

Chapter 21

Optically Enhanced Solar Selective and Thermally Stable Absorber Coating for Concentrated Solar Thermal Application



S. R. Atchuta, B. Mallikarjun and S. Sakthivel

Abstract Spectrally selective absorber coating for concentrated solar thermal (CST) receiver tube application has been developed on economically available stainless steel grade (SS-J4) substrate. The novel composite coating comprises of zirconia and silica networks to enhance the optical properties, thermal stability, and corrosion resistance. A solar absorptance of 0.91 ($\alpha_{\text{AMI},5}$; 300–2400 nm) and low spectral emittance of 0.15 (2.5–25 μm) are achieved in the gradient layer matrix. Coating has a superior thermal stability at 400 °C in open-air atmosphere with a low value of performance criterion ($\text{PC} < 0.02$), and comparable corrosion resistance, low thermal emissivity characteristic of 0.15 at 400 °C temperature obtained, which are essential for the coating to give significant shelf lifetime to the receiver tube in CST application.

Keywords Spectrally selective absorber coating · Concentrated solar thermal · Solar absorptance · Emittance and optical enhancement layer

21.1 Introduction

Solar energy is the best renewable energy source in the present day requirement for the generation of power. There are two leading conversion technologies for the solar, one is the photovoltaic (PV) method, and the other one is a thermal method. PV attracted a greater attention compared to that of CSP because of its simple conversion technology and economic feasibility [1]. In CSP, the power generation is a two-step process—generation of heat and then utilization of heat to run a conventional turbine. This complex process and economics made CSP costlier than PV. CSP can be viable if the plant operated with thermal energy storage in higher capacity (hundreds of Megawatt). Apart from CSP, solar thermal systems have more potential in process heat applications of the temperature < 400 °C. In concentrated solar thermal (CST) [2], there are few technologies like (compound parabolic collector, parabolic

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trough, linear Fresnel reflector, and solar dish) which can be fit for the process heat applications like solar drying, cooling, cooking, space heating, desalination, and other steam applications.

In CST, receiver tube is one of the key components in the solar collector, where the concentrated solar radiation will be converted into thermal energy [2]. The design of the solar receiver tube should be in such a way that it absorbs maximum solar radiation with minimum thermal emittance over the desired spectral range, which depends on the operating temperature and transition wavelength at that particular temperature. In order to get more efficiency, solar receiver tube should have exceptional spectrally selective absorber coating, which exhibits high solar absorptance over the entire solar spectrum (0.3–2.5 μm) and low thermal emittance in the infrared region (2.5–25 μm) [3]. Apart from spectral selectivity, coatings should also have thermal stability at operating temperature and corrosion resistance in the air (if the vacuum seal is broken) for practical applications of CST [4].

Most of the absorber coatings developed and commercialized for practical field application in power plants are based on vapor deposition method [5], which leads to higher cost. From past few decades, researchers also developed some of the efficient coatings by using different coating methods such as electroplating, sputtering, anodization, and oxidation route, but they have not commercialized due to the drawbacks of reproducibility of the same properties on a larger scale such as uniformity, adherence, and stability. To achieve the high spectral selectivity, coatings should have a proper thickness in nanometer range with excellent optical properties. Sol-gel is one of the promising routes for reproducibility at smaller and larger scale by maintaining specific conditions [6, 7].

In this present work, we have been developed a thermally stable solar selective absorber coating on a highly polished mirror finished stainless steel substrate by controlled thermal oxidation process and then optical enhancement layer developed, which has the property of 91% absorptance in the solar region (300–2400 nm) and emittance of 15% in the infrared region (2.5–25 μm). To get high spectral selectivity, we developed different barrier layers with different sols. We optimized process parameters like thickness, annealing temp, process duration, and different optical enhancement layers.

21.2 Experimental

21.2.1 Sample Preparation

The preliminary step of the process was to make the sample surface free of any external impurities. The mirror-polished SS J4 samples (50 × 25 × 1.5 mm L × OD × T—having the composition of C: 0.1, Mn 8.5–10, Cr 15–16, Ni 1–2, Cu 1.5–2.0, P 0.08, S 0.01, Si 0.75, and Fe 69–73 wt%, respectively) were cleaned with a mild detergent solution and rinsed with tap water followed by deionized water and finally

Table 21.1 Composition of the Sol's used for developing different barrier and optical enhancement layer

Sample	Molarity ratio of Zr & Si
Sol-1	1: 0
Sol-2	1:0.1
Sol-3	1:0.3
Sol-4	1:0.8
Sol-5	0:1

wiped with a soft cotton cloth with an organic solvent, preferably isopropyl alcohol (IPA). The cleaned substrate is then dried at 100 °C for 20 min in an air oven.

21.2.2 Sol and Coating Preparation

After cleaning the substrate, the novel composite thin films were deposited on the SS substrate by dip-coating process using a composite solution prepared by mixing the zirconium (IV) propoxide solution (70 wt% in 1-propanol—Make: Sigma Aldrich), glycidoxypropyltrimethoxysilane (>98%—Make: Sigma Aldrich) as precursors with 2-Iso-Propoxy Ethanol and Isopropyl alcohol (1:1 ratio) as solvents. The ratio of Zr and Si was varied in a systematic manner (as shown in Table 21.1), to develop the barrier and optical enhancement coating formulation with regards to both the coating quality and shelf life.

21.2.3 Design of Solar Absorber Coating

Soon after the deposition process, the coated samples were initially cured at 100 °C for 30 min and then transferred to a muffle furnace and annealed at 400–600 °C for 15–90 min to form a suitable optical layer (I) on the stainless steel substrate by controlled thermal oxidation. During this process, the coating will act as a barrier layer to control the metal atoms oxidation in the SS substrate, a thin composite oxide layer sandwiched between the developed barrier layer and the substrate [8]. After the annealing process, the substrates turned into different colors like dark gray, gray, bluish gray, blue, yellow, and greenish yellow depending upon the applied coating properties such as refractive index and thickness along with the process conditions like temperature and duration (Fig. 21.1).

Thin layers of different refractive index coatings (II) were developed on the composite layer to capture the maximum solar energy and high photothermal conversion.

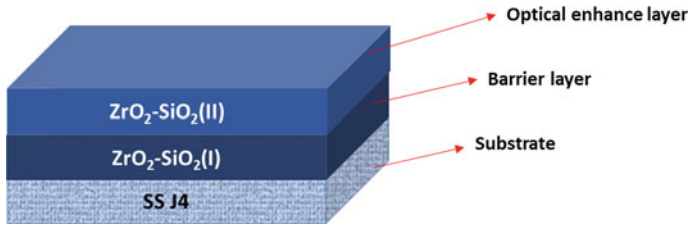


Fig. 21.1 Schematic representation of the developed solar selective absorber coating

21.3 Characterization Methods

A detailed analysis of optical and structural properties of the surface has been done during the optimization and finalization of the selective solar absorber coating. A Cary 5000 spectrophotometer equipped with a standard integrating sphere (110 mm Dia) is used to study the total reflectance measurements in the UV-VIS-NIR region at room temperature in a spectral region of 300–2400 nm with a scanning speed of 1200 nm/min. Bruker vertex 70 Fourier transform infrared (FTIR) spectrometer equipped with a standard integrating sphere used for characterizing the emittance of the absorber thin films in the spectral range of 2.5–25 μm using a standard evaporated gold mirror as a reference. Based on the standard equations as described in the literature, the average absorptance (α) and emittance (ε) values are calculated using Eqs. (21.1) and (21.2). The solar absorptance α_{sol} of the sample calculated as a weighted average fraction of absorbed radiation and incoming solar radiation using an AM 1.5 spectrum, according to the standard ISO 9845-1 (1992), the direct normal solar irradiance, I , is measured with an air mass of 1.5 and the emittance is calculated according to Kirchoff's law

$$\alpha_{\text{sol}} = \frac{\int_{\lambda_1}^{\lambda_2} (1 - \rho(\lambda)) I(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} I(\lambda) d\lambda} \quad (21.1)$$

$$\varepsilon(\lambda) = 1 - R(\lambda) \quad (21.2)$$

For thermal emissivity calculation, FTIR spectrometer equipped with the standard accessories of black body furnace and a high-pressure cell (sample compartment) supplied by Bruker optic GmbH used for the measurement of thermal radiative emission. Initially thermal radiative emission spectra (2.5–25 μm) of the sample coated with absorber layer and then black body were measured separately one after another at a particular temperature. The emissivity calculations were done using Eq. (21.3) and measurements were done at different temperatures from 100 to 500 $^{\circ}\text{C}$ [9].

$$\varepsilon_t = \frac{\text{sample emission}}{\text{Black body emission}} \quad (21.3)$$

Ellipsometer (Model: M-2000 V, J.A. Woollam Co. Inc.) used for measuring the thickness and refractive index of the composite layers between 350 and 1000 nm wavelength [10]. X-ray photoelectron spectrometer (Omicron-ESCA+) equipped with Al K α anode is used to find the chemical composition and oxidation state of the composite layers.

An Atlas cyclic corrosion testing chamber (Model: CCX 2000, Atlas Materials Testing Solutions) is used for testing the relative corrosion resistance information of the samples/coating; salt spray test is an accelerated corrosion test that produces a corrosive environment to the coated samples to predict its life in the normal environment [11]. Samples are kept in corrosion testing chamber according to the ASTM B117 standard; 5% NaCl aqueous solution is used to produce mist to circulate in the chamber at 35 °C temperature and 95% humidity. The samples are monitored at successive intervals, and the optical properties were studied.

Muffle furnace (Nabertherm) is used to check the thermal stability of the coatings; the samples were placed in the furnace with a heating rate of 10 °C/min to 500 °C and dwell for 2 h and then sudden cooling to room temperature.

21.4 Results and Discussion

21.4.1 Composite Oxide Layer Formation with Different Barrier Layers of Sol's

Different barrier layers of Zr: Si sols have been applied on manganese-rich SS substrate to form the composite oxide coating with the optimized parameters of 3 mm/s withdrawal speed, 550 °C annealing temperature, and 30 min' dwell time. Optimized results of the coatings shown in Table 21.2. From the table, it is observed that Zr: Si (1:0.3) molarity ratio of the Sol has formed optimized thickness and refractive index with good optical properties of absorptance 83.7% and emittance of 14% (Fig. 21.2a).

Table 21.2 Solar absorptance and emittance data of absorber layers generated by different barrier layers with refractive index and thickness data

Zr: Si ratio	Thickness (in nm)	Refractive index	Solar absorptance (%) (AM1.5)	Emittance (%)
1:0	41.6	1.81	78.8	13
1:0.1	42.4	1.80	82.1	14
1:0.3	56.9	1.71	83.7	14
1:0.8	71.9	1.66	79.1	13
0:1	32.6	1.47	82.4	19

Note The mentioned ratio is molarity ratio of Zr: Si composite present in the Sol
The bold values indicates optimized parameters for the better optical properties

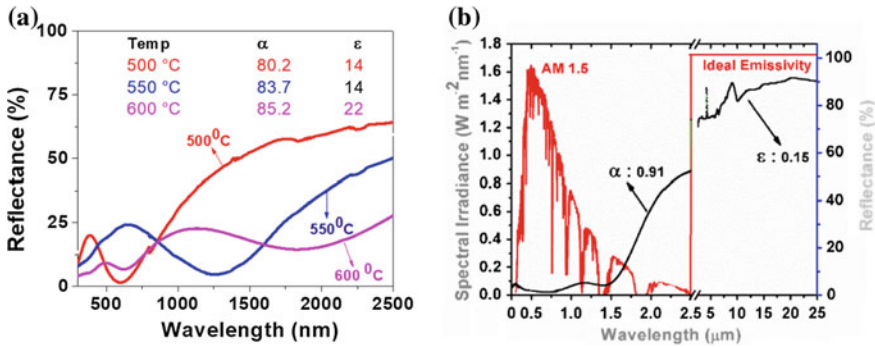


Fig. 21.2 a The Reflectance spectra of composite absorber layer as a function of optimized conditions and b Optical properties of the best composite layer with comparison of AM1.5 and ideal spectral data

The higher absorption was attained because of the composite oxide formation and the refractive index of the coating; Composite oxide layer formation is directly proportional to the thickness of the barrier layer (as thickness increases composite oxide formation is less) and the refractive index of the coating is caused by particular wavelength absorption in the solar spectra. Hence, from Table 21.2, the coating has an optimum thickness of barrier layer ~ 57 nm and the refractive index of 1.71 matches to the solar spectrum to absorb more solar radiation for the photothermal conversion of 83.7% with an emittance value of 14% for the composite solar selective absorber coating.

21.4.2 Development of Optical Enhancement Layer

To improve the optical properties of the coatings to tap more solar energy for efficient photothermal conversion process, we have applied different layer stack of coatings on optimized composite oxide absorber coating (83.7% absorption and emittance of 14%). From Table 21.3, the best optical properties observed are 90.5% absorption and 15% emittance, by the approach of gradient layer (refractive index) coating method.

Here, on high refractive index layer of composite oxide (1.71), low refractive index (1.66) layer of coating is applied to get best optical properties [12]. Whereas in the case of silica, very low refractive index coating (1.47) helped to improve the absorption to 91.8% but at the same time, emittance values increased drastically to 21%.

Table 21.3 Absorption and emittance data of optical enhancement layer coatings

Sample	First layer	Second Layer (Zr: Si) ratio with 3 mm/s	Solar absorptance (%) (AM1.5)	Emittance (%)
Type-1	Zr: Si (1:0.3) 3 mm/s	1:0	84.1	13
Type-2	Zr: Si (1:0.3) 3 mm/s	1:0.1	84.4	13
Type-3	Zr: Si (1:0.3) 3 mm/s	1:0.3	86.8	14
Type-4	Zr: Si (1:0.3) 3 mm/s	1:0.8	90.5	15
Type-5	Zr: Si (1:0.3) 3 mm/s	0:1	91.8	21

The bold values indicates optimized parameters for the better optical properties

21.4.3 Thermal Emissivity of the Coating

Selective solar absorber coating should absorb more light in UV-Visible and NIR region, depends upon the transition wavelength at that particular operating temperature, and it should reflect more in mid and far IR radiation to get low radiation loss. Here, thermal emissivity characterizations of composite absorber layer having high optical properties developed on the surface of SS J4 were carried out by FTIR spectrophotometer as said in characterization methods. Samples were measured for the emissivity at different temperatures from 100 to 400 °C with an interval of 100 °C as shown in Table 21.4.

Typical thermal emittance spectra of uncoated SS substrate, developed composite absorber layer, and the black body were shown along with different temperatures in Fig. 21.3. The emittance intensities from the composite absorber layer and the bare sample are increased with increase in temperature as observed in a black body sample. From Table 21.4, composite oxide layer developed on SS substrate shows little high thermal emittance compared to the bare substrate due to the metal oxides content in the layer and also due to the presence of silica, whereas zirconia will help to increase the thermal stability. Moreover, the thermal emissivity of composite absorber layer deposited on the substrate was observed to be, 0.15 at 400 °C, which is essential for the coating to get more efficiency.

Table 21.4 Thermal emissivity of different samples at various temperatures

Sample	Temperature			
	100 °C	200 °C	300 °C	400 °C
Uncoated SS	0.07	0.10	0.12	0.14
Solar selective absorber coated SS	0.09	0.12	0.14	0.15

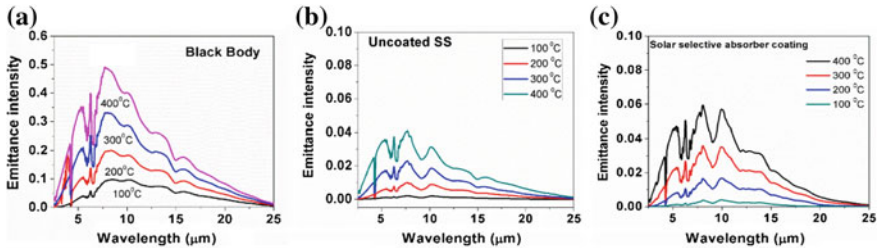


Fig. 21.3 Thermal emittance spectra of **a** black body **b** uncoated SS substrate **c** solar selective absorber layer at different temperatures

21.4.4 Compositional Analysis of the Coatings—X-Ray Photoelectron Spectroscopy (XPS)

The barrier and optical enhanced solar absorber coating compositions were characterized by XPS, to determine the elemental percentage of the thin film and compare the Zr and Si atomic proportions. According to the XPS analysis report for the barrier layer coating over on the SS J4 substrate by using Sol 3 (1:0.3 ratio of Zr: Si) shown in Fig. 21.4, the peaks appeared at a binding energy of 182.0 ± 0.2 eV (Zr 3d $\frac{5}{2}$) and 184.4 ± 0.2 eV (Zr 3d $\frac{3}{2}$) correspond to ZrO_2 . For SiO_2 , the peak appears at the binding energy of 101.5 ± 0.2 eV. Further, the mentioned oxidized species are also confirmed by observing the O 1s peak. From the O 1s spectrum, it is confirmed that the peak appears at 530.8 ± 0.2 eV corresponding to the oxygen in SiO_2 , whereas peak appears at 529.9 ± 0.2 eV corresponding to the oxygen in ZrO_2 . The atomic proportion (%) of Zr, Si, and Oxygen, is 20.19%, 3.36% and 76.46%, respectively.

XPS analysis report for the optical enhanced solar absorber coating using Sol 4 (1:0.8 ratio of Zr: Si) deposited over on the SS barrier layer composite oxide layer shown in Fig. 21.5; the peaks appeared at the binding energy of 182.5 ± 0.2 eV (Zr 3d $\frac{5}{2}$) and 185.0 ± 0.2 eV (Zr 3d $\frac{3}{2}$) correspond to ZrO_2 species. For SiO_2 , the peak appears at the binding energy of 102.0 ± 0.2 eV. Further, the mentioned oxidized species are also confirmed by observing the O 1s peak. From the O 1s spectrum, it is

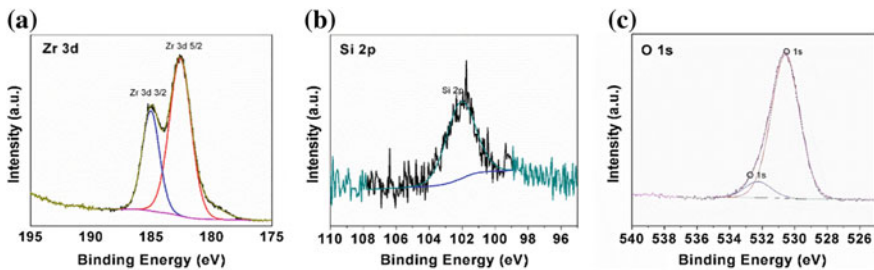


Fig. 21.4 Resolved XPS peaks of Zr, Si, and O of barrier layer composite absorber coating using Sol 3 on SS substrate

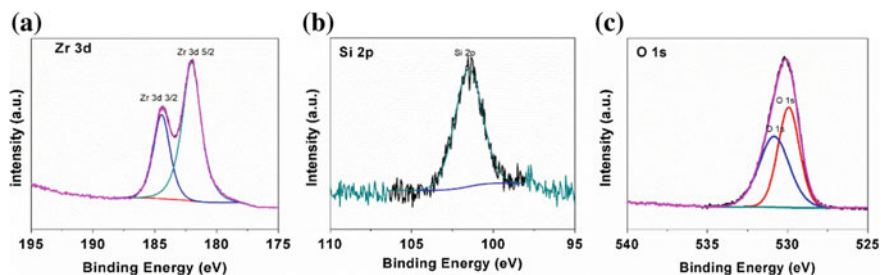


Fig. 21.5 Resolved XPS peaks of Zr, Si, and O of optical enhanced composite solar absorber coating using Sol 4 on barrier layer composite oxide coating

Table 21.5 Coating compositions of the absorber layer generated on SS J4 substrate

Sample	Elemental concentration (%)		
	Zr	Si	O
Barrier layer composite oxide layer	20.19	3.36	76.46
Optical enhanced solar absorber coating	18.27	10	71.72

confirmed that the peak appears at 532.57 ± 0.2 eV corresponding to the oxygen in SiO_2 , whereas peak appears at 530.56 ± 0.2 eV is corresponding to oxygen in ZrO_2 . The atomic (%) proportion of Zr, Si, and O is 18.27%, 10%, and 71.72% respectively.

It is also clearly observed that optical enhanced solar absorber coating developed by a high content of silica in the composite sol (Zr: Si-1:0.8) show a high atomic percentage of SiO_2 compared to barrier layer composite oxide coating using Zr: Si-1:0.1 composite Sol (Table 21.5).

21.4.5 Corrosion Resistance Test

An accelerated corrosion test was conducted according to ASTM B117 standard for the developed absorber layer on SS J4 substrate; the test coupons were placed in the chamber at a 45° angle and corrosive fog generated at 35°C by bubble tower using 5% solution of sodium chloride with 95% humidity condition. The time taken for decolorization of the coatings or formation of spots was carefully observed and for every 12 h duration optical properties measured and noted in Table 21.6. The test indicated adequate stability of the coating till 50 h duration, after that there was a slight change in optical properties and corrosion spots are observed. These corrosive spots are may be because of the substrate oxides start to expose to the corrosive environment.

Table 21.6 Optical properties of the corrosion tested sample at different durations of time

Time taken (h)	Solar absorptance (%) AM1.5	Emittance (%)
0	90.5	15
50	90.5	15
100	87.2	17

Table 21.7 Effect of annealing at 400 °C in the air on the solar absorptance, emittance, and PC values of the composite absorber layer developed on SS J4 substrate after completion of each thermal cycle test

Thermal cycle	α_s	ε	$\Delta\alpha_{sol}$	$\Delta\varepsilon$	PC
0	0.905	0.15	0	0	0
5	0.903	0.15	0.002	0.000	0.002
10	0.900	0.18	0.005	-0.030	0.020

21.4.6 Thermal Stability Test

The long-term thermal stability till 400 °C in open-air atmosphere for the absorber coating is an essential requirement for concentrated solar thermal application. The process temperature, duration, and material properties also play a role in the thermal stability of the receiver in the open-air atmosphere. Since thermal instabilities and degradation of the solar absorber layers are the major parameters of interest for the long-term stability of the selective solar absorbers, the stability of the selective absorber layer developed on the SS J4 substrate was tested by a high-temperature thermal cycle test [13]. Thermal stability tests of the samples were carried out under air at 400 °C for 2 h for each cycle. The cycle comprises of 10 °C/min heating rate to attain the testing temperature of 400 °C, 2 h dwelling at 400 °C and then sudden cooling to reach the ambient temperature. In this way, thermal cycle test repeated for ten times. The optical properties were measured and shown in Table 21.7.

The influence of the changes in the solar absorptivity in the thermal cycles is calculated by the change of solar absorption and emittance ($\Delta\alpha_{sol}$ and $\Delta\varepsilon$). This change in the solar absorptance and emittance is used to calculate the performance criterion (PC):

$$PC = \Delta\alpha_s - 0.5\Delta\varepsilon \leq 0.05$$

It can be inferred that the developed novel composite absorber layer did not show much change in the optical properties of thin-film performance criterion study (Table 21.7). Hence, a PC of approximately 0.02 was observed, indicating superior stability of the coating at 400 °C.

21.5 Conclusion

A novel Zr-Si, selective composite absorber layer, is developed on austenitic stainless steel (SS J4) substrate proved to show high thermal stability and moderate corrosion resistance (400 °C, >100 h) in open-air atmosphere with good optical properties (α_{sol} : 0.91, $\varepsilon_{400\text{ °C}}$: 0.15). This novel absorber coating will ensure that there will be an increase in the solar fields operating temperature maximum up to 400 °C, which leads to improved performance and reduced cost of concentrated solar thermal (CST) systems. The optical enhanced layer improves the absorption by 8% and made suitable for CST with an economic process of fabrication at large scale is simple and do not demand sophisticated equipment and processing conditions, which can help the receiver tube cost in an economic way.

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References

1. P. Bhubaneswari, S. Iniyamb, G. Ranko, A review of solar photovoltaic technologies. *Renew. Sustain. Energy Rev.* **15**, 1625–1636 (2011)
2. V.K. Jebasingh, G.M.J. Herbert, A review of solar parabolic trough collector. *Renew. Sustain. Energy Rev.* **54**, 1085–1091 (2016)
3. A. Dana, H.C. Barshilia, K. Chattopadhy, B. Basu, solar energy absorption mediated by surface plasma polaritons in spectrally selective dielectric-metal-dielectric coatings: a critical review. *Renew. Sustain. Energy Rev.* **79**, 1050–1077 (2017)
4. C.E. Kennedy, H. Price, Progresses in development of high temperature solar selective coatings, in *International Solar Energy Conference* (Orlando, Florida USA, 2005)
5. N. Selvakumar, H.C. Barshilia, Review of physical vapor deposited (PVD) spectrally selective coatings for mid- and high-temperature solar thermal applications. *Sol. Energy Mater. Sol. Cells* **98**, 1–23 (2012)
6. C.J. Brinker, G.C. Frye, A.J. Hurd, C.S. Ashley, Fundamentals Of Sol-Gel dip coating. *Thin Solid Films* **201**, 97–108 (1991)
7. B. Usmani, A. Dixit, Spectrally selective response of ZrOx/ZrC–ZrN/Zr absorber–reflector tandem structures on stainless steel and copper substrates for high temperature solar thermal applications. *Sol. Energy* **134**, 353–365 (2016)
8. A. Srinivasa Rao, S. Sakthivel, A highly thermally stable Mn–Cu–Fe composite oxide based solar selective absorber layer with low thermal loss at high temperature. *J. Alloy. Compd.* **644**, 906–915 (2015)
9. X. He, Y. Li, Lidong Wang, Y. Sun, S. Zhang, High emissivity coatings for high temperature application: progress and prospect. *Thin Solid Films* **517**, 5120–5129 (2009)
10. H.G. Tompkins, S. Tasic, J. Baker, D. Convey, Spectroscopic ellipsometry measurements of thin metal films. *Surf. Interface Anal.* **29**, 179–187 (2000)
11. B. Carlsson, K. Moller, M. Kohl, U. Frei, S. Brunold, Qualification test procedure for solar absorber surface durability. *Sol. Energy Mater. Sol. Cells* **61**, 255–275 (2000)

12. J.H. Rouse, G.H. Ferguson, Preparation of thin silica films with controlled thickness and tunable refractive index. *J. Am. Chem. Soc.* **125**, 15529–15536 (2003)
13. M.K. Öhl, M. Heck, S. Brunold, U. Frei, B. Carlsson, K.M. Öller, Advanced procedure for the assessment of the life time of solar absorber coatings. *Sol. Energy Mater. Sol. Cells* **84**, 275–289 (2004)