Colored selective absorber coating with excellent durability

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Abstract

The colored solar-thermal collectors can provide advantages of architectural integration over energy performance. The colour appearance of the solar-thermal collectors can be achieved by increasing the number of layers. W/WAlN/WAlON/Al_2O_3 coating, fabricated by DC and RF magnetron sputtering showed a high solar absorptance of 0.948 and the low thermal emittance of 0.08 with a sky blue color appearance. The tandem absorber exhibited excellent long-term thermal stability at 500 °C in air for 100 hrs. The absorber deposited on SS substrates showed high solar selectivity (α/ε) of 0.918/0.11**,** even after heat treatment in air up to 500°C for 100 hrs. The selective performance of the coating can be stable more than 25 years. The humidity test confirms the significant moisture resistant of the coating. In summary, the new W/WAlN/WAlON/Al_2O_3 –based coating with its colourful appearance is appropriate to be used in solar thermal collectors.

Key words: Solar-thermal collectors, colored coatings, spectral selectivity, optical properties, thermal stability

1. Introduction

The solar energy is the most popular alternative source of energy to supply world's expanding needs of energy without environmental detriment. The solar-thermal power systems can efficiently transform the solar energy to heat or electricity. The flat plate collectors are most widely used solar thermal power systems for residential or commercial water heating [1]. Spectrally selective absorbers are very important in solar water heaters to improve the efficiency of the solar-thermal systems. The desired properties of the spectrally selective absorbers are high absorptance in the solar spectrum range (0.25 – 2.5 μm) and less emittance in the infrared region (2.5 – 25 μm) [2]. The absorptance is an optical characteristics which depends on the intrinsic property of the materials and the structure of thin film of the selective coatings whereas low thermal emittance is dependent on the metallic substrates. The flat plate collectors are usually prepared black in colour to achieve highest absorption of solar energy. In order to improve the aesthetic appearance of building roofs and facades, it is important to deposit the colourful solar selective coating on the flat plate collectors keeping high performance at the same time [3]. These coating should possess high selective performance in an elevated temperature. The spectrally selective coloured paints are one of the well-known approaches to fabricate the colored solar selective absorbers coatings. The only thing that limits the use of spectrally selective coloured paints is the high emittance. The thermal emittance of the paint coatings are > 20% due to high thickness (> 1μm) [4]. There is a newer approach to deposit the solar selective absorber coating in which the metallic property of the layers decreases from bottom to top. These selective coatings consist of four layers from substrate to substrate (1) an infrared metallic reflector, (2) an absorber layer with higher metallic content, (3) a semi-transparent layer with lower metallic content and (4) a dielectric on top as an anti-reflection layer [5]. Such a colored tandem absorber with high absorptance and low thermal emittance can be used in the collectors.

In our previous work, we have deposited W/WAlN/WAlON/Al_2O_3-based solar selective coating by DC and RF magnetron sputtering. The W layer is pure metallic whereas the Al_2O_3 layer is dielectric in nature. The metallic property of WAlN and WAlON was tailored by varying the amount of O_2/N_2 in the film such that WAlON has less metallic character than WAlN. The coating exhibited a high absorptance of 0.948 and a low thermal emittance of 0.08. In addition, we have investigated the short-term thermal stability of the coating from 300 - 550 °C in air for 2 hrs. The coating showed very high thermal stability up to 500 °C in air for 2 hrs Long term thermal stability is a very critical issue for photo thermal applications. The coating exhibited excellent thermal stability upto 350 °C in air for 550 hrs. The details of the work can be found elsewhere [6, 7].

In the present work, we report the role of individual layer with appropriate properties to produce a color appearance of the coating. The absorptance, emittance and associated colorimetric data of these coatings are discussed. In addition, the long-term (150 hrs) high temperature stability of the coating at 500 °C in air has been investigated. The colour appearance of the coating after the prolonged heat treatment has also been studied. In order to evaluate the moisture resistance of the coating, humidity test has been carried out for 50 hrs at 40 °C condensation.

2. Experimental details

The W/WAlN/WAlON/Al_2O_3 has been deposited by DC/RF magnetron sputtering using W, Al and Al_2O_3 targets with a purity of 99.99%. The substrates were polished mechanically for a longer time to obtain a very less roughness (3.23 nm). The polishing of the substrate is very crucial for fabrication of solar selective absorber coating as the emissivity of the coating depends on the substrate roughness. The substrates were cleaned with detergent and flushed with de-iodized water. Finally these were ultrasonicated for 15 mins in absolute ethanol, acetone separately. Before starting the deposition, the sputtering chamber was

pumped down to a base pressure of 8.5×10^{-6} mbar by a rotary pump backed by turbo-molecular pump. The deposition of W layer was performed in Ar atmosphere. The W and Al targets run simultaneously in Ar, N_2 and O_2 environment to deposit WAlN and WAlON layers. The Al_2O_3 layer has been deposited using Al_2O_3 target in Ar + O_2 environment. The design of the coating has been presented in Fig. 1.

2.1. Optical characterization

The absorptance (α) of the coating can be defined by the ratio of the amount of energy absorbed by the coating to the total incident radiation while the emittance (ε) weighted fraction between the emitted radiation from the sample and the perfect blackbody, and both can be determined in terms of the reflectance ($R(\lambda)$) using the following equations [8]:

$$\alpha = \frac{\int_{0.3}^{2.5}[1-R(\lambda)]I_S(\lambda)d\lambda}{\int_{0.3}^{2.5} I_S(\lambda)d\lambda} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$\varepsilon = \frac{\int_{2.5}^{25}[1-R(\lambda)]I_b(\lambda,t)d\lambda}{\int_{2.5}^{25} I_b(\lambda,t)d\lambda} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Where λ is the wavelength, $R(\lambda)$ is the reflectance at λ, $Is(\lambda)$ is the solar spectral radiation at and $I_b(\lambda,t)$ is the black body spectral radiation, t = 80 °C is used for the normal temperature solar–thermal application. The finite integral limit has been considered in the range of 0.25 to 2.5 μm and 2.5 to 25 μm for solar radiation spectrum and infrared radiation spectrum, respectively.

The total hemispherical absorptance and total hemispherical emittance of the tandem absorber were measured using solar spectrum reflectometer and emissometer (M/s. Devices and Services). The absorptance of the coatings was measured at room temperature. The coating was illuminated by a tungsten-halogen lamp. The reflected rays from the samples were detected at an angle of reflection of 20° using four filtered detectors. The solar spectrum measurement was achieved by summing the output from these four detectors in appropriate

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proportion. The emissometer has been used to measure the total hemispherical emittance of absorber coatings used for flat plate solar thermal collector. The maximum working temperature of the collector is 82 °C. The instrument was calibrated using standard samples. The absorptance and the emittance values were measured at four different positions and the average values of these measurements has been considered. The optical properties of the coating has been characterized by UV-Vis-NIR spectrophotometer (Perkin Elmer) from 300 – 2500 nm in near normal incident angle. BaSO$_4$ was used as reference sample to measure the diffuse reflectance. Basically this instrument is divided into two spectral ranges from 0.25 to 0.8 μm and 0.8 to 2.5 μm with the source of deuterium and tungsten lamps. The colour appearance of the heat treated samples were also studied by the color software.

To investigate the long-term thermal stability of the coating, the samples were subjected to keep at 500 °C in air for 150 hours inside a muffle furnace. The temperature of the coating was increased at a rate of 3 °C/min. The structural change of the annealed coating has been evaluated using XRD. To conduct the humidity test, the samples were kept at 40 °C under condensation for 50 hrs. The optical properties of the samples after annealing and humidity test were also examined by UV-Vis-NIR spectrometer.

2.2. Color version:

The colours of the samples are numerically specified in a plane described by a set of tristimulus values X, Y, Z in CIE chromaticity diagram. The X, Y and Z values are calculated from three similar integration of the spectral power distribution of light P (λ) emitted from a coloured object, using the following equations,

$$X = \int P(\lambda)x(\lambda)d\lambda \qquad \text{...} \quad (3)$$

$$Y = \int P(\lambda)y(\lambda)d\lambda \qquad \text{...} \quad (4)$$

$$Z = \int P(\lambda)z(\lambda)d\lambda \qquad \text{...} \quad (5)$$

Where λ is the wavelength. x (λ), y(λ) and z(λ) are the set of CIE-1931 standard spectrum tristimulus values. The P (λ) can be represented as a R(λ), measured from the reflectance spectra for a neutral light source.

$$P(\lambda) = R(\lambda)$$ ……………………………………………………… (6)

The colour coordinates x, y and z can therefore be calculated by the following equations,

$$x = \frac{X}{X+Y+Z}$$ ……………………………………………………… (7)

$$y = \frac{Y}{X+Y+Z}$$ ……...……………………………………………… (8)

$$z = 1 - (x + y)$$ ……………………………………………………… (9)

The colours can be determined by combing a given set of three primary colours, such as red, blue and green. Then, any colour can be provided in the three-point gamut in the chromaticity diagram [9].

3. Results and Discussions:

Essentially, the performance of a selective coating is determined by two parameters such as absorptance and emittance. The important aspect of the present work is the color tuning of the solar selective absorber coating during the deposition of consecutive layers. It is desirable to obtain a color appearance of the coating for photo-thermal applications keeping high selective properties. In practice, it is very challenging to satisfy both the conditions simultaneously. We have successfully prepared a colourful selective coating of WAlN/WAlON/Al$_2$O$_3$ with a very high absorptance of 0.948 and low emittance of 0.08. The color appearance of the selective coating can be analysed based on the reflectance spectra of the coatings in visible range, which are shown in Fig. 2. The reflectance spectra in the visible wavelength is influenced by the absorption of light in the multilayer coating due to the interband electronic transitions. The high absorptance of the multi-layer stack can also be

explained by the interference phenomenon between different layers in the coating. Due to the destructive interference, two interfering waves are trapped inside the multilayer which enriches the absorptance. The absorptance and emittance of pure stainless steel substrate is 0.387 and 0.12. The deposition of the successive layers on SS such as W, WAlN, WAlON, Al_2O_3 boost the absorptance to 0.948. WAlN layer increased the absorptance of the coating to 0.753. The deposition of WAlON layer enhanced the absorptance of the coating to 0.902 further. Finally the absorptance reaches a value of 0.948 after deposition of Al_2O_3, as an anti-reflection layer. The reflectance spectra of the individual layer also is in good agreement with the absorptance value of $W/WAlN/WAlON/Al_2O_3$. The Fig. 2 indicates that the deposition of subsequent layers decreases the reflectance of the coating. The wider minima in the reflectance spectra of $W/WAlN/WAlON/Al_2O_3$ –based coating at 870 to 1345 nm represents the destructive interference which helps to exhibit highest maximum for the multilayer absorber. The detail explanation of the absorptance mechanism of $W/WAlN/WAlON/Al_2O_3$ can be found elsewhere [7]. The thermal emittance is determined mainly by the W layer. After deposition of W layer, the thermal emittance is maintained at 0.08 for all other layers.

Reflectance of the multilayer coating in the solar spectrum should be less for high absorptance, but it is also necessary to enhance the reflection in the visible wavelength range i.e. 380 − 780 nm to ensure the color appearance of the selective absorber. Therefore, we need to inevitably compromise the absorptance value to achieve a colourful coating. A number of studies have been reported explaining the effect of different parameters such as thickness, rate of gas flow, anti-reflection layer on the color of a selective coating [3, 9, 10]. In the present investigation, we have studied how number of layers has been optimized so that the sample exhibit a color in the visible spectral region. We have tuned the no of layers in such a way so that we can prepare a coating of sky blue in color. The reflectance spectra of the individual layer also suggests us that the colour of the tandem absorber coatings are

highly sensitive to the no of layers. For the W layer (Fig. 2a), only one interference minimum was observed, which is located at about 465 nm, and no peaks were found in the visible wavelength range. The surface appears grey because of the 57% reflectance in the visible wavelength range. When the WAlN layer was incorporated on top of W surface, no change in the number of interference minimum has been observed. However (Fig. 2b) a shift of the interference minimum towards the higher wavelength side occurs. The interference mimimum for W/WAlN has shifted to 1258 nm with a reflectance of 20%. The colour of the W/WAlN sample is also grey as no interference peak is present in the visible wavelength range. After deposition of WAlON layer, a sudden change has been observed in the reflectance spectra of the coating in Fig. 2c. Two interference minima at 360 and 1293 nm have been found in the solar wavelength range. The colour of the sample become slightly yellowish. The reason of this colour change can be attributed to the fact that the reflectance of the coating in visible range is almost < 10% for W/WAlN/WAlON sample. In addition, the WAlON has extended the absorption of the coating up to 1293 nm by decreasing the reflectance. With the deposition of Al_2O_3 layer, an interference maximum has been observed at 485 nm and this results the bluish appearance of the coating (Fig. 2d). The reflectance at the interference maximum is about 17%. The antireflection dielectric layer helps to decrease the reflectance all over the solar spectrum except an interference maximum in the visible wavelength range i.e. at 485 nm. Finally, a peak in the visible region has been achieved by increasing the number of layers. The thickness of the entire coating is 160 nm where WAlN, WAlON, Al_2O_3 layers have a thickness of ~ 87, 50, 23 nm [7].

In order to understand the color change of SS/W/WAlN/WAlON/Al_2O_3, the colors of the layer-added coatings are shown in the CIE chromaticity diagram (Fig. 3.) and table 1. The point, located at x = y = 0.33 is known as neutral point as the reflectance in the visible wavelength range has equal value for that point. The colour at the location is white, black or

grey. The location of the W and W/WAlN sample is very close to the neutral point as no interference peak has been observed in the visible range for these coatings. After deposition of WAlON layer, the sample colour turns remarkably different. The colour of the coating turned to yellowish. The last layer of this design is more sensitive than other layers in color appearance. The Al_2O_3 layer changed the colour of the coating entirely from yellowish to sky blue. The dominating interference peak at 485 nm in the visible region gives such strong color appearance.

The W/WAlN/WAlON/Al_2O_3 coating not only exhibited the color appearance, but also an excellent long- term thermal stability at 500 °C in air. The absorptance and the emittance of the as-deposited coating was 0.948 and 0.08, respectively. After heat treatment at 500 °C for 150 hrs, the absorptance and the emittance changed slightly to 0.912 and 0.11 ($\Delta\alpha = 0.036$; $\Delta\varepsilon = 0.03$), respectively. The variation of the absorptance and emittance value with respect to annealing time has been presented in Fig 4a. According to international Energy Agency, the Performance Criterion (PC) of a flat plate collector can be expressed in terms of a change in the absorptance ($\Delta\alpha$) and emittance ($\Delta\varepsilon$) values by the following relation [4]:

$$PC = -\Delta\alpha + 0.25\Delta\varepsilon \leq 0.05$$ …………………………………………………………… (10)

This relationship indicates the average life time of the flat plate collector for at least 25 years with a decrease in annual solar fraction 5%. In the present case, the performance criteria value is 0.043, which does not exceed 0.05. Therefore, it can be stated that the service life time of W/WAlN/WAlON/Al_2O_3- based solar thermal collector can exceed 25 years.

The reflectance spectra of the as-deposited and heat treated coating for 20, 60, 80 and 100 and 150 hrs has at 500 °C in air have been presented in Fig. 4b. A small change has been observed in the reflectance spectra of the heat treated coating with respect to as-deposited coating. The negligible change in the reflectance spectra is also evident from the absorptance

value obtained from the reflectometer. To investigate the high temperature annealing effect on the composition of the coating, we have studied the XRD spectra of the as-deposited and heat treated coating (see Fig. 5.) and we have also compared the spectra with our previous work where the coatings were annealed at 350 °C for 550 hrs [6]. The as-deposited coating shows a high intensity and a low intensity peaks at interplanar spacings of 2.238 Å and 1.582 Å respectively, corresponding to the crystallographic plane (110) and (200) of tungsten. Another peak at an interplanar spacing of 2.520 Å can be attributed to crystallographic plane (111) of cubic AlN. The heat treated coating shows an additional peak which can be attributed to the (110) plane of WO_3 with an interplanar spacing of 3.728 Å. The partial oxidation of W causes the formation of WO_3.

There are several reasons to explain the high temperature stability of the coating The Al_2O_3 with high thermal and chemical stability act as the protection layer of the underneath coating. In addition, the W as diffusion layer restricts the diffusion of the Fe, Cr atoms from stainless steel substrates towards the coating. Moreover the component of the coatings, such as WN, AlN, AlON are very stable which helps to protect the coating from degradation [11, 12]. The XRD data confirms the formation of WO_3 during heat treatment of the coating at high temperature. It has been reported that the oxide layer has better resistance to prevent the oxygen diffusion than oxide and oxynitride layers [13]. Therefore, the formation of WO_3 along with the presence of Al_2O_3 on top layer protect the underlying layers from further oxidation. The nano-crystalline and amorphous nature of the layers without grain boundary also prevent the delamination of the coatings.

In addition, interface of the four layers of the coating prevents the formation of any pinholes or cracks inside the coating. Therefore, the diffusion of the unwanted atoms from air of stainless steel substrate has been blocked [14]. The CIE points in Fig. 6 of all the heat-treated coatings overlap with the point corresponds to as-deposited coating. Therefore, it can

be concluded that the color of the absorber coating has not been changed even after long-heat treatment.

The humidity test on the coatings have not showed any adverse effect on the optical properties of the coatings. Fig. 7. represents the reflectance spectra of the coating before and after humidity test. A small change has been observed in the reflectance spectra of the coating after humidity test. Therefore it can be concluded that the humid environment has not significantly affected the selective property of the coating which confirms the excellent moisture resistance property of the environmentally stable coating.

4. Conclusions:

In an effort to develop a colored flat plated collector, $W/WAlN/WAlON/Al_2O_3$ absorber coating was developed by DC and RF sputtering on stainless steel substrates. The effect of each layer on changing the color of the coating has been discussed. The coating showed outstanding thermal stability at 500 °C in air for 100 hrs. Long-term thermal stability tests demonstrated that the predicted service lifetime of the coatings is more than 25 years. The color of the absorber coating does not change after long-term annealing. The humidity test on the coating ascertain the extreme suitability of the coating for practical applications. Taken together, $W/WAlN/WAlON/Al_2O_3$ coating shows high aesthetic compatibility, high temperature stability and moisture resistance as solar thermal collectors for building integrations.

Table 1

Color co-ordinates of successive layers

| Layers	X	Y	Color appearance
W	0.33	0.33	Grey
W/WAlN	0.32	0.32	Grey
W/WAlN/WAlON	0.46	0.41	Yellowish
W/WAlN/WAlON/Al$_2$O$_3$	0.30	0.34	Sky blue

List of figures

**Fig. 1.** Schematic of the design of W/WAlN/WAlON/Al$_2$O$_3$-based solar selective absorber coating

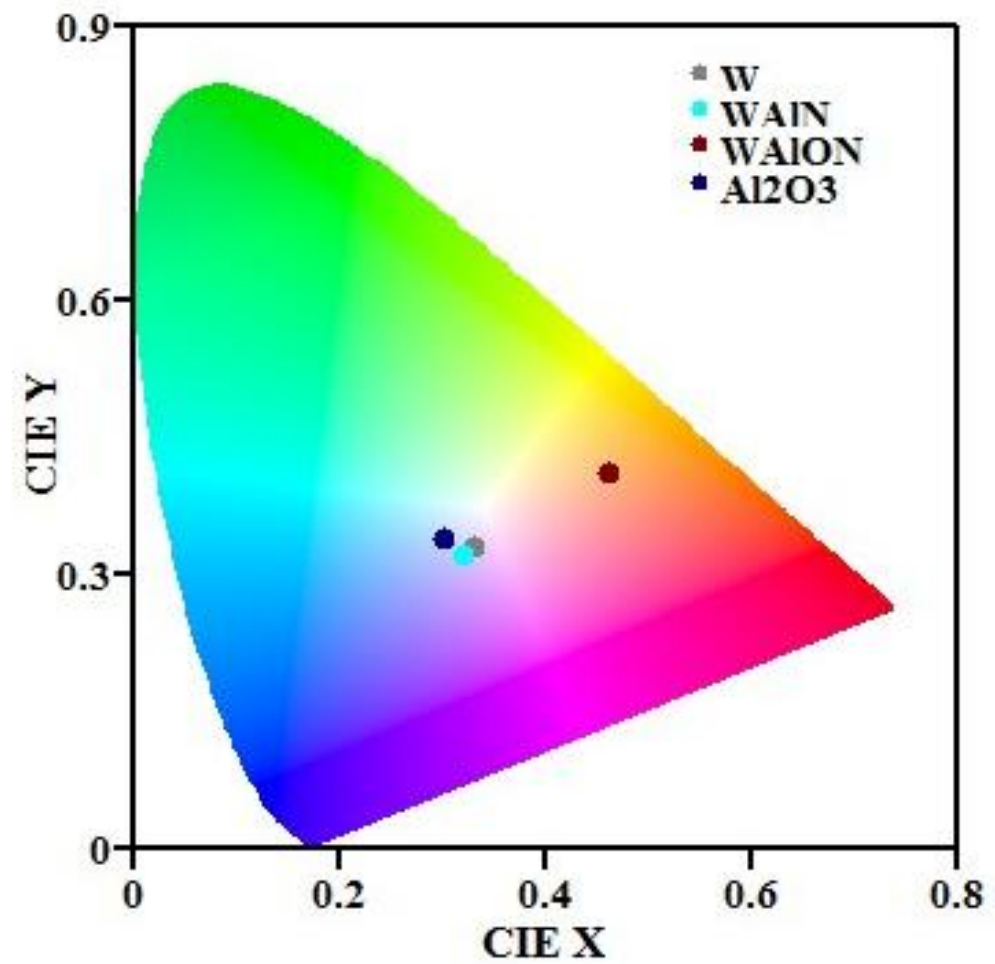**Fig. 2.** Reflectance spectra of a) W; b) W/WAlN; c) W/WAlN/WAlON; d) W/WAlN/WAlON/Al$_2$O$_3$ layer

Fig. 3. Chromaticity diagram layer-added absorbing coatings

Fig. 4. a) Variation of absorptance and emittance value with respect to annealing duration;

b) Reflectance spectra of the as-deposited and heat treated coating at 500 °C in air for different time

Fig. 5. XRD spectra of as-deposited and heat treated coatings

Fig. 6. Chromaticity diagram of as-prepared and heat-treated absorbing coatings

Fig. 7. Reflectance spectra of the coating before and after humidity test

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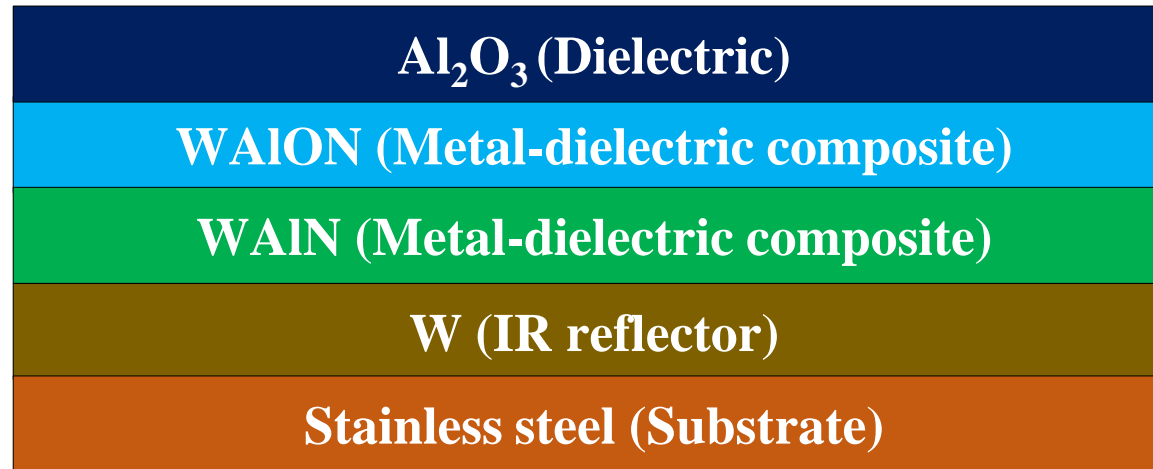
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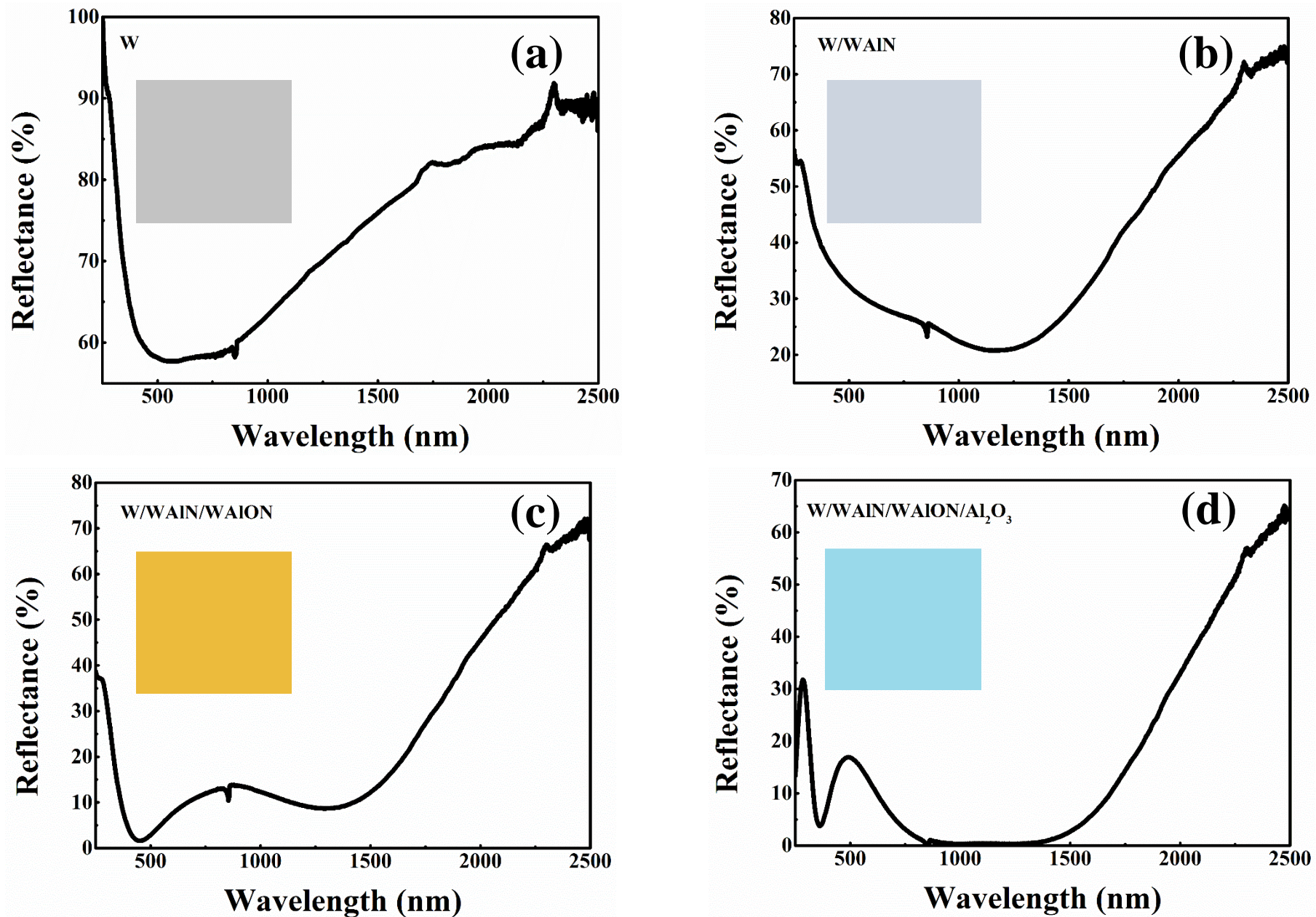
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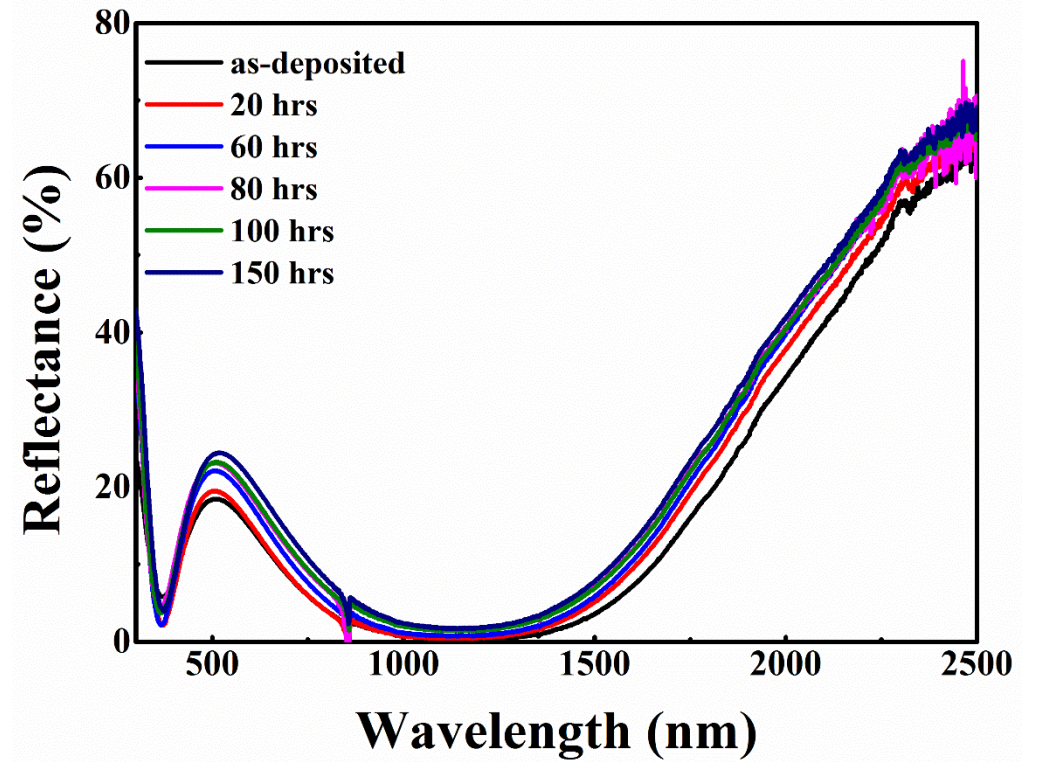
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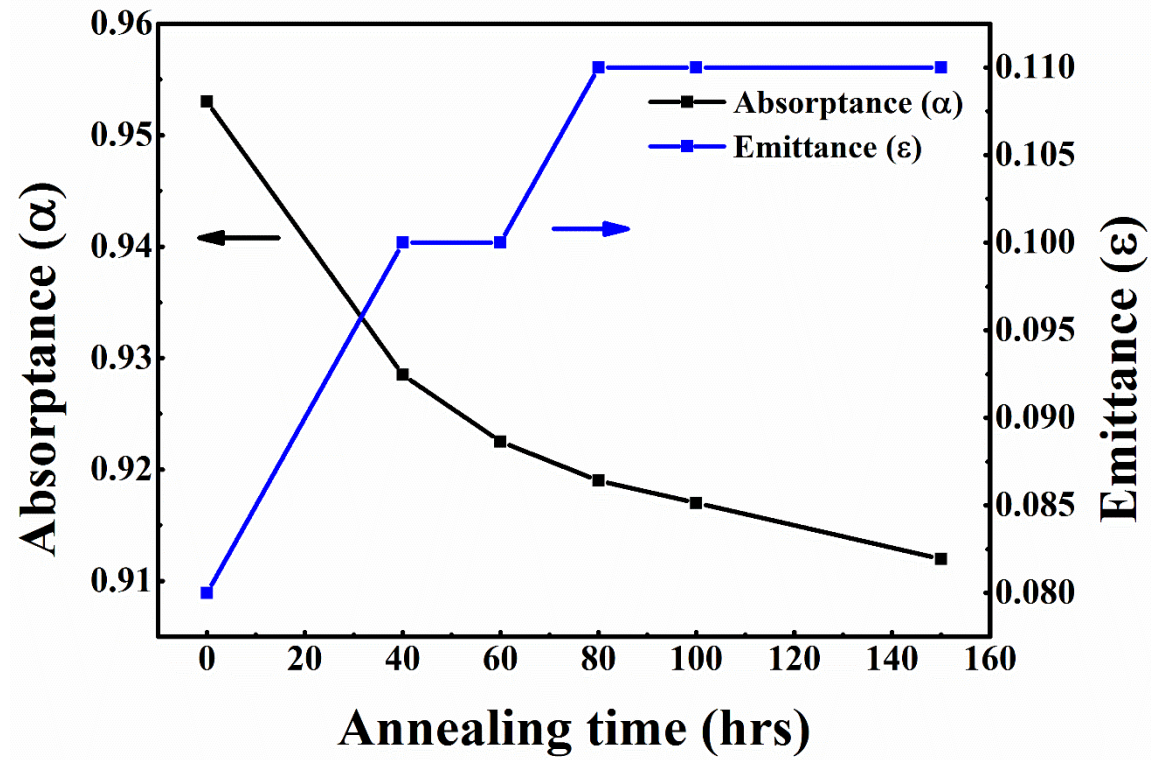
(a)

(b)

Fig. 4. a) Variation of absorptance and emittance value with respect to annealing duration;
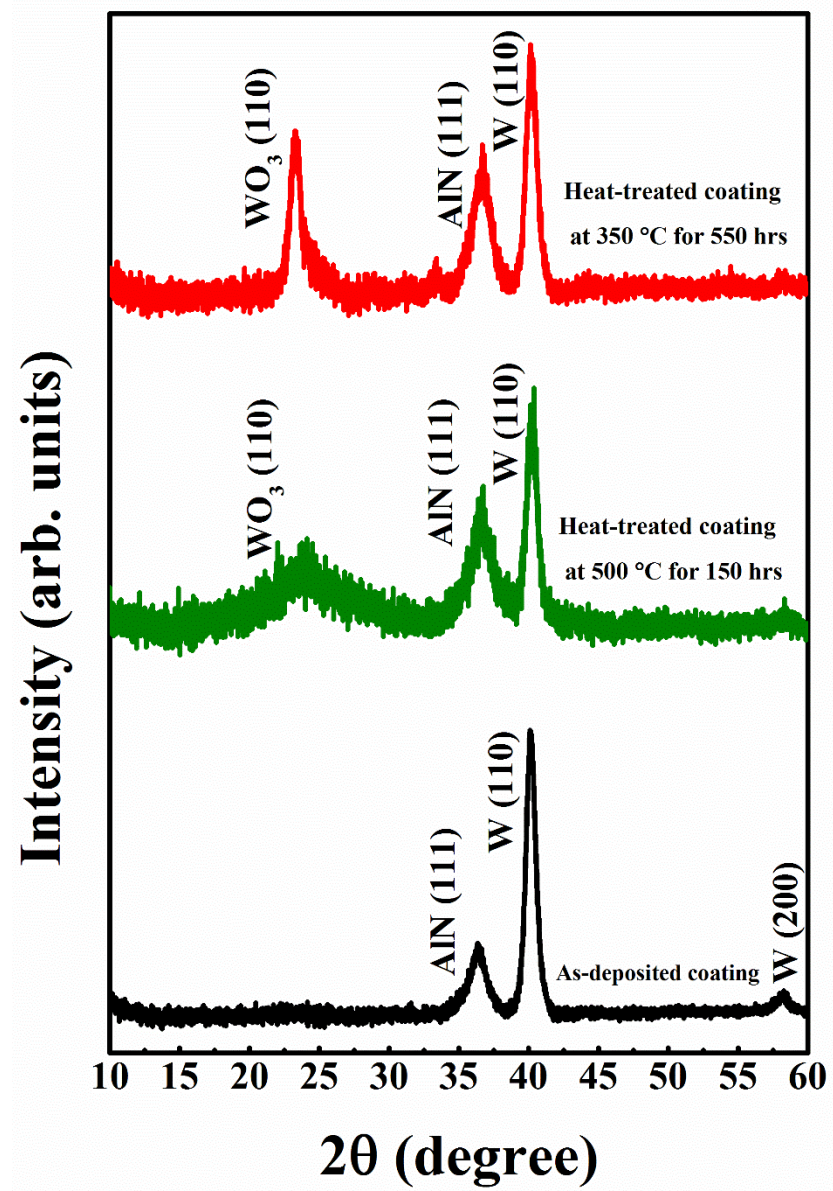b) Reflectance spectra of the as-deposited and heat treated coating at 500 °C in air for different time

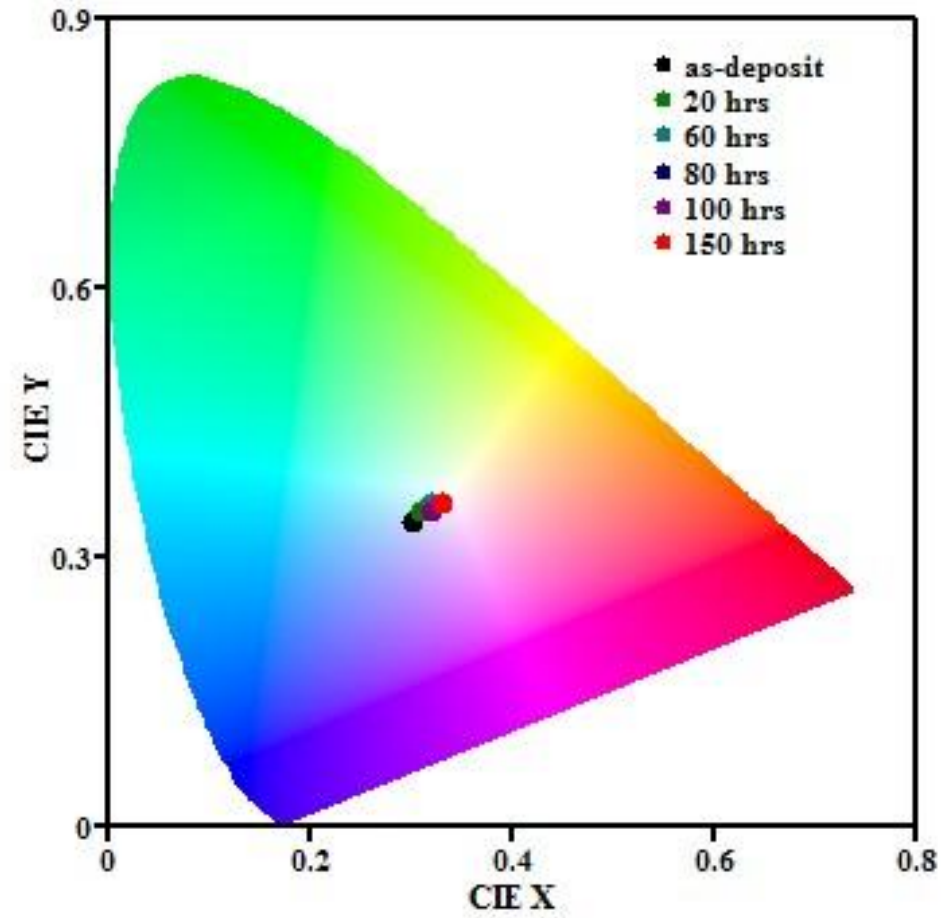Fig. 5. XRD spectra of as-deposited and heat treated coatings

Fig. 6. Chromaticity diagram of as-prepared and heat-treated absorber coatings
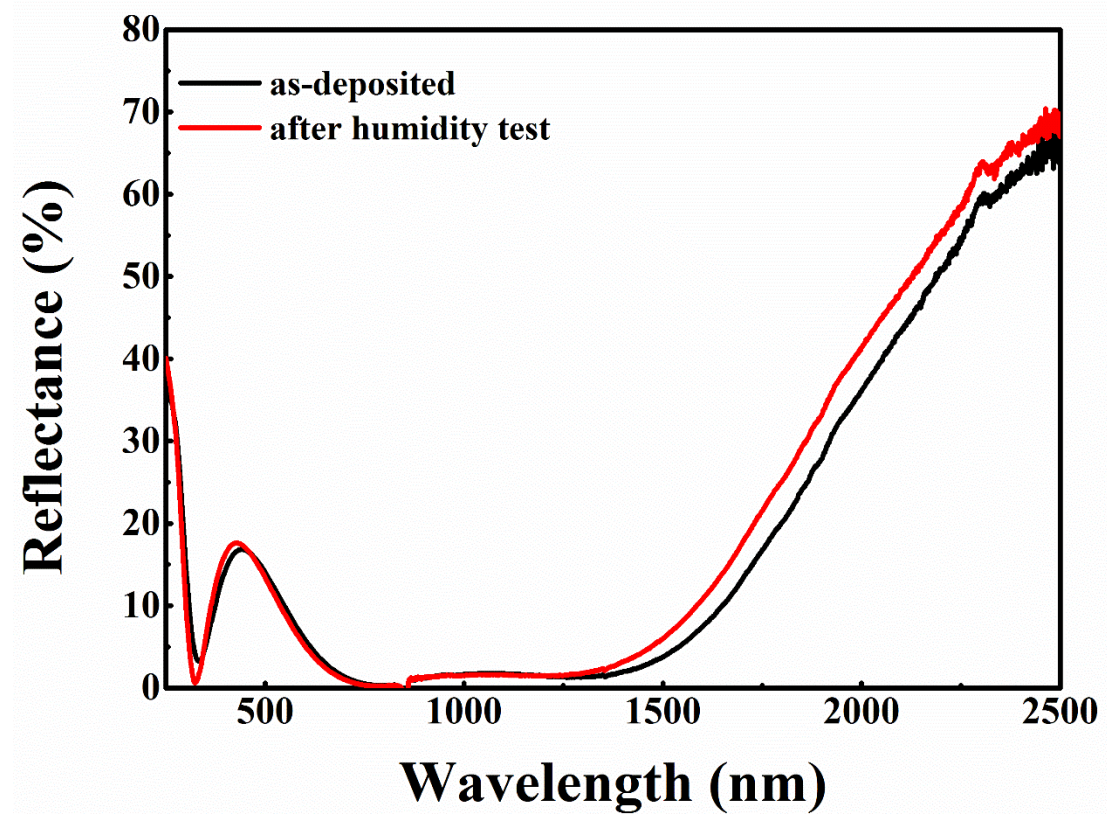
Fig. 7. Reflectance spectra of the coating before and after humidity test