposition, one can change the optical properties of the coating. Such solar absorbers based on a multilayer of a-C:H/Cr nanocomposites are produced on a large scale by the “Ikarus coatings”, Germany [9]. An advantage of the a-C:H/Cr is the absence of grain boundaries, which may be susceptible to corrosion. Therefore, for such coatings a life time of more than 25 years is expected, although oxidation of the metal particles could decrease the absorber life time. Deposition of such a-C:H/Cr coatings, however, is a complicated process, while chromium as a heavy metal is environmentally harmful and should be avoided.

Recently, we succeeded in fabricating a DLC solar absorber made without metal inclusions [10]. In our coatings, the necessary variation of the optical properties is achieved by simply changing the bias voltage during DC PECVD deposition. A typical design of our solar absorber is shown in figure 1. It consists of 5 sublayers deposited on an aluminum substrate at 2.5 kV; 2 kV; 1.5 kV; 1 kV and 0.5 kV.

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The first sublayer is softer than the others, with small mechanical stress and good adhesion to the substrate. The following sublayers are deposited with decreasing bias voltages, which make them more optically transparent and harder. The top sublayer is hard and plays also the role of a protective coating of the whole absorber.

The necessary thickness of such an absorber has been estimated earlier [11]. Using the measured absorption coefficient and assuming ~ 95% absorption, we have found that the absorber film thickness should be at least 0.6 μm. In this work, these conclusions were proved experimentally and an accelerated ageing test was carried out, which predicts long life behavior of our absorbers.

2. Experimental

Thin films of diamond-like carbon were deposited in DC a PECVD reactor [10]. Benzene vapors diluted with argon were chosen as a precursor. Both silicon and aluminum substrates were used for the experiments. Aluminum was chosen as a substrate material because of its good adhesion to the DLC and its high thermal conductivity. The DLC films deposited on aluminum are very smooth with roughness about of 0.5 nm as the AFM image shows (figure 2).

To reduce further the reflectance from the absorber surface, rough Al substrates were also used. The roughness of such a substrate was about 4 μm, just as needed to obtain small, broadband and omnidirectional reflection from the absorber surface in the visible optical range.

Three sets of absorbers were fabricated with 6 min, 12 min and 18 min deposition time of each of the 5 sublayers. The total absorber thickness, measured by a surface profilometer, were found to be \( d_1 = 0.88 \) μm; \( d_2 = 1.76 \) μm and \( d_3 = 2.41 \) μm, respectively. The reflectance \( R(\lambda) \) of the complete absorber was measured by a Shimadzu 3600 UV-VIS-NIR spectrometer equipped with an integrating sphere in the wavelength range from 350 nm to 2500 nm to estimate the total solar absorption \( \alpha \).

In order to simulate accelerated ageing [12] the absorbers were subjected to high-temperature treatment at 200°C for 10 h and at 300°C for 10 h in air. After the absorbers were exposed to these temperatures, the reflectance was measured again and compared with the values prior to the thermal treatment.

The solar absorption \( \alpha \) of the samples before and after thermal ageing treatment was calculated using the relation:

\[
\alpha = \frac{\int_{0.39 \mu m}^{2 \mu m} W(\lambda)(1 - R(\lambda))d\lambda}{\int_{0.39 \mu m}^{2 \mu m} W(\lambda)d\lambda},
\]

where \( W(\lambda) \) is the solar radiation intensity at different wavelength for air mass 1.5 (ISO9845-1:1992).

The degradation of the diamond-like carbon coatings on silicon substrates after annealing at 300°C was monitored also by Raman spectroscopy with a laser operating at wavelength of 633 nm.
3. Results

Figure 3 shows the reflectance spectra of the 3 fabricated absorbers. All have spectrally selective properties: reflection below 10 % at solar maximum radiation and increasing reflectance toward 2500 µm. Interference pattern are observed in all samples, whose position depends obviously on the film thickness. The absorber 1 (d₁) with 5 sublayers deposited at 6 min each shows a minimal reflectance of 3.7 % at 780 nm. As expected, the three absorbers (d₁, d₂, d₃) have sufficient absorptance: $\alpha₁ = 0.9150$, $\alpha₂ = 0.9163$ and $\alpha₃ = 0.9292$.

Figure 4 shows the reflectance spectra changes after the heat treatment at 200 °C for 10 h – figure 4a and at 300 °C for 10 h – figure 4b. No significant changes can be seen in the spectra. Slight shifts of the interference pattern were only observed connected probably with small films thickness changes due to carbon oxidation.

As seen in figure 5, the positions of the reflectance maxima differ slightly, i.e. there is no considerable temperature influence on the optical thickness.

A possible degradation of the coatings caused by the accelerated ageing was monitored by Raman spectroscopy [13]. Figure 6 shows the Raman spectra of the tree absorbers after annealing at 300°C. The spectra were almost identical with two broad maxima: the so-called G-peak at about 1580 cm⁻¹ and D-peak at about 1350 cm⁻¹. These peaks are well known to originate from sp²-bonded graphite-like regions and from disordered carbon, respectively. It is also well known that by analysing their position and width one can determine the size of the sp²-bonded regions [14]. The narrow peaks, as well the increased D-peak of our samples are indication for the existence of graphite-like regions in the absorbers.

In our coatings we did not observe any shift in the position of both peaks from their typical positions. These Raman spectra, however, should be interpreted with caution, because the samples are not homogeneous in depth and some modification of the samples by the laser beam power was noticed during the Raman measurements. The modification is caused due to the high absorption of the samples at the laser wavelength of 633 nm, which falls in the middle of the solar spectrum. However, this is the best demonstration of the excellent properties of our solar absorbers. In single films one cannot observe any modification because their absorption is not so high.
Table 1. Solar absorption of 3 mulilayered absorber coatings with different thicknesses.

| Absorption $\alpha$ | before annealing | after $T = 200^\circ C$ | after $T = 300^\circ C$ |
|---------------------|------------------|-------------------------|-------------------------|
| $\alpha_1 (d_1)$   | 0.9150           | 0.9123                  | 0.9132                  |
| $\alpha_2 (d_2)$   | 0.9163           | 0.9223                  | 0.9211                  |
| $\alpha_3 (d_3)$   | 0.9291           | 0.9156                  | 0.9183                  |

4. Discussion
In the experiments described, no substantial difference was found in the absorption of the three sets of samples, although the thickness of absorber 2 exceeds that of absorber 1 by factor of 2, and that of absorber 3, by a factor of three. The thinnest one (0.88 µm) has already the necessary absorption and should be preferred because of the lower emittance, a (probably) better adhesion and the lower cost. In addition, only small changes were found in $\alpha_1$ after a high-temperature test (table 1). Furthermore, the interference maxima in reflection measured after the annealing (figure 5) show small shifts only, indicating that the optical thickness of the sample is not decreased considerably.

5. Conclusions
In conclusion we would like to point out that we succeeded in fabricating a solar absorber made of diamond-like carbon thin films without metal inclusions consisting of 5 sublayers deposited on an aluminum substrate with a total thickness of 0.88 µm. Accelerated thermal ageing performed at 200°C and 300°C in air showed that there are not substantial differences in the absorption and the structure of the DLC layers. Therefore long-life behavior of our absorber should be expected.

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References

[1] Bogaerts W F and Lampert C M 1983 J. Mater. Sci. 18 2847
[2] Granqvist C G and Wittwer V 1998 Sol. Energy Mater. Sol. Cells 54 39
[3] Bostrom T, Westin G and Wackelgard E 2007 Sol. Energy Mater. Sol. Cells 91 38
[4] Lee T K, Kim D H and Auh P C 1993 Sol. Energy Mater. Sol. Cells 29 149
[5] Nunes C, Teixeira V, Colares-Pereira M, Monteiro A, Roman E and Martin-Gago J 2002 Vacuum 67 623
[6] Barshilia H, Selvakumar N, Rajam K and Biswas A 2008 Sol. Energy Mater. Sol. Cells 92 1425
[7] Gampp R, Oelhafen P, Gantenbein P, Brunold S and Frei U 1998 Sol. Energy Mater. and Sol. Cells 54 369
[8] Milde F, Dimer M, Hecht Ch, Schulze D and Gantenbein P 2000 Vacuum 59 825
[9] Oelhafen P and Schuler A 2005 Solar Energy 79 110
[10] Tinchev S, Nikolova P, Dyulgerska Y, Danev G and Babeva Tz 2005 Sol. Energy Mater. Sol. Cells 86 421
[11] Nikolova P, Tinchev S and Alexieva Z 2009 J. Optoelectr. Adv. Mater. - Symposia 1 327
[12] Carlsson B, Moller K, Kohl M, Frei U and Brunold S 2000 Sol. Energy Mater. Sol. Cells 61 255
[13] Baek S, Parks S-J, Lee K-R and Seok C-S 2008 Mater. Sci. Engin. A 483–484 245
[14] Ferrari A and Robertson J 2000 Phys. Rev. B 61 14095