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Spectrally selective response of ZrO_x/ZrC–ZrN/Zr absorber–reflector tandem structures on stainless steel and copper substrates for high temperature solar thermal applications

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ZrO_x/ZrC–ZrN/Zr absorber–reflector tandem layered structures were fabricated on stainless steel (SS) and copper (Cu) substrates using DC/RF magnetron sputtering system. ZrC–ZrN absorber layer was grown on the Zr infrared reflector, in conjunction with the top ZrO_x anti-reflecting layer. Absorbing properties, of ZrC–ZrN absorber layer, were optimized by varying nitrogen flow during deposition of this layer. The optimized ZrN fraction in a ZrC–ZrN layer showed additional plasmonic absorption in ~1.0–2.5 μm wavelength range, together with other intrinsic absorptions, providing enhanced solar absorption in 0.3–2.5 μm wavelength range. The detailed structural, micro-structural, surface and optical characterization showed the strong structure – solar thermal property correlation. We observed that absorber–reflector tandem structures, fabricated at ~12.5 sccm nitrogen flow rate, exhibit the best solar thermal response among investigated structures with absorptance $\alpha \sim 0.88$ and 0.85 and emittance $\varepsilon_{27^\circ C} \sim 0.04$ and 0.1 on stainless steel and copper substrates. Thermal studies showed high temperature stability at ~700 °C and 600 °C in vacuum for these solar selective coatings on SS and Cu substrates, whereas at or below 200 °C in the air. These studies suggest that ZrO_x/ZrC–ZrN/Zr absorber–reflector tandem structures may be a good choice for high temperature applications under vacuum/inert conditions.

1. Introduction

Solar energy has always been of interest to researchers and scientists due to its potential as a possible green energy source. This energy can be converted into thermal energy by concentrating onto a receiver. These receivers are designed to absorb the maximum solar radiation with minimum emittance over the desired spectral range. The desired maximum absorptance and minimum emittance may be achieved using spectrally selective coatings on absorber tubes with materials exhibiting high solar absorptivity over the entire solar spectrum (0.3–2.5 μm), and low emissivity in the infrared region (2.5–25 μm). An ideal spectrally selective surface exhibits absorptance "$\alpha \sim 1$" in the solar wavelength range and emittance "$\varepsilon \sim 0$" in the infrared wavelength region to convert the entire incident solar irradiation into thermal energy, without any probable thermal losses (Selvakumar and Barshilia, 2012; Duffie and Beckman, 1991). In practice, these spectrally selective coatings show deviations from these values. Thus, the design and deposition of materials in the thin film geometries become important to realize an enhanced solar thermal performance. The surface properties also have an impact on emissivity of these solar selective coatings, and thus, on receiver performance. In addition, these coatings should also withstand high operating temperatures and large thermal cycling, without any significant degradation in their performance (Barshilia, 2014). Numerous oxide and nitride based solar selective coatings are investigated for high temperature applications. The most common ones are W–AlN, SS–AlN, Mo–Al_2O_3, Mo–Si_3N_4, W–Al_2O_3, Ti/AlTiN/AlTiON/AlTiO, HfMoN/HfON/Al_2O_3, HfO_x/Mo/HfO_2, Al/$Ti_{0.5}Al_{0.5}N$/$Ti_{0.5}Al_{0.25}N$/AlN, etc. (Zhang and Shen, 2004; Zhang, 1998; Zhang et al., 1996; Céspedes et al., 2014; Antonaia et al., 2010; Selvakumar et al., 2012,2010; Du et al., 2013). Among them, titanium, zirconium, or hafnium metal carbides, oxides, and nitrides exhibit higher degree of spectral selectivity, showing promise for spectrally selective coatings. These carbides and nitrides absorber–reflector tandem structures such as TiN_x, ZrN_x, and ZrC_xN_y on silver (Ag) have been investigated as solar selective coatings for desirable solar absorptance and thermal emittance properties (Kennedy, 2002). The absorptance and emittance for such structures show large variation, 0.66–0.97 and 0.02–0.42 respectively. These data were calculated from the measured reflectance data on such thin film structures

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(Blickensderfer et al., 1977; Blickensderfer, 1977a, 1978). These structures exhibit good solar performance at room temperatures yet suffer from an agglomeration of silver metal infrared reflector film at ∼350 °C, in vacuum (Ihara et al., 1977). This agglomeration of silver layer degrades infrared reflecting surface properties, thus causing an enhancement in emissivity. Similarly, sputtered ZrC_xN_y selective absorbers on aluminum-coated oxidized stainless-steel are thermally stable up-to 600 °C (likely in a vacuum but not specified in reported work) (Ihara et al., 1977). Lazarov et al. has replaced Ag with Zr as an infrared reflector layer in sputtered ZrO_x/ZrC_x/Zr absorber–reflector tandem solar selective structures and observed high optical selectivity with α/ε (20 °C) = 0.90/0.05 and thermal stability on stainless-steel and quartz substrates up-to 600 °C and 800 °C in vacuum respectively (Lazarov and Mayer, 1997, 1998). The explored solar selective coatings exhibit enhanced thermal stability at elevated temperatures in the range of ∼550–580 °C in vacuum and at relatively lower temperatures in air (Antonaia et al., 2010; Esposito et al., 2009). There are still challenges associated with such solar selective coatings, especially for their long term thermal stability and cyclability. Considering such constraints, continuous efforts are ongoing to develop such coatings with enhanced spectral selectivity and thermal stability to realize the better power generation efficiencies. The present work aims (i) to develop zirconium carbonitride based solar selective coatings with enhanced solar performance and temperature stability and (ii) to understand the microscopic origin of absorptance and emittance in such systems. We investigated the effect of nitrogen flow rate on synthesis and physical properties of ZrC–ZrN absorber layers on stainless steel (SS) and copper (Cu) substrates for desired solar absorptivity and emissivity parameters. Structural and microstructural properties, including surface roughness, are investigated using X-ray diffraction (XRD), scanning electron microscope (SEM) and atomic force microscopic (AFM) measurements. UV–Vis-NIR and Fourier transform infrared (FTIR) spectrometers are employed to characterize the optical properties, such as absorptivity and emissivity of fabricated structures in the desired wavelength range. We investigated the thermal stability of these coatings at elevated temperatures in vacuum and air. The investigated thermal response suggests that fabricated structures are stable up to 700 °C and 600 °C in vacuum and up to 200 °C in the air on SS and Cu substrates, respectively. The solar absorptivity and emissivity of fabricated structures are nearly unaffected after heat treatment under vacuum and deteriorate in air, suggesting that investigated solar selective structures can be used for high temperature applications under vacuum/inert ambient.

2. Design of ZrO_x/ZrC–ZrN/Zr absorber–reflector tandem structures for solar selective coatings

We designed and investigated ZrO_x/ZrC–ZrN/Zr tandem absorber–reflector as a promising solar selective surface for high temperature applications. The schematic representation of ZrO_x/ZrC–ZrN/Zr absorber–reflector tandem structure is shown in Fig. 1, for stainless steel and copper substrates. The average thicknesses of the respective layers, estimated from the fabricated structures, are listed in Fig. 1. Here, a metallic Zr layer is used to achieve infrared reflection in the desired wavelength range, on SS and Cu substrates against the conventional infrared reflecting layers such as silver and aluminum, where stability is limited upto ∼350 °C, even in a vacuum because of their agglomeration at elevated temperatures (Ihara et al., 1977). Against these conventional infrared reflectors, Zr metal reflector provides high infrared reflectivity with thermal stability against high temperature because of it's refractory nature (Zhang et al., 2003). In conjunction with the infrared reflector layer, the absorber layer is also critical and needs to be optimized for the maximum absorption of incident solar radiation. ZrC–ZrN absorber layers are investigated and optimized by controlling the free electron density in the ZrC–ZrN absorber layer. This can be achieved by manipulating the stoichiometry and nitrogen concentration in ZrC–ZrN absorber layers. The enhanced electron density in ZrC–ZrN spectrally selective absorber layers will introduce plasmonic absorption in the long wavelength region of solar spectrum. In conjunction with intrinsic absorption, this additional plasmonic absorption, in ZrC–ZrN absorber layers, will enhance the total absorption of incident solar radiation over an extended wavelength range (Seraphine, 1979; Kittel, 1995). We utilized these concepts to optimize the optical properties of ZrC–ZrN absorber layers to achieve the maximum spectral selectivity and thus, the enhanced solar absorption, by varying nitrogen concentration. Antireflection structures are used to minimize the back reflection into the ambient and any microstructural damages to the absorber layer directly. In this work, ZrO_x antireflecting layer was fabricated on ZrC–ZrN absorber layer, as explained in Fig. 1. ZrO_x antireflection layer not only reduces the back reflection, but also enhances the thermal and environmental resistivity of fabricated solar selective structures. We observed that ZrO_x/ZrC–ZrN/Zr absorber–reflector tandem layered structures exhibit absorptance 0.81–0.88 and emittance ∼0.04 on SS substrates, whereas the same on Cu Substrate are 0.80–0.90 and 0.1 respectively. The detailed synthesis process and intensive characterization of these designed solar selective coatings are discussed in the following sections.

3. Experiment details

Spectrally selective absorber–reflector ZrO_x/ZrC–ZrN/Zr tandem structures were prepared on 304 SS (dimension: $35 \times 25 \times 1$ mm^3) and Cu (dimension: $35 \times 25 \times 0.6$ mm^3) substrates using DC and RF magnetron sputtering systems. These substrates were metallographically polished with 2000 grade silicon carbide (SiC) abrasive paper to remove the surface defects such as oxide layers and to reduce the surface roughness. The polished substrates were then chemically cleaned for 10 min in acetone and alcohol using ultrasonic agitator to remove the grease and other impurities such as dust and residual surface debris during abrasive polishing. Finally substrates were rinsed with deionized water and dried in air. Cleaned substrates were mounted on six inch diameter substrate holder in a sputtering chamber for deposition of the proposed layered structures. High purity Zr (99.8%) and ZrC (99.9%) targets (diameter: 101.6 mm; thickness: 6.35 mm) were integrated on magnetron sources for sputtering of thin film structures. After mounting sputtering targets and substrates, the chamber was evacuated down to the base pressure ∼5.0–6.0 × 10^{-6} mbar and targets were pre-sputtered for ∼15 min to remove any surface contaminations, prior to the thin film fabrication process. The deposition of thin film structures was carried out at a constant working pressure ∼2.0–2.2 × 10^{-2} mbar using respective gas environment. The Zr infrared reflecting layer was fabricated using DC magnetron sputtering at 110 W power and 50 sccm argon flow rate to maintain the constant working pressure (∼2.0 × 10^{-2} mbar). The substrate temperature was maintained at 350 °C and deposition was carried out for 2 h. We observed that the optimized synthesis process for Zr metal resulted into ∼200 nm and ∼650 nm thick layers on SS and Cu substrates under identical growth conditions. ZrC–ZrN absorber layers were then, grown on a Zr metal layer, using reactive RF magnetron sputtering of ZrC target at 200 W power in the presence of Ar and N_2 working gases environment. ZrC–ZrN thin layers were deposited at 80 °C temperature for 3 h by varying the N_2 ratio in the working gas environment. The detailed growth conditions for ZrC–ZrN absorbing layer are listed in Table 1