Solar Energy 173 (2018) 192–200

Contents lists available at ScienceDirect

Solar Energy

journal homepage: www.elsevier.com/locate/solener

Shifting of the absorption edge in $TiB_2/TiB(N)/Si_3N_4$ solar selective coating for enhanced photothermal conversion

Atasi Dan[a], Kamanio Chattopadhyay[b,c], Harish C. Barshilia[d,*], Bikramjit Basu[a,b,*]

[a] Materials Research Centre, Indian Institute of Science, Bangalore 560 012, India
[b] Interdisciplinary Centre for Energy Research, Indian Institute of Science, Bangalore 560 012, India
[c] Materials Engineering, Indian Institute of Science, Bangalore 560 012, India
[d] Nanomaterials Research Laboratory, Surface Engineering Division, CSIR-National Aerospace Laboratories, Bangalore 560 017, India

ARTICLE INFO

Keywords:
Spectrally selective absorber
Magnetron sputtering
Thin films
Spectroscopic ellipsometry

ABSTRACT

The concentrated solar power systems for solar energy applications demand the development of solar absorber coatings with high spectral selectivity. This is possible by careful compositional selection of absorber thin films with an aim to shift the optical absorption edge towards higher wavelength side. In this context, the present work aims at developing such a coating, based on $TiB_2/TiB(N)/Si_3N_4$ by tailoring magnetron sputtering parameters. This multilayer exhibits a high absorptance of 0.964 and a moderately low emittance of 0.18 at 82 °C. The attainment of excellent spectral selectivity has been explained in terms of systematic variation or gradient in refractive index and extinction co-efficient throughout the multilayer stack.

1. Introduction

The solar thermal power systems have a strong potential to emerge as a leading technology in contributing significantly to world's energy supply (Duffie and Beckman, 2013; Gauché et al., 2017; Thirugnanasambandam et al., 2010). These systems require solar collectors to convert significant amount of solar energy into thermal energy (Kalogirou et al., 2016). Solar collectors consist of spectrally selective solar absorber coatings, which should maximize the efficiency of the photothermal systems by absorbing maximum amount ($\alpha \geq 0.95$) of solar radiation with minimizing thermal heat loss ($\varepsilon \leq 0.05$) (Dan et al., 2017; Granqvist and Niklasson, 2018; Selvakumar and Barshilia, 2012). The selective performance of a material can be achieved by introducing a sharp discontinuity of the reflectance around absorption edge (Selvakumar et al., 2014). The tuning of optical properties in line with this specific requirement demands careful selection of materials in the absorber thin film.

The structures include intrinsic absorbers (Chen and Boström, 2016), semiconductor-metal tandems (Jeong et al., 2017), multilayer stacks (Dan et al., 2016a), cermets (Klochko et al., 2015), textured absorbers (Gupta et al., 2018), etc. In recent years, the design of several multilayer architectures ($WAlN/WAlON/Al_2O_3$ (Dan et al., 2016b, c), $ZrO_x/ZrC\text{-}ZrN/Zr$ (Usmani and Dixit, 2016), $TiAlN_x/TiAlN_y/Al_2O_3$ (Soum-Glaude et al., 2017), CrTiAlN/TiAlN/AlSiN (Valleti et al., 2014), $TiAlN/TiAlON/Si_3N_4$ (Barshilia et al., 2006), $CrAlN/CrAlON/Al_2O_3$ (Zou et al., 2015), $Al_2O_3(L)\text{-}WC/Al_2O_3(H)\text{-}WC/Al_2O_3$ (Gao et al., 2016), $MoSi_2\text{-}Si_3N_4/Si_3N_4/Al_2O_3$ (Rodríguez-Palomo et al., 2018)) are extensively investigated as these structures allow multiple reflections at the interfaces of different layers to enhance the absorption in solar wavelength range, while maintaining a low thermal emittance.

However, an extensive literature survey reveals that spectrally selective properties of TiB_2-based multilayer thin film have not yet been explored. The above-mentioned studies also indicate that various absorber thin films emerged over the years and it could be found that multilayer spectrally selective absorbers are very sensitive to the composition of individual layer. For capturing significant amount of solar radiation, the metallic property and refractive index of each layer should decrease from substrate to surface in a typical multilayer absorber. Considering the conductive property of TiB_2, it can be featured as the first layer of the selective coating. On the other hand, dielectric Si_3N_4 emerged as one of the most promising anti-reflecting layer, an essential part of optically selective films (Feng et al., 2015; Kim et al., 2013). Moreover, the incorporation of nitrogen may lower the refractive index of TiB(N) than TiB_2 and also lead to an intermediate property between conducting TiB_2 (high refractive index) and insulating Si_3N_4 (low refractive index).

Apart from material selection, the choice of processing strategy is equally important. Worldwide, advanced deposition technologies, such

* Corresponding authors at: Materials Research Centre, Indian Institute of Science, Bangalore 560 012, India (B. Basu). Nanomaterials Research Laboratory, Surface Engineering Division, CSIR-National Aerospace Laboratories, Bangalore 560 017, India (H.C. Barshilia).
E-mail addresses: harish@nal.res.in (H.C. Barshilia), bikram@iisc.ac.in (B. Basu).

https://doi.org/10.1016/j.solener.2018.07.002
Received 28 March 2018; Received in revised form 10 June 2018; Accepted 2 July 2018

Table 1
Sputtering conditions during TiB_2/TiB(N)/Si_3N_4 deposition.

Parameter	Condition
System	Balanced magnetron sputtering
Target	TiB_2 and Si
Power supply	Pulsed DC and RF
Substrate	Stainless steel (SS)
Substrate temperature	Room temperature
Target-substrate distance	5 cm
Base pressure	5×10^{-4} Pa
Sputtering gas	Ar
Reactive gas	N_2
Target power	Varying
Reactive gas flow rate	Varying
Deposition time	Varying

as, electrodeposition, chemical vapour deposition, sputtering, and allied techniques were utilized to fabricate such selective coatings using multiple material systems. For last two decades, the fabrication of spectrally selective absorbers using sputtering is appreciated from an industrial perspective. However, the deposition during sputtering is a complex process. In the present study, we have primarily varied target power, deposition time and gas flow rate to study their influence on the selective optical performance of thin film. The sputtering parameters for the present deposition process is listed in Table 1. Our main aim was to develop a multilayer thin film with a graded refractive index profile, which will exhibit enhanced absorption at a wider window of solar wavelength and reduced emittance in infrared range.

In the above backdrop, we have investigated the possibility of designing a novel TiB_2/TiB(N)/Si_3N_4–based graded absorber coating for photothermal systems. Attempts are made to explore deposition conditions for achieving spectral selectivity. The underlying physics of high absorption of solar radiation and low thermal emittance have also been discussed.

2. Experimental

2.1. Deposition of the coating

TiB_2/TiB(N)/Si_3N_4 films were deposited on stainless steel (SS) substrates (35 mm × 35 mm × 2 mm) by DC and RF magnetron sputtering of highly pure (> 99.99%) TiB_2 and Si targets (diameter = 0.076 m). Prior to deposition, the substrates were metallographically polished and chemically cleaned. The base pressure of the vacuum chamber was pumped down to 5.0×10^{-4} Pa. The vacuum system was equipped with a rotary and a turbomolecular pump. The gas flow rates inside the chamber were controlled by standard mass flow controllers. The TiB_2 layer was developed in Ar plasma, while deposition of TiB(N) and Si_3N_4 layers was performed in Ar + N_2 environment. The Ar gas flow rate was kept constant at 20 sccm for all layers. . All the layers were deposited at a substrate temperature of ∼40 °C. The structure of the coating has been presented in Fig. 1.

2.2. Characterization of the coating

The total hemispherical absorptance (α) and emittance (ε) of the coatings were measured using solar spectrum reflectometer (Model SSR) and emissometer (Model AE) of M/s. Devices and Services, the details of which can be found elsewhere (Selvakumar et al., 2010). The solar reflectometer was calibrated using air mass 2. The emittance was measured at 82 °C. It is important to mention that the emissometer is a special kind of instrument, which is usually operated to evaluate the emittance of solar absorber coatings developed for flat plate thermal collectors having maximum working temperature of 80–90 °C (Saleh and Mosa, 2014; Wallner et al., 2008). The absorptance and the emittance values were evaluated at four different positions. The averages of

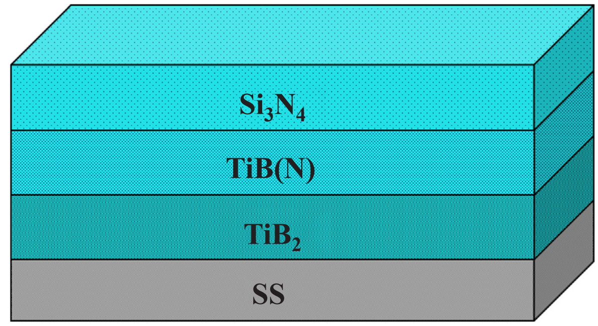

Fig. 1. Architecture of SS/TiB_2/TiB(N)/Si_3N_4 multilayer coating.

these values are reported in the preset paper. While offering a resolution up to 0.001, the solar spectrum reflectometer ensures the accuracy of measured absorptance values within ± 2%. The reproducibility of the emittance values measured by the emissometer is ± 0.01 emittance units.

The spectral response of the absorbers was recorded using UV–Vis–NIR spectrophotometer (PerkinElmer Lambda 950) in solar wavelength range (0.3–2.5 µm), with an illumination spot size of 5 mm × 5 mm. The spectrophotometer was equipped with a 150 mm integrating sphere to measure total reflectance. FTIR spectrometer (PerkinElmer Frontier) with an integrating sphere attachment was used to collect the reflectance spectra of the samples in the operating range of 2.5–25 µm. Transmission electron microscopy (FEI Tecnai T20 U-TWIN TEM) was utilized to determine thickness of the coating. Cross-sectional samples prepared using the UHR dual beam focused ion beam system (FIB, Helios NanoLab 600i, FEI). The coatings were characterized by a VASE spectroscopic ellipsometer (SE) M-2000 (JA Woolam Co, Inc, USA) in the spectral range of 200–1000 nm. The analysis of acquired data was performed using completeEASE software, supplied with the ellipsometer.

3. Results

The spectrally selective properties of thin films are strongly dependent on the deposition parameters. It has been observed that a slight change in the sputtering environment can significantly influence the optical properties. Hence, we have tried to find how the spectral performance of TiB_2/TiB(N)/Si_3N_4 thin film is controlled by deposition parameters. A brief discussion of the strategy that was followed will now be presented.

3.1. Reactive sputtering conditions

3.1.1. Influence of sputtering power and deposition time on TiB_2 layer

In the optimization process, the first aim was to achieve the highest possible absorptance of first layer, i.e., TiB_2. In order to reach the goal, the efforts were made in selecting the sputtering power of TiB_2 target. The low limit must maintain the DC glow discharge in the abnormal discharge regime, which is the operative domain for sputtering power. Fig. 2(a) represents the reflectance spectra of four different TiB_2 coatings, deposited at 50, 75, 100 and 150 W, respectively, keeping deposition time constant at 3 min. The coating deposited at 150 W exhibits high reflectance in the wavelength range of ∼400–2500 nm, which results in a low absorptance in solar spectrum. On the other hand, the coating fabricated at 75 W possess < 14% reflectance from 415 to 775 nm, i.e., the most intense part in the solar radiation, which gives rise to a high absorptance. The absorption edges shift to higher wavelength for the films prepared with different TiB_2 target powers. The absorption edge can be observed at ∼414, 566 and 840 nm for target powers of 50, 75 and 100 W, respectively (see Fig. 2(b)). The absorption edge disappears on further increase of target power to