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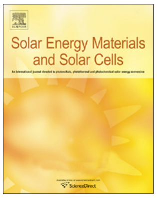

Hafnium carbide based solar absorber coatings with high spectral selectivity

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ABSTRACT

Single layer coatings of hafnium carbide were deposited on stainless steel, copper and silicon substrates by means of reactive sputtering. The deposition process was optimized for maximum solar absorptance by varying the process parameters. In the case of coated stainless steel substrates, we obtained a maximum solar absorptance of 0.925 along with a thermal emittance of 0.13. For coated copper substrates we obtained a maximum solar absorptance of 0.948 along with a thermal emittance of 0.03. Reflectance spectra of SS and Cu substrates coated at optimized parameters were measured in the wavelength range 250 nm to 20 µm. Detailed x-ray photoelectron spectroscopy (XPS) studies were carried out to investigate the chemical composition of the coatings. XPS analysis of coated samples showed that because of the tendency of HfC to oxidize, the coating had a surface consisting mostly of HfO_2 but the extent of oxidation reduced with depth and partially oxidized HfC was present on the subsurface layers of the coatings. Along with the absorbing nature of HfC and appropriate coating thickness, the high solar absorptance of the coating can be partially attributed to the presence of HfO_2 near the surface which acts similar to an antireflection layer. Assuming a two-layer model of the coating, an upper HfO_2 layer and a HfC layer underneath it, reflectance spectra of the coated samples were simulated using SCOUT software and compared to the experimentally obtained spectra. For all the samples, best fit values of coating thicknesses were in the range 120–130 nm.

1. Introduction

Electricity production is responsible for around one-quarter of the total greenhouse gas emission globally [1]. Concentrated solar power (CSP) systems are a vital cleaner alternative to fossil fuels based systems of electricity production. These systems are predicted to provide around 11% of the global electricity by the year 2050 [2]. A key component of CSP systems is the absorber surface which intercepts solar radiation. The efficiency of these systems is enhanced by application of a solar selective coating on the absorber surface [3].

Transition metal carbides and nitrides have been proposed as promising candidates for solar absorber coatings because of their inherent selectivity long ago [3]. Optical properties of these materials are different than pure metals because of the contribution to dielectric function from interband transitions of bound electrons. In metals a steep drop in reflectance is observed at the plasma frequency. Whereas, in case of transition metal carbides and nitrides this drop in reflectance is shifted towards lower frequencies because of the contribution from interband transitions [4]. This extends the high absorption frequency range in these materials which leads to higher solar absorption. Sputter deposited films of TiN, ZrN, ZrC, ZrC_xN_y and ZrO_xN_y have been reported to have solar absorption ranging from 0.80 to 0.93 [5].

Hafnium carbide (HfC) is one the most refractory binary compounds known. It has a melting point of 3928 °C, which is among the highest melting point for binary compounds [6]. Sayir [7] has reported the mechanical properties of a carbon fiber - HfC composite material, which has a potential to be used as a structural material for high-temperature aerospace applications. To make the composite, HfC was deposited on substrates made of graphite and carbon fiber cloth using CVD process. The fact that HfC can withstand high-temperature environment makes it more suitable to be used in solar absorber coatings. Structure and mechanical properties of HfC films deposited using other processes have also been reported by many researchers. Teghil et al. [8] have reported the hardness of HfC coating deposited by pulsed laser ablation. Shuo et al. [9] sputter deposited HfC films on Si substrates and observed how hardness, microstructure and tribological behavior change with a change in the carbon content of the film. Oxidation of hafnium carbide has also been studied thoroughly [10–12]. At an oxygen pressure of 1.3 kPa, oxidation of HfC begins at 430 °C. During the oxidation of HfC, a dense hafnium oxide layer with carbon dissolved in it (HfC_xO_y) is formed, which separates HfO_2 from HfC [10]. This layer acts as an effective diffusion barrier for oxygen. Sani et al. [13] have investigated

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the use of ZrC, TaC and HfC in concentrating solar power applications. They have reported solar absorptance (α) of 0.88 and thermal emittance (ε) of 0.55 for an HfC bulk sample prepared by hot pressing.

To the best of our knowledge, optical properties of hafnium carbide thin films in the context of solar selective coatings have not been reported yet. In the present work, we have sputter deposited HfC films on stainless steel (SS) and copper (Cu) substrates. The process was optimized to maximize solar absorption of the deposited film. Optical properties of the obtained coatings were investigated using different techniques. Detailed X-ray photoelectron spectroscopy (XPS) studies were carried out to analyze chemical composition of the coatings. The obtained coatings showed good solar absorption without applying any anti-reflection layer. With only one absorbing layer, the coatings had almost up to 95% solar absorptance in some samples. Solar selective coatings are usually made of more than one layers of different materials. The possibility of achieving very high solar absorptance with a single layer of one material can potentially make the process of manufacturing solar selective coatings much simpler.

2. Experimental details

Hafnium carbide coatings were deposited on SS and Cu substrates using a balanced reactive magnetron sputtering system. The SS substrate dimensions were: 33 mm × 33 mm × 2 mm and the Cu substrate dimensions were: 33 mm × 33 mm × 1.5 mm. The substrates were polished using alumina powder which had a particle size of 1 µm. After polishing, the substrates were cleaned by sonicating while dipped in isopropyl alcohol for 10 min. Before the deposition, pressure inside the chamber was brought down to 7.9×10^{-6} mbar using a turbomolecular pump. Before depositing the HfC layer, a thin titanium interlayer was sputter deposited on the substrate. This interlayer aids the adhesion of the HfC layer to the substrate. Inside the chamber, the substrates were kept 5 cm apart from the target. Hafnium and titanium targets used for the deposition were 99.9% pure and 75 mm in diameter. Argon (Ar) at a flow rate of 20 sccm was supplied to the chamber for deposition. A DC power supply was used for the titanium interlayer which maintained a constant supply of 150 W during the deposition. The interlayer was deposited for 30 s. For the HfC layer, acetylene (C_2H_2) was also supplied to the chamber along with Ar. C_2H_2 flow rate was varied from 3 to 5 sccm and the deposition time was varied from 1 min 15 s to 3 min 40 s. A pulsed DC power supply was used (frequency = 100 kHz, pulse width = 2796 ns) to maintain a constant supply of 78 W during the deposition of HfC.

Solar absorptance and thermal emittance values of the deposited coatings were measured using solar spectrum reflectometer (model SSR) and emissometer (model AE) of M/s. Devices and Services. The source of illumination in the solar spectrum reflectometer was a tungsten-halogen lamp. Reflectance spectra of the coatings in the UV, visible and NIR regions were measured using PerkinElmer Lambda 950 spectrophotometer. FTIR measurements were done in PerkinElmer Frontier™ MIR/FIR instrument consisting of an integrating sphere. An x-ray diffractometer (XRD, Bruker, D8 Advance) was used with a Cu K_α x-ray source to obtain x-ray diffraction patterns of the coating. The measurements were done in thin film mode with a glancing angle of 0.75° and at very slow scan speed (0.3°/min). A nanoprofilometer (Nanomap, Bruker) was used to measure the coating thickness.

To investigate the chemical composition of the coatings XPS was recorded with SPECS spectrometer using non-monochromatic Al K_α radiation (1486.6 eV) as an X-ray source operated at 150 W (12.5 kV and 12 mA). The binding energies reported here were referenced to C1s peak at 284.6 eV. All the spectra were obtained with a pass energy of 40 eV and step increment of 0.05 eV. Depth profile studies were carried out by successive sputter etching with focused Ar^+ ion beam using IQE12/38 ion gun for 5, 15, 30 and 50 min, respectively. After each sputter etching, all the spectra were recorded with same parameters used for as-deposited coating. CasaXPS program was employed for curve-fitting of C1s and Hf4f core level spectra into several components with Gaussian-Lorentzian peaks after Shirley background subtraction.

3. Results and discussion

3.1. Optimization of process parameters

HfC Coatings deposited directly on the substrates, without any interlayer, had poor adhesion to the substrate. Depositing the thin titanium (Ti) interlayer of 14 nm thickness before the HfC layer solved the adhesion issue. Introduction of Ti interlayer on SS substrate increased the absorptance to 0.477 from 0.361, whereas, the emittance remained almost unaffected ($\varepsilon_{SS} = 0.12$ and $\varepsilon_{Ti+SS} = 0.13$). The deposition process of the HfC layer was optimized for maximum solar absorptance by varying C_2H_2 flow rate, power supplied to the Hf target and deposition time. The explored ranges of the process parameters were: (a) Power (Hf target): 76–125 W, (b) Deposition time for HfC layer: 1 min 15 s–3 min 40 s and (c) C_2H_2 flow rate: 3–4 sccm. Maximum solar absorptance was obtained at a C_2H_2 flow rate of 4 sccm, 78 W of power supplied to the Hf target and deposition time of 1 min 40 s for the HfC layer. The chemical composition of the coating depends on the power supplied to the target and gas flow rates. A higher value of power supplied leads to a higher sputtering yield and a higher metal content in the coating, similarly, the carbon content in the coating depends on the acetylene flow rate. Changing the power supplied to the target or the gas flow rate changes the chemical composition of the coating and also its optical constants. As it will be discussed in the following sections, the reflectance spectra of the substrates coated with HfC contains a local minimum. The position of this local minimum in the reflectance spectrum depends on the coating thickness which depends on the deposition time. A change in coating thickness leads to a change in solar absorption because of a shift in the position of reflectance minimum. This is also accompanied by a change in color of the coating. Table 1 depicts the optimized process parameters used for deposition of the absorber coating as well as the absorptance and emittance values of the optimized coating deposited on SS (α = 0.925; ε = 0.13) and Cu (α = 0.948; ε = 0.03) substrates. The optimized coatings were dark blue in color which indicates high solar absorptance. The thickness of the Ti interlayer was around 14 nm and the thickness of the optimized coating was ~ 126 nm (Fig. 1).

3.2. Crystal structure of the coating

HfC exists in NaCl like cubic phase in which hafnium atoms form a face-centred cubic cell and carbon atoms are present in the interatomic spaces also forming a face centred cubic cell [6]. Fig. 2 shows the XRD pattern of hafnium carbide thick coating deposited for 30 min on a

Table 1
Optimized experimental parameters for HfC coating deposited on SS and Cu substrates.

Substrates	Polished SS and Cu
Target material	Ti and Hf
Target size	75 mm diameter × 6 mm thickness
Distance between substrate and target	0.052 m
Ultimate vacuum	$< 7.9 \times 10^{-6}$ mbar
Operational pressure	$\sim 5.8 \times 10^{-3}$ mbar
Argon flow rate	20 sccm
C_2H_2 flow rate	4.0 sccm
Substrate temperature	35 °C
Hf target power	78 W pulsed DC
Ti target power	150 W DC
Target cleaning	1 min
Deposition time for Ti interlayer	30 s
Deposition time for HfC layer	1 min 40 s
Absorptance and emittance	SS (α = 0.925; ε = 0.13) Cu (α = 0.948; ε = 0.03)