Amorphous hydrogenated carbon coatings for thermal solar collectors

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Abstract. Selective solar thermal collectors were prepared by plasma enhanced deposition of pure amorphous hydrogenated carbon (a-C:H) films on aluminium substrates. By only varying the bias voltage in the DC PECVD system coatings were fabricated composed of five sublayers with graded optical properties. An absorption spectrum well matched to the solar spectrum was obtained. A very low value of the optical hemispherical reflectance of graded a-C:H films was achieved. The selective optical properties of the coatings were further confirmed by the high transmittance measured in the infrared region.

1. Introduction
Extensive investigations on solar absorbers with the purpose of saving natural sources of energy have been performed recently [1, 2]. Solar thermal collectors can convert unlimited amounts of solar energy into usable heat. The efficiency of such solar collectors depends mostly on the solar selectivity of the absorber surface. To accomplish this, new and more efficient selective coatings are needed that manifest high solar absorption and low thermal emission together. There are several ways such as manufacturing absorber/reflector, semiconductor/metal tandems or interference multilayers to achieve this [3]. Amorphous hydrogenated carbon (a-C:H) being a semiconductor is an interesting absorber material whose bandgap, refraction index, adhesion, hardness and durability can be tailored. Layers of a-C:H are used as antireflection coatings for solar cells [4, 5]. Films of a-C:H containing transition metals are a promising material for the fabrication of selective solar absorbers[6, 7]. Usually, such coatings are deposited by a combined PECVD-magnetron sputtering process. By varying the metal content it is possible to control the optical properties of the deposited coatings and thus optimise their absorption coefficient. This makes however the technology more complex. We report here a simple process, where the selective solar absorbers are made of pure a-C:H without metal inclusions. This is achieved by varying the bias voltage during the PECVD deposition. In such a way a five-sublayer system with graded optical properties was fabricated. In our previous work [8] we report our investigations of a matched to the solar spectrum a-C:H absorber layer deposited on glass. For thermal...
solar collectors, however, it is important to use substrates with high thermal conductivity like copper (Cu) and aluminium (Al). In this work a-C:H coatings for thermal solar collectors were fabricated on Al-substrates.

2. Experimental
Thin films of amorphous hydrogenated carbon were deposited in DC plasma CVD reactor. Benzene vapours diluted by argon were chosen as a processed hydrocarbon. Rough Al substrates were used for the experiments. However glass substrates were needed for the UV-VIS transmittance measurements and Si wafers were used for the IR transmittance measurements. Aluminium was chosen as a substrate material because of earlier experience, relatively low cost, good adhesion of a-C:H to it [9], its high reflectivity in the IR range of wavelengths and its high thermal conductivity [10]. Before the film deposition the substrates were cleaned by acetone and deionized water in an ultrasonic bath and placed upon the water-cooled cathode. The metal vacuum chamber acted as an anode. 10 min Ar ion sputtering at 2 kV provided for an additional cleaning of the surface. The samples were prepared at five different DC voltages (0.5 kV, 1 kV, 1.5 kV, 2 kV and 2.5 kV) with 6 min deposition time of each layer and one graded layer which consisted of the same five layers with a 30 min total deposition time. The voltage decreases from bottom (film-substrate interface) to top (air-film interface). The other conditions in the reactor are kept constant. The voltage variation from 2.5 kV to 0.5 kV changes the optical bandgap of an a-C:H material from 1.2 eV to 2.1 eV, thus covering almost the whole solar spectrum [8].

A double-beam spectrophotometer type Shimadzu UV-190 with integrating sphere was used for the measurement of the layer hemispherical reflectance on Al substrates and transmittance and reflectance on glass substrates in the solar spectrum wavelength range. A FTIR Shimadzu Prestige 21 spectrophotometer operating in the infrared wavelength range from 1.25 μm to 28.5 μm was used for the measurements of the transmittance of the a-C:H sublayers and of the multilayer system as a whole.

3. Results

3.1. UV - VIS Region
To obtain thermal solar collectors one have to prepare coatings, which can actually absorb the whole solar spectrum. According to Kirchoff’s law, the absorption \( \alpha(\lambda) \) for opaque surfaces is related to the total hemispherical reflectance \( R(\lambda) \) as:

\[
\alpha(\lambda) = 1 - R(\lambda).
\]  

The ideal behaviour of solar absorber surfaces is that of high absorption (\( \alpha(\lambda) \approx 1 \)), i.e. \( R(\lambda) \approx 0 \) in the 250÷2500 nm wavelength range, where almost all solar radiation is concentrated.

The optical hemispherical reflectance of a-C:H films deposited on Al substrates at different DC voltages is shown in figure 1. The thin films formed at higher voltages exhibited lower values of \( R \) and in the measured region the average value of \( R \) varies between 0.490 for DC = 0.5 kV and 0.114 for DC = 2.5 kV.

In figure 2 are shown the visible region reflectance of a pure rough Al surface and of a graded a-C:H film on the same Al substrate. As the average value of \( R \) for Al is 0.62, an Al substrate covered with a graded a-C:H thin film has average value of \( R = 0.078 \). The reflectance of the graded film is lower than the reflectance of all single layers. The effect of destructive interference [11] due to the combination of five layers can be seen by comparing figure 1 with figure 2.

In figure 3 is shown the absorption of the graded film in the whole 250÷2500 nm wavelength range. Very good matching of \( \alpha \) to the solar spectrum is observed.

3.2. IR region
Since the maximum radiance of an absolute black body at 80 °C (the operating temperature of low temperature thermal collectors) is at about 7.5 μm, the thermal emittance of optically selective
absorbers has to be minimal, i.e. $R(\lambda) \approx 1$, in the infrared range ($2.5 \mu m < \lambda < 25 \mu m$).

Our a-C:H/Al tandem actually act as a heat mirror. Since an Al substrate has very good reflectance we have to prepare coating which is transparent for infrared radiation. In figure 4 are shown the transmittances of five single layers and of the graded layer in the IR region. It is seen that with decreasing the voltage of film deposition increases the film transmittance, the graded layer having the highest transmittance.

![Graph 1](image1.png) ![Graph 2](image2.png) ![Graph 3](image3.png) ![Graph 4](image4.png)

**Figure 1.** The hemispherical reflectance of the five a-C:H films deposited on Al substrate at different bias voltages. **Figure 2.** The hemispherical reflectance of the graded a-C:H coating compared with the reflectance of the Al substrate. **Figure 3.** Absorption of the graded film in the whole solar spectrum. **Figure 4.** The transmittances of the single sublayers and of the whole absorber in the infrared region.

5. Conclusion

Only by varying the bias voltage during the PECVD deposition we prepared selective solar absorbers made of pure a-C:H without metal inclusions. As a result of our experiments we could optimize the film arrangement inside the multilayer structure. By decreasing the voltage from 2.5 kV to 0.5 kV we obtained five films with increasing bandgap width. The funnel-like shape of the bandgap of a-C:H is the main reason for the high absorption in the optical range and the good solar spectrum matching.
This layer arrangement has further advantages: the first a-C:H layer upon the aluminum substrate has a maximum number of sp²-bonds [8], hence best adhesion to Al substrate and the top layer is the hardest one. Therefore no passivation or protection covering is needed.

It is obvious that our further investigations should be aimed at increasing the transparency in the near infrared. The fabricated absorbers for thermal solar collectors manifest a very low reflectance in the optical range, but their near IR transparency should be increased in order to improve the optical selectivity.

Acknowledgments

The authors would like to acknowledge the financial support of Project NNP E-04-01 by the Bulgarian NCSR.

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