Optical properties and enhanced photothermal conversion efficiency of SiO_2/amorphous diamond-like carbon selective absorber films for a solar energy collector

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Abstract: - Solar energy could become the most attractive alternative energy source. In this study we test an attractive candidate material for solar energy collectors. It can be found that the higher the gas pressure is, the higher the sp^2/sp^3 area ratio, the greater the sputtering rate and the greater the optical absorption. The photothermal conversion efficiency of a SiO_2 coating on the amorphous diamond-like carbon (a-DLC) selective absorber films deposited on the Cr/mirror like Al substrate is 93.2% as the film thickness of a SiO_2 coating is 105 nm. The coatings also increase the protective properties for a longer service life. This makes the SiO_2 coated a-DLC film a promising candidate material for solar selective absorber films.

Key-Words: - selective absorber film, solar energy collector, amorphous carbon, silicon oxide, photothermal conversion efficiency

1. Introduction

Solar energy is non-polluting, inexhaustible and available in amounts several orders of magnitude greater than that needed for all present-day energy requirements world-wide. These factors make it possibly the most attractive alternative future energy source. It could for example, easily be utilized to a far greater extent for residential heating and industrial heat generation. Efficient systems will likely be in widespread use. One main component of these systems is the solar energy collector, which converts the incident solar radiation to heat and transfers it to a fluid circulating through the tubes in an absorber plate. For efficient photothermal conversion, the surface of solar absorber plate must have a high solar absorptance (α) and a low thermal emittance (ε) at the operational temperature. The ideal solar absorber plate surface should be spectrally selective, that is it should completely absorb the 0.3-2.4 μm wavelengths, and completely reflect the 2.4-20 μm wavelengths.

The diamond-like carbon (DLC) films have been widely used for many applications such as optics [1], [2], corrosion protection [3] and wear resistance [4], [5], because of the good properties they exhibit: low friction, wear-resistance, chemical inertness and advantageous optical characteristics. An amorphous DLC (a-DLC) films could be a good solar absorber film. But an a-DLC film is not stable because it deteriorates too rapidly at moderate temperatures in air. However a transparent ceramic film could function as a protective layer and as a layer for enhancing photothermal conversion efficiency, when deposited on the a-DLC selective absorber and SiO_2 could be a good material for this ceramic film.

In this study, we examine the optical and thermal properties of solar selective absorber films on the surface of mirror like Al substrates and extruded aluminum sheet substrates for use as heat energy collectors. The selective absorber films of SiO_2/a-DLC thin films are produced by rf reactive unbalanced magnetron sputtering technology at room temperature.

There are five main aspects discussed in the remainder of this paper:

1. the fabrication and material properties of the studied a-DLC film;

2. the optical properties and the photothermal conversion efficiency of the a-DLC selective absorber films for use in a solar energy collector;

3. improving the adhesion between a solar selective absorber film and a Al substrate;

4. the anti-reflective optical properties and the enhanced photothermal conversion efficiency of

SiO_2-coated a-DLC selective absorber films for solar energy collectors;

6. the thermal protective properties of SiO_2 films on a-DLC selective absorber films for lengthening the service time.

2. Experimental details

a-DLC films were deposited on the Si wafers, the Al extrusion substrates (which are with rough surface.) and the mirror like Al substrates using r.f. reactive unbalanced magnetron sputtering from a C target (99.999% purity) in an atmosphere of C_2H_6 and Ar at room temperature. A denser thin film was obtained because a higher ion density can be obtained with an unbalanced magnetron sputtering system than a balanced one [6]. The target-to-substrate distance was 15 cm. The substrates were rotated during the deposition process to yield uniform thin films. The substrates were cleaned in an ultrasonic bath by a series of processes: in trichlorethane for 50 min., deionized (D. I.) water for 10 min., acetone for 5 min., D. I. water for 10 min., ethanol for 5 min. and D. I. water for 10 min. The deposition chamber was surrounded by heating girdles. It was evacuated to a base pressure of less than 1.33×10^{-4} Pa using a cryo pump. Prior to deposition, the target was pre-sputtered for 30 min. at 1.60 Pa Ar pressure. The gas flow rate was accurately controlled by a mass flow meter. All carbon films were deposited according to the following parameters: pressures of 0.147, 0.293, 0.440, 0.600 and 0.800 Pa; an Ar/C_2H_6 flow rate ratio of 5; a substrate bias of -30 V; and a sputtering power of 1000 W. All SiO_2 films were deposited according to the following parameters: a pressure of 0.600 Pa; an Ar/O_2 flow rate ratio of 5; a substrate bias of -30 V; and a sputtering power of 1200 W.

The thickness of the DLC film was measured using an atomic force microscope (AFM) (Digital Instruments, D3100) operated in tapping mode with an etched silicon cantilever having a tip radius of 10 nm and an apex angle of 35°. The AFM was set on an optical table (IDE, ETC-10LM2), which acted as an active isolation system. The reflectance spectra in the 300-2400-nm wavelength range was measured by an optical spectrometer then averaged over ten measurements. The refractive index n and extinction coefficient k for the films can be obtained using the reflection (R) method in which the multiple reflection effects are taken into account using the measured R data. The reflectance spectrum of a-DLC films coated on the surface of the Al extrusion substrates was measured by an optical spectrometer with an integrating sphere. Raman spectroscopy is an essential tool in the carbon industry. Raman analysis was performed on a RENISHAW micro-Raman spectroscopy. The excitation wavelength of the Ar ion laser is 514.5nm (power output 2 mW). Service lifetime testing was performed by exposing the absorber coatings for 70 h at 250 °C. The adhesion between the films and the substrates was analyzed using the ASTM Crosshatch tape testing method.

3. Results and discussion

3.1 The fabrication and material properties of the studied a-DLC film for the solar selective absorber

A DLC film makes it a more suitable thin film material for application in the selective absorber in a solar energy collector. Therefore, a DLC film must be prepared. Except for the film deposited on the mirror like Al substrate at a pressure of 0.800 Pa, the adhesion of all the DLC films deposited on the Si wafer and the mirror like Al substrate is good.

The Raman spectra of the DLC films are dominated by two features: the graphite-peak (or sp^2 bond) at around 1550 cm^{-1} and the diamond-mode (or sp^3 bond) at around 1350 cm^{-1}. The Raman spectra of the films (Fig. 1) were deconvoluted using two Gaussian curves. A look at Fig. 1 shows that the type of the DLC film is slightly dependent on the gas pressure. The results are much like the results of the sputtered a-C reported by Prof. J. Robertson [7]. The higher the gas pressure is, the higher the sp^2/sp^3 area ratio and the more the peak wavenumber of the sp^2 bound. No any diffraction patterns are found when the DLC films were measured by low angle high power X-Ray. Therefore, the DLC films could be amorphous.

3.2 The optical properties and the photothermal conversion efficiency of a-DLC selective absorber films

The reflectance spectrums of the a-DLC films coated on the Si wafers were measured by an optical spectrometer as shown in Fig. 2. Except for the interference effect, the longer the wavelength is, the greater the reflectance. When the wavelength is longer, the refraction index is larger and the extinction coefficient is smaller. It can be found that the higher the gas pressure is, the greater the sputtering rate, and the greater the optical absorption.

The photothermal conversion efficiency (PTCE) is calculated by fitting the reflectance data to the spectral power density in the standard AM 1.5 spectrum

$$PTCE = \frac{\int_{0.2}^{2.5} \alpha(\lambda) \cdot SD(\lambda) d\lambda}{\int_{0.2}^{2.5} SD(\lambda) d\lambda} \text{ ,……… (1)}$$

$$\alpha(\lambda) = 1 - R(\lambda) \text{ ,…………………….(2)}$$

where $\alpha(\lambda)$, $R(\lambda)$ and $SD(\lambda)$ are the absorption coefficient, the reflectance and the spectral power density at the wavelength of λ, respectively.

The PTCE of the a-DLC selective absorber film deposited on the mirror like Al substrate at the 0.600 Pa pressure is 76.8% as shown in Fig. 3. The a-DLC film is not a good selective absorber film. Therefore, for enhancing film photothermal conversion efficiency, an anti-reflective optical coating is needed for a-DLC selective absorber films for solar energy collectors. An oxide film has more stable oxidation properties than an oxynitride or nitride film. Therefore, we select a SiO_2 film for the anti-reflectance coating material. But, after heat treatment, the adhesion of SiO_2/a-DLC films is not good as deposited on the mirror like Al substrate.

3.3 Improving the adhesion between a solar selective absorber film and a Al substrate

It is very important that SiO_2/a-DLC films adhere well to the Al substrate. An investigation, using adhesive tape and the ASTM Crosshatch tape testing method, was carried out on films. For improving the adhesion, there are two methods: with rough surface and with the interface layer [8]. After heat treatment and the ASTM Crosshatch tape test, the adhesion of SiO_2/a-DLC films is well as deposited on Al extrusion substrates with rough surface. SiO_2/a-DLC films are deposited on a Cr (5nm)/mirror like Al substrate. The Cr layer is the interface layer. After heat treatment and the ASTM Crosshatch tape test, the adhesion of SiO_2/a-DLC films also is well as deposited on a mirror like Al substrate.

3.4 The optical properties and the enhanced photothermal conversion efficiency of SiO_2 coating on a-DLC selective absorber films

From Eqs. (1) and (2), it is easy to find that the smaller the $R(\lambda)$, the greater the PTCE. After fabrication, the measured thickness of the SiO_2 coated on the a-DLC selective absorber film is 89 nm. The measured reflectance spectrum is also shown in Fig. 3. It is found that when the wavelength is greater than 350nm, the $R(\lambda)$ of the SiO_2 coating on the a-DLC film is lower than that of the a-DLC film. It forms a highly absorbent coating for the solar spectra and is also a highly IR-reflective material. The PTCE of the SiO_2 coating on the a-DLC selective absorber film is 91.5%. When the thickness of the SiO_2 films are 98 nm, the PTCE of the SiO_2 coating on the a-DLC selective absorber film are 92.8%. When the thickness of the SiO_2 coating increases, it modifies the wavelength range so as to increase the absorption red shift. When the thickness of the SiO_2 films coated on the a-DLC selective absorber film deposited on the Al extrusion substrates is measured to be 105 nm. The measured reflectance spectrum is shown in Fig. 4. The PTCE was 93.2%, which is optimized. And it is easy to find that the longer the wavelength, the higher the reflectance and then the smaller the thermal emittance for λ > 2000 nm. Therefore, its thermal emittance could be small.

3.5 The thermal protective properties of SiO_2 films for a-DLC selective absorber films

It is an important requirement for a solar energy collector that the solar selective absorber film have long-term thermal stability so as to ensure a long service lifetime. To test the service lifetime, the absorber coating was exposed in air in a heat-treating furnace for 70 h at 250˚C. The a-DLC absorber film disappeared after the heat-treatment, meaning that the a-DLC absorber film does not have sufficient long-term thermal stability. However the measured reflectance of a SiO_2 coated a-DLC selective absorber film did not change as also shown in Fig. 3. The PTCE after the heat treatment was 91.9% greater than before the heat treatment. The protective properties of the SiO_2 coated a-DLC selective absorber films deposited on the Al extrusion substrate or Cr/mirror like Al substrate are good enough to ensure a long service life.. Therefore, the SiO_2 coated a-DLC film is a good candidate material for a solar selective absorber.

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4. Conclusion

Following the oil crisis of the last few years, research and development of thermal solar collector systems has become a very important topic. The most important component of a thermal solar collector is the spectrally selective absorber surface. A DLC film makes it a more suitable thin film material for application in the selective absorber in a solar energy collector. Therefore, a DLC film must be prepared. The lower the gas pressure is, the lower the sp^3/sp^2 ratio. The higher the gas pressure is, the greater the sputtering rate, and the greater the optical absorption. The PTCE of the a-DLC selective absorber film deposited on the mirror like Al substrate at the 0.600 Pa pressure is 76.8% but the a-DLC absorber film does not have good long-term thermal stability. For improving the adhesion, two methods: with rough surface and with the interface layer are used. After heat treatment and the ASTM Crosshatch tape test, the SiO_2/a-DLC films still adhere well to the Al extrusion substrates and the Cr/mirror like Al substrate. The photothermal conversion efficiency and thermal stability can be enhanced by the deposition of an SiO_2 coating on an a-DLC film. The PTCE before and after heat treatment are 91.5% and 91.9%, respectively. The best PTCE was 93.2% when the thickness of an SiO_2 coating is 105nm. Its thermal emittance could be small. Therefore, the SiO_2 coating on a-DLC film could be a good candidate material for a solar selective absorber.

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Figure Captions

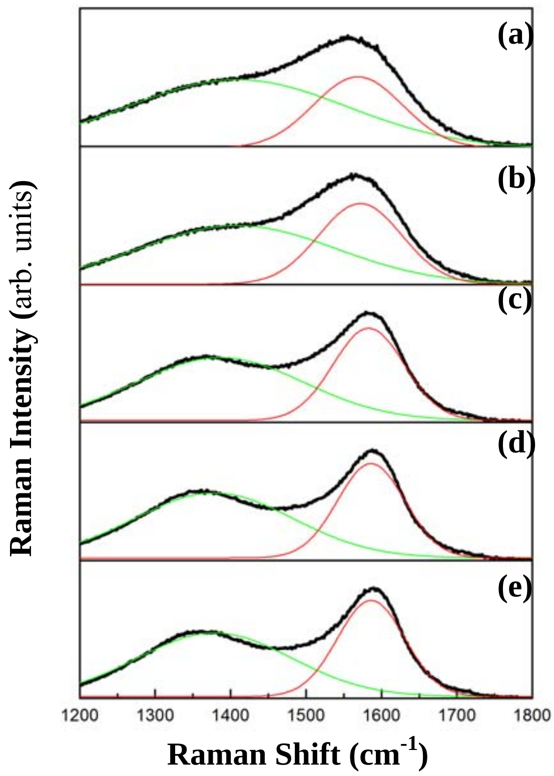
1. Raman spectra of DLC films deposited at the pressure of (a) 0.147, (b) 0.293, (c) 0.440, (d) 0.600 and (e) 0.800 Pa. The lower the gas pressure, the lower the sp^3/sp^2 ratio.

2. Reflectance spectra of a-DLC films deposited on the Si wafers at the pressure of (a) 0.147, (b) 0.293, (c) 0.440, (d) 0.600 and (e) 0.800 Pa.

3. Reflectance spectra of the: (a) a-DLC film; (b) SiO_2/a-DLC film before heat treatment; and (c) SiO_2/a-DLC film after heat treatment, and the spectral power density in the standard 1.5 spectrum.

4. Reflectance spectra of SiO_2/a-DLC film deposited on the substrate. The substrate is Cr (5nm)/mirror like Al. SiO_2 film thickness is 105 nm.

Fig. 1



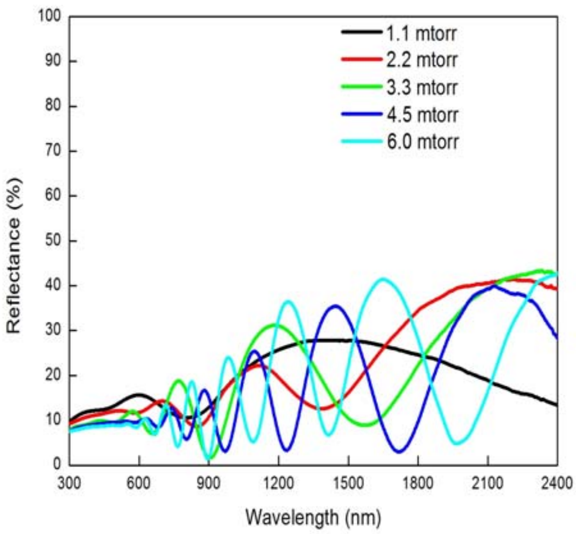

1.1 mtorr
2.2 mtorr
3.3 mtorr
4.5 mtorr
6.0 mtorr
Reflectance (%)
Wavelength (nm)

Fig. 2

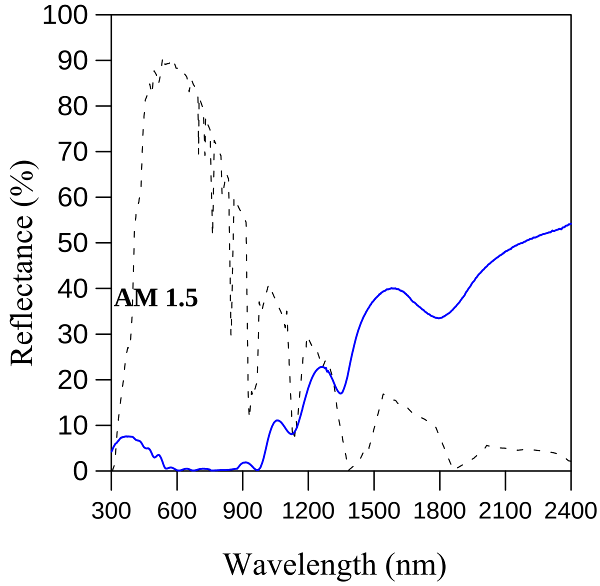
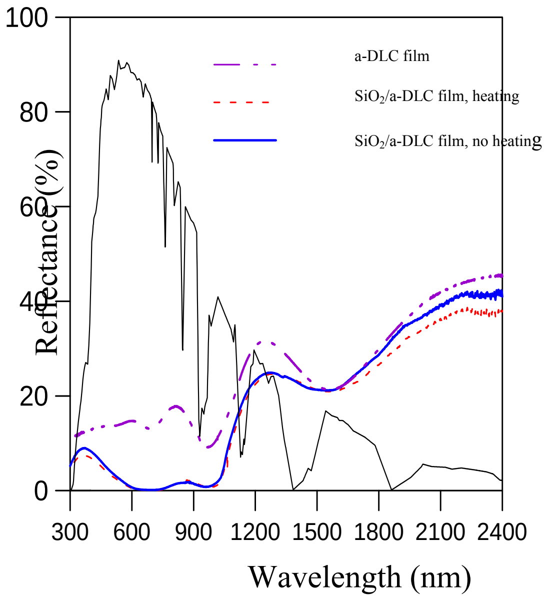

AM 1.5
Reflectance (%)
Wavelength (nm)

Fig. 4


a-DLC film
SiO2/a-DLC film, heating
SiO2/a-DLC film, no heating
Reflectance (%)
Wavelength (nm)