Solar energy technology has gained attention in both academia and industry due to its abundance as a renewable energy source, which can be utilized for mitigating the everyday increasing energy demands. The aim of the solar energy technology is to harness the maximum for possible humankind applications. Solar thermal technology is the direct method to harness solar energy through solar collectors and receivers. The receiver consists of absorber tube, for absorbing the maximum incident solar energy and minimizing the thermal losses. The primary objective is to develop the thermally stable spectrally selective absorber coatings using low processing and maintenance cost. This chapter presents a brief review on solar electromagnetic radiation, optical properties such as absorptance, emittance, and the historical development of solar selective absorber materials for low, mid-to-high temperature applications. This will also include a section on commercially developed solar selective coatings and associated challenges/problems in the present context of solar thermal applications.

2.1 ELECTROMAGNETIC RADIATION

Electromagnetic radiation consists of electric and magnetic field vectors, perpendicular to each other and also perpendicular to the direction of propagation. The energy will propagate along the direction of electromagnetic radiation and is known as the pointing vector. James Clerk Maxwell, a Scottish scientist, was the first one, who proposed the theory of classical electromagnetism in 1862 and predicted that light itself is a form of electromagnetic radiation. Electromagnetic radiation is divided into different energy bands based on the frequency distribution. The stipulated frequency range of electromagnetic radiation, such as solar radiation, which covers the ultraviolet-visible-near infrared (UV-Vis-NIR) range (0.3 – 2.5 µm), and thermal radiation, from mid infrared (MIR) to far infrared (FIR) range (2.5 – 50 µm), are very important for solar thermal energy applications.

2.1.1 Thermal Radiation

Thermal radiation is also the large wavelength electromagnetic radiation and a temperature dependent radiation distribution is emitted by all bodies/objects. All objects, above absolute zero temperature, emit thermal radiation, whose wavelength and intensity depend on the temperature of the object and its optical properties. A black body is an ideal system, which can absorb all the incident radiation, and to maintain a constant temperature, it emits an equal amount of energy simultaneously. The wavelength distribution of a black body at a given temperature, T K, is given by Plank's Law [Richtmyer and Kennard, 1947].

$$E_{\lambda b} = \frac{C_1}{\lambda^5 [\exp(C_2 / \lambda T) - 1]} \ , \tag{2.1}$$

where $E_{\lambda b}$ is the energy per unit area per unit time per unit wavelength interval at wavelength λ. The subscript b indicates the blackbody, h is Plank's constant and k is Boltzmann's constant. $C_1 = 2\pi h C_0^2$ and $C_2 = h C_0 / k$ are often called Plank's first and second radiation constants. The values of C_1 and C_2 are 3.7405 x 10^-16 m²W and 0.0143879 mK respectively. The total emitted energy is calculated by integrating Plank's radiation distribution over the desired wavelength range. The total energy emitted by a blackbody is found to be

$$E_b = \int_0^\infty E_{\lambda b} d\lambda = \sigma T^4 , \tag{2.2}$$

Where σ is the Stefan-Boltzmann constant, equal to 5.6697 x 10^{-8} W/m^{2}K^4.

2.1.2 Solar Radiation

The sun is considered as a spherical system with a diameter of 1.39 x 10^9 m and is ~ 1.5 x 10^{11} meter from the earth. It emits about 3.84451 x 10^{23} kW energy using nuclear fusion reactions. The radiated solar energy spectrum consists of the long wavelength infrared radiation to the very short wavelength gamma radiations. However, most of this radiation is absorbed or scattered in the ionosphere, the ozone layer or by the atmospheric constituents such as nitrogen, oxygen, ozone, water vapor, carbon dioxide etc. The intensity of solar radiation is constant outside the earth's atmosphere, due to the sun and earth's spatial relation. The constant solar radiation is known as solar constant, G_{sc}, which is 1367±1% W/m^2 throughout the year. This solar constant is also defined as the energy received per unit area per unit time from the sun on a surface perpendicular to the direction of propagation of the incident radiation [Duffie and Beckman, 1991]. Solar radiation consists of about 8.03% UV, 46.41% visible and rest of 46.40% near infrared (NIR) fractions (Figure 2.1 (Right panel)). The sun's effective blackbody temperature can be calculated using the following equation [Iqbal, 1983].

$$T = \left[\frac{G_{sc}}{\sigma} \left(\frac{r_0}{r_s} \right)^2 \right]^{1/4} , \tag{2.3}$$

Where G_{sc} is solar constant, r_0 and r_s are the sun-earth distance and the mean radius of the sun respectively. The effective blackbody temperature of the sun is 5777K. However, spectral distribution of the sun as a blackbody does not strictly follow the extraterrestrial solar spectrum; therefore, it cannot be used for characterizing solar selective absorbers [Iqbal, 1983].

A fraction of solar radiation is absorbed by different atmospheric gases, giving an irregular and rough shape of the terrestrial spectrum, as shown schematically in Fig. 2.1(Left panel). The absorption of extraterrestrial radiation is due to the resonance with vibrational energy levels of CO_2, NO_2, CO, O_2 and CH_4 gases. Simultaneously, the scattering takes place because of the gaseous molecules as well as atmospheric dust particulates [Sukhatme and Nayak, 2008]. The radiation is also characterized by air mass (AM), which is defined as the path length of sun's rays passing through the atmosphere, divided by minimum sun rays path length (Figure 2.1(Right panel)). Thus, an air mass 1 (AM1) implies that the sun is directly on the head. AM0 represents the same at no atmospheric conditions, that is, in the extraterrestrial region. The AM1.5 is defined as an average solar spectrum at the earth's surface. The AM1.5 solar spectrum consists of 2% UV, 54% visible, and 44% infrared fraction in the solar spectrum [Masters, 2004] and is used for higher latitudes. For lower latitudes, smaller AM solar spectrum is suggested. However, air mass variations have not shown much difference on the solar thermal performances for spectrally selective absorbers [Lind *et al.,* 1980].

There are two types of solar radiations: (i) beam or direct radiation termed as the Direct Normal Irradiance (DNI), directly received at earth's surface without changing its direction and (ii) diffuse radiation, received at the earth's surface from all parts of the atmosphere. The sum of these beam and diffuse radiation is called the global or total radiation [Sukhatme and Nayak, 2008]. Moreover, in concentrated solar thermal plants, electricity generation is directly affected by the availability and variability of solar resources and more specifically by DNI. Therefore, direct normal irradiation is crucial for concentrating direct sunlight to drive CSP plants [Blanc *et al.*, 2014; Nou *et al.*, 2016; Prasad *et al.*, 2015].
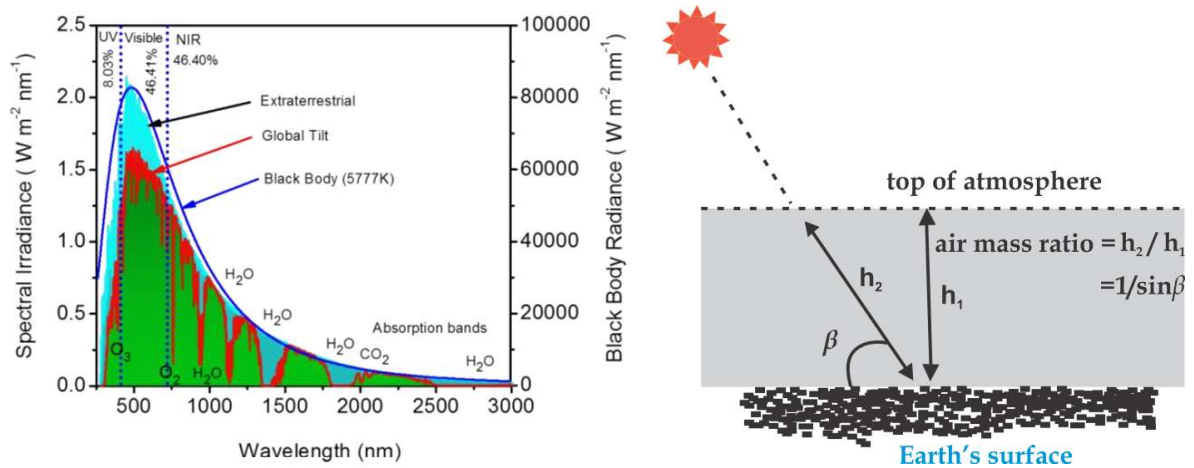
Figure 2.1 : (Left panel) Spectral distribution of solar radiation (i) extraterrestrial radiation, (ii) total radiation incident on the inclined (37°) earth's surface, and (iii) black body radiation at sun's surface temperature 5777K with O_3, O_2, H_2O, and CO_2 absorption bands (Source: Rredc, 2015). **(Right panel)** The air mass ratio (AM) and it's numeric analog (Source: Masters, 2004).

2.2 SPECTRAL SELECTIVITY OF ABSORBING SURFACES

The spectral distribution of sun and blackbody spectrum at a given temperature needs to be understood in order to know the spectral selectivity of absorbing surfaces. After passing through the atmospheric layers, solar insolation on the earth surface is confined in 0.3 to 2.5 µm (UV-Vis-NIR) wavelength range and is shown in Figure 2.2 for the clear atmospheric conditions. This spectrum corresponds to American Society for Testing and Materials (ASTM) G173 for air mass 1.5 (AM1.5). Figure 2.2 also shows 100°C, 200°C, and 300°C temperatures black body spectra, calculated using Plank's law [Duffie and Beckman, 1991]. As temperature rises, the total thermal radiation increases and the peak wavelength has shifted towards the shorter wavelength. The sun is a radiative source with surface temperature > 5500°C, emitting 95% of its output at wavelengths < 2 µm, and a terrestrial receiver kept at 650°C (an upper temperature limit for the most technological applications) emits 95% of its thermal radiation at wavelengths > 2 µm. Therefore, the spectral distribution of solar radiation and respective thermal losses are well separated on the wavelength scale, with ~ 5% overlap on either side of 2 µm, as illustrated in Figure 2.2 [Seraphin, 1979].

A selective absorber surface absorbs the maximum fraction of the incident solar energy while at the same time suppresses the thermal emittance in the infrared region. Neither perfect solar absorption nor perfect thermal suppression is possible [Seraphin, 1979]. For an ideal selective absorbing surface, the absorption is equal to one ($\alpha = 1$) and emittance is equal to zero ($\varepsilon = 0$) at given temperature, as shown in Figure 2.3. However, a real selective absorber surface has absorptance less than one ($\alpha < 1$) and thermal emittance greater than zero ($\varepsilon > 0$).
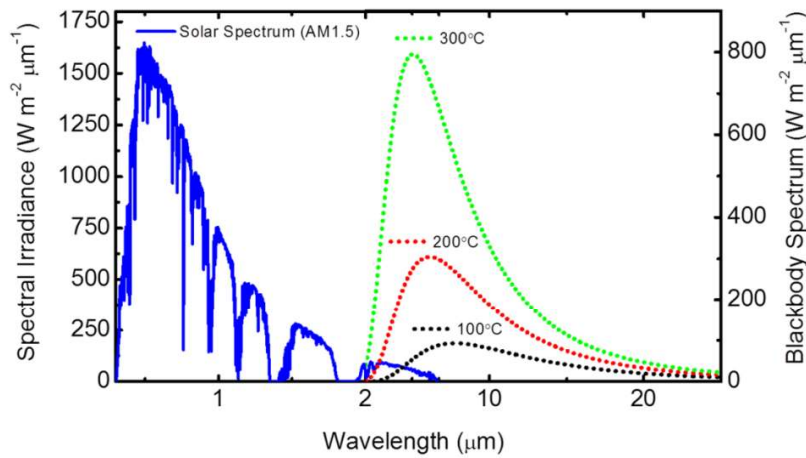
Figure 2.2 : Solar spectral irradiance for AM1.5 in 0.3 to 2.5 μm wavelength range (Source: Rredc, 2015). A blackbody radiation spectrum calculated using Plank's law for different temperatures. (Source: Duffie and Beckman, 1991)
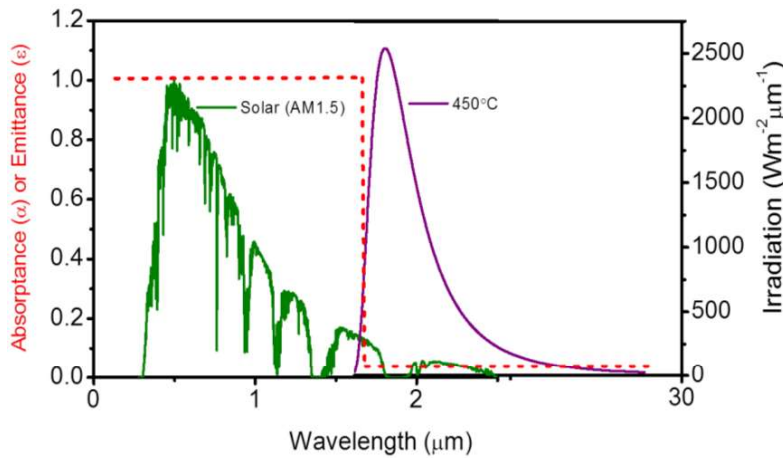
Figure 2.3 : AM1.5 solar spectral irradiance in the wavelength range 0.3 to 2.5 μm (Source: Rredc, 2015). The blackbody radiation for 450°C temperature (Source: Duffie and Beckman, 1991). The red dashed curve represents the ideal spectral response for an absorber.

Solar absorptance and thermal emittance are two essential parameters to evaluate the spectral selectivity of an absorber surface. The solar absorptance is defined as the fraction of incident solar radiation absorbed by the absorber surface. According to the Kirchhoff's Law, a material which does not allow any transmittance to the incidence radiation, the spectral absorptance can be expressed in terms of total reflectance, R (λ, θ) [Duffie and Beckman, 1991],

$$\alpha\,(\lambda,\,\theta) = 1 - R\,(\lambda,\,\theta), \tag{2.4}$$

where λ is the wavelength and θ is the incidence light angle from the normal of the absorber surface. The solar absorptance is calculated by weighting the spectral absorptance with spectral solar irradiance. The integration of weighted solar insolation I_{sol} over the desired wavelength range is expressed as,

$$\alpha(\theta) = \frac{\int_{\lambda_1}^{\lambda_2}[1-R(\lambda,\theta)]I_{sol}(\lambda)d\lambda}{\int_{\lambda_1}^{\lambda_2}I_{sol}(\lambda)d\lambda} \quad , \tag{2.5}$$

where, λ_1, λ_2 represent the lower and upper solar wavelengths. Solar radiation reflectance R (λ, θ) is commonly measured in the range of 0.3 – 2.5 μm wavelength at near normal incidence using UV-Vis-NIR spectrophotometer.

Another parameter, thermal emittance, is used to characterize the performance of the solar selective absorber surface in the range of 2.5 – 25 μm wavelengths. The thermal emittance is calculated as a fraction of emitted radiation from the heated body as compared to the blackbody radiation at the same temperature. According to the Kirchhoff's law, for an opaque selective surface, the thermal emittance relates to the absorptance:

$$\varepsilon (\lambda, T) = 1 - R(\lambda, T), \tag{2.6}$$

At a given temperature T, the total emittance is calculated as:

$$\varepsilon(T) = \frac{\int_{\lambda_1}^{\lambda_2}[1-R(\lambda,T)]E_{\lambda b}d\lambda}{\int_{\lambda_1}^{\lambda_2}E_{\lambda b}d\lambda} \quad , \tag{2.7}$$

where, $E_{\lambda b}$ is the blackbody spectrum given in equation (2.1). The denominator of equation (2.7) is the total thermal energy radiated by a black body at temperature T.

An efficient selective absorber is defined as having a high absorptance α in the solar spectrum range and low emittance ε in extended infrared range to reduce the thermal radiation loses, for temperature below 500ºC. The 98% of this radiation occurs above 2 μm wavelength. The design of spectrally selective coatings is possible because of non-overlapping wavelength regions of these two properties: solar absorptance and emittance [Pettit and Sowell, 1976]. A quantity that has been used to characterize a spectrally selective coating is the ratio of the solar absorptance (α) to the thermal emittance (ε), known as the figure of merit or spectral selectivity of solar selective coatings [Jaworske, 2002]. A good spectrally selective coating might be expected to have α/ε ~ 10, with large solar absorptance values [Pettit and Sowell, 1976]. For efficient spectrally selective structures, solar absorptance, α, should be as large as possible. Sandia research group has demonstrated that an increase in α is more effective in improving the operating efficiency than a corresponding decrease ε for focused solar collector system [Peterson and Ramsey, 1975]. For example, an increase 0.05 in α (e.g., from 0.90 to 0.95) achieves the same increase in efficiency as decreasing the emittance by 0.20 (e.g., from 0.30 to 0.10) [Pettit and Sowell, 1976].

2.3 DEPOSITION TECHNIQUES USED IN THE DEVELOPMENT OF COATINGS

Several deposition techniques are employed to develop the low to mid and high temperature stable spectrally selective absorber coatings such as physical vapor deposition (PVD), chemical vapor deposition (CVD) and plasma enhanced chemical vapor deposition (PECVD), electrochemical methods, sol-gel derived process such as dip-coating, spin-coatings, spray and painting etc. In this section, the commonly used deposition techniques are discussed, which are especially employed for the development of spectrally selective structures.

2.3.1 Physical Vapor Deposition

Physical vapor deposition (PVD) techniques are based on atomistic deposition process, in which material is vaporized from a solid or liquid source in the form of atoms or molecules. The vaporized atoms are transported in the form of a vapor through a vacuum or low pressure gaseous environment to the substrate, where it condenses. PVD technique can be used for fabricating uniform films with variable thickness ranging from few nanometers to micrometers [Mattox, 1997]. Various physical deposition techniques are explored by researchers such as evaporation, sputtering, cathodic arc evaporation and ion plating for the development of spectrally selective absorber coatings.

2.3.1.1 Evaporation

Both thermal and electron beam evaporation techniques are employed to develop spectrally selective absorber coatings for photothermal applications. The raw material is heated in vacuum, where vaporized atoms and molecules are transported to the substrate. The rate of atom/molecule vapor transport can be controlled for the desired quality of the thin film structures. The necessary thermal heating is achieved by using a resistive coil or boat, made of refractory tungsten or molybdenum materials. In contrast to the resistive heating, used in case of thermal evaporation, a magnetically focused energetic electron beam is used in electron beam evaporation [Holland, 1956]. However, films deposited with evaporation do not bond well with the substrate and difficult to evaporate high melting temperature materials such as platinum and molybdenum. The major drawback of the evaporation techniques is the scaling issues for large area deposition [Selvakumar and Barshilia, 2012]. There are limited reports on evaporation based spectrally selective coatings. Niklasson et al., developed a $Co-Al_2O_3$ cermet coatings with Al_2O_3 as antireflection layer employing co-evaporation of Co and the absorptance and emittance values for optimized $Co-Al_2O_3$ cermet are ~ 0.94 and ~ 0.04 at 100°C respectively [Niklasson and Granqvist, 1983]. Several other cermet coatings such as $Ag-Al_2O_3$, $Cr-Al_2O_3$ and $Au-Al_2O_3$ etc., have also been reported for solar thermal applications [Mckenzie, 1979].

2.3.1.2 Sputtering

Sputtering or sputter deposition relies on the sputtering or etching of target particles from its surface by the physical sputtering process. In this process, surface atoms are physically ejected from a solid surface by transferring momentum from the atomic sized energetic particles bombarding onto the target surface. It is an extensively employed technique for large area deposition for spectrally selective absorber coatings. In sputter deposition, control on film uniformity is relatively easier as compared to the evaporation deposition, especially in case of large area depositions. Several coating structures have been investigated for absorber applications. For example, $Cr-Cr_2O_3$ cermet coating with Cr_2O_3 as an antireflection coatings on nickel coated stainless steel (SS) substrate has been developed using sputtering process, with enhanced solar thermal properties such as absorptance $\alpha = 0.98$ and emittance $\varepsilon = 0.08$ at 100°C [Fan and Spura, 1977]. A multilayer stainless steel – Carbon (SS-C) coating is developed by Harding et al, with high absorptance ~ 0.94 - 0.95 and low emittance ~ 0.05 - 0.06 values at room temperature [Harding, 1979]. Zhang reported an optimized Al-AlN based three layer cermet coatings, with absorptance, $\alpha = 0.95$, and emittance, $\varepsilon = 0.05$, at 80°C temperature [Zhang, 1999].

2.3.1.3 Arc Evaporation

A high current and low voltage *dc* arc is used to evaporate the cathodic (cathodic arc) or anodic (anodic arc) electrode material. The evaporated electrode material is used to deposit on a substrate. The substrate is biased to accelerate the ionized materials vapor. This process has extensively been used to deposit different metallic and compound thin films for various applications. However, one of the major disadvantages of this technique is the emission of macro particles from metal electrodes, which affects the optical properties of a solar selective coating. Yin et al. employed cathodic arc evaporation technique and prepared Al-AlN and a-C:H-SS (hydrogenated amorphous carbon – stainless steel) metal-ceramic structures on different substrates. Al-AlN metal-ceramic coating with AlN anti reflecting coatings exhibited good

absorption of ~ 0.90 and emittance of ~ 0.06 at room temperature. However, a-C:H-SS cermet with a-C:H antireflection coating exhibited very low reflection in the visible region and thus high absorption > 0.95 in conjunction with relatively lower emittance values [Yin *et al.*, 1996].

2.3.1.4 Ion Plating

In this process, highly energetic atomic–sized particles are periodically bombarded on the substrate to deposit the desired thin film structures. The flux and mass of the bombarding species, ratio of bombarding particles to the depositing particles on the substrate are important process variables for the deposition of thin film structures [Mattox, 1997]. Ion plating system has been employed to develop TiA/TiAlN/TiAlON/TiAlO spectrally selective coating by Lei et al., coated on SS and Cu substrate and showed high absorptance of 0.90 and low emittance of 0.08 - 0.19 values. These structures are stable in air up to 650ºC for 1hour [Lei *et al.*, 2009].

2.3.1.5 Pulsed Laser Deposition

Pulsed laser deposition (PLD) is a very simple and elegant deposition technique and has been employed to deposit a broad range of materials such as optical coatings, high temperature superconducting, magneto-resistive, metallic and insulating thin film structures [Cheung, 1994; Tang *et al.*, 2010]. However, the major disadvantage of PLD technique is the available deposition area, which is relatively smaller than that of other deposition methods [Cheung, 1994]. Therefore, PLD technique has not been used extensively to deposit spectrally selective absorber coatings. Limited literature is available, where PLD technique has been employed to deposit cermet based spectrally selective coatings. Chen et al. have studied the optical properties of Ti:Al$_2$O$_3$ selective coatings deposited using PLD and shown very low reflectance in the visible region and very high reflectance in the infrared region [Chen *et al.*, 2008].

2.3.2 Chemical Vapor Deposition (CVD) and Plasma Enhanced CVD

In this process, atoms or molecules of interest are deposited by using the high temperature decomposition of a chemical vapor precursor. The high temperature thermal activation is used to achieve the desired decomposition of a chemical vapor precursor, whereas reduction is carried out by using hydrogenous environment at elevated temperatures. However, in the case of plasma enhanced CVD, plasma can be used to induce decomposition and reactions [Mattox, 1997]. In general, CVD technique has been used to produce coating structures for the electronic applications. However, different CVD processes have been investigated to synthesize the absorber coatings including borides, carbides, oxides and nitrides of transition and other metals [Lampart, 1979; Kennedy, 2010]. For example, SiC:H thin films are grown from Ar/tetramethylsilane plasma enhanced chemical CVD as absorber layers for high temperature solar receiver applications including the seven layer stacks with alternating metal and SiC:H layers. The structure showed high absorptance ~ 0.92 and low thermal emittance of ~ 0.08 at 500ºC [Glaude *et al.*, 2013].

2.3.3 Electrochemical Deposition Technique

Electrochemical deposition techniques such as electrodeposition (electroplating) and anodic oxidation have been extensively employed to develop spectrally selective absorber coatings. However, very few researchers have used electroless deposition technique for spectrally selective coatings. These techniques are briefly described for their applications in the development of spectrally selective coatings:

2.3.3.1 Electrodeposition Technique

Electrodeposition is an electrolytic process, where metal ions are moved in the solution by applying an electric field to deposit on one of the electrode. The substrate to be coated is termed as a cathode in the electrodeposition cell. Electrodeposition has been extensively used to develop the absorber coatings, especially black chrome ($Cr-Cr_2O_3$). In electrodeposition process, the performance of deposited solar selective coatings are affected by the several deposition parameters such as plating current density, bath temperature, plating time, substrate etc. However, an environmental concern is a major challenge with electrodeposition. The process is well suited for electrically conducting substrates. However, insulating substrates such as glass and ceramics cannot be coated using electrodeposition [Atkinson *et al.*, 2015]. It has also issues of non-uniform film thickness and high thermal emittance.

2.3.3.2 Anodic Oxidation Technique

It is also an electrochemical process for the deposition of oxide films on the conducting substrates. In this process, electrons are repelled from an electrode, which oxidizes the anode in an electrolyte to produce a coating. For example, anodization of aluminum is carried out in an aqueous solution of H_2PO_4 acid. Aluminum is used as an anode and immersed in the electrolyte and connected to the electrical circuit. A porous oxide layer is formed on the aluminum substrate. The anodized alumina is partially covered by metallic nanoparticles using electrodeposition to enhance the selectivity and absorptivity in the desired wavelength range.

Balin et al., reported the detailed experimental and theoretical study on solar selective surfaces, produced by anodization and cobalt 'Co' coloration of Al. The Selective surfaces have shown a very high selectivity, absorptance $\alpha = 0.94$ and emittance $\varepsilon = 0.1$ [Blain *et al.*, 1985]. Andersson et al., have discussed a novel selective surface for efficient photothermal conversion of solar energy, comprised of Ni pigmented anodic Al_2O_3 coatings on Al sheet [Andresson *et al.*, 1980].

2.3.4 Sol-gel Technique

Sol-gel technique is a chemical process and has been extensively used for spectrally selective absorber coatings' development. Sol-gels are colloidal solutions of constituent elements, where viscosity of the solution is controlled by using different solvents, required for deposition of the desired film structures. Mostly metal alkoxides are used for synthesizing the gels. This process is attractive for receiver tubes and absorbers as it can be extended on intricate shapes and sizes, employing simple dipping or spray coatings techniques. The thickness of coatings can be tailored from few hundreds of nm to several micrometers. In terms of fabrication, there are different deposition options such as dip coating, spin coating, spray coating, flow- and roll- coatings, which can be used to coat a surface. However, industrially viable processes are spray-, flow- and roll- coatings techniques. Sol-gel processing does not usually need expensive vacuum equipment and allows coatings of oxides at relatively low temperatures [Atkinson *et al.*, 2015]. Kaluza et al., prepared a novel black coloured coating with $CuCoMnO_x$ compositions using sol-gel technique on Al substrate showing $\alpha = 0.9$ and $\varepsilon = 0.05$ [Kaluza *et al.*, 2001].

2.3.5 Painting

Painting is an extremely simple process, where materials in liquidous states can simply be painted and dried to get the desired solar thermal properties. A paint solution usually consists of desired materials in organic solvents. The distribution of particles and their sizes are important to control the rheological properties of the paints, which may affect the solar thermal properties of the painted structures. In addition to the constituent elements, binder is also used in paint solutions to enhance the adhesion properties of paint materials with the substrates. The physical properties of painted film structures depend on the paint composition, solvent and binder components and their appropriate ratios etc. These individual components are very important for the synthesis of thin film structures with desired thermophysical properties. High

quality black paint, e.g. Pyromark, has been developed and still in use for high concentration solar tower applications [Atkinson *et al.*, 2015]. FeMnCuO$_4$/Silicon binder, PbS/polyacrylin resin are typical materials, used for painted coatings. The painting technique is an easy and low cost process, suitable for large scale applications. However, the major disadvantage of painted coatings is the relatively large emittance values and very poor bonding of selective surface with the substrate, causing peel off with time.

2.4 HISTORICAL DEVELOPMENT OF SPECTRALLY SELECTIVE ABSORBER SURFACES

The basic concept of spectrally selective coatings was developed by H. Tabor, J. T. Gier and R. V. Dunkel for efficient photothermal conversion during mid- 1950s [Tabor, 1956, 1961; Gier, 1958]. Initially, coatings were successfully developed for flat plate collectors including black nickel, black chrome and black copper oxides using different fabrication methods. Electrochemical deposition has shown promise for such coatings with high absorptance and relatively higher emittance, as compared to the other physical processes. Solar absorptance (α) and thermal emittance (ε) of electroplated black nickel onto a bright nickel plated copper are 0.901 and 0.05 at T = 20°C respectively [Tabor, 1956; Gier and Dunkle, 1958]. The extensive research on solar selective absorber coatings was carried out in late 1970s, after realizing oil crunch [Boffey, 1970]. The alternative renewable energy sources were attracting attention and among them, solar thermal has been realized as the potential candidate. Thus, the development of selective surfaces became essential for the solar thermal energy applications. Several types of absorber surfaces such as intrinsic absorber, absorber – reflector tandem and semiconductor – reflector tandem, multilayer interference stacks, optical trapping systems, composite material films, and quantum size effect based structures are developed by researchers across the globe. There is no such material, which may exhibit the ideal solar selective properties. However, there are several materials, which show very high selectivity. Due to physical properties of materials, intrinsic solar selective properties can be found in two types of materials such as transition metals and semiconductors. Mostly, metals have a plasma reflection edge at about 0.3 μm, it can be shifted towards infrared side by creating internal scattering centers. Moreover, tungsten (W) metal is one of the most wavelength selective metals [Agnihotri and Gupta, 1981]. On the other hand, by using the highly degenerate semiconductors, it may be possible to shift plasma frequency in the infrared region [Dixit *et al.*, 2009]. Absorber – reflector tandem surface, show high absorptance in the solar wavelength range and deposited on a highly reflective metal substrate. The onset of high absorption in the exterior coatings may be either of intrinsic nature or geometrically enhanced or the combined effect. Seraphin and Meinel have discussed the basic requirements of absorber – reflector tandem structures in detail [Seraphin and Meinel, 1976]. In the case of Semiconductor – reflector tandem selective surfaces, a thick semiconductor film is coated on an opaque metal having high thermal infrared reflectivity. Semiconductor films with energy band gap of about 0.5 eV (2.5 μm) to 1.26 eV (1.0 μm), could absorb radiation but transparent to IR radiation. The spectral selectivity in multilayer stack is a result of multiple passes through the dielectric layers of the stack sandwiched between semi transparent and totally reflecting surface. Meinel and Meinel have discussed the basic physics of multilayer stacks [Meinel and Meinel, 1977]. In optical trapping systems, surface texturing is a usual technique to get physical wavelength discrimination optical trapping of solar energy. Composite spectrally selective coatings, such as cermets, where small metal particles embedded in a dielectric matrix, have good optical properties for spectrally selective coatings. Cermet surfaces absorb maximum solar spectrum due to the interband transition in metal and the small particle resonance, while they are transparent in the thermal infrared region. Resonant scattering depends upon both the size and optical properties of the particles and surrounding medium. Quantum size effects occur in ultrathin films of degenerate semiconductors, resulting into the high solar absorptance and simultaneously high thermal reflectance. The detailed mechanism of optical properties of spectrally selective coatings is discussed by Agnihotri and Gupta, Seraphin and Kennedy [Agnihotri and Gupta, 1981; Seraphin, 1979; Kennedy, 2002]. In this section, we give an overview of historical developments of spectrally selective absorber

surfaces. Historical development of spectrally selective coatings categorized on the basis of temperature range such as low, mid and high temperature applications. We classified the temperature ranges based on their applications such as low temperature range is less that 200°C (T < 200ºC), mid-temperature range is more than 200°C but less than 350ºC (200°C < T < 350ºC) and high temperature range is greater than 350ºC (T > 350°C).

2.4.1 Low Temperature (T < 200°C) Spectrally Selective Absorber Materials

Normally, low temperature spectrally selective surfaces are used in water heating applications. Black nickel (Ni-Zn-S alloy) solar selective surfaces are used in absorber – reflector tandem structures since 1955 and commercialized long back for solar water heating applications [Agnihotri and Gupta, 1981]. Chronological development of low temperature spectrally selective surfaces is summarized in Table 2.1. The black nickel absorber structures are stable at relatively low temperatures. However, it starts degrading in the humid and high temperature environments, especially at or above 200ºC and thus, poor humidity resistant structure [Wäckelgård, 1998]. Black copper oxide (CuO) based spectrally selective absorber surfaces have also been developed in 1956 by Tabor et al. and later commercialized for industrial applications. High-temperature stability of the coatings is limited due to the defoliation and corrosion instability [Agnihotri and Gupta, 1981]. Table 2.1 illustrates the chronological developments of copper oxide spectrally selective coatings, using different synthesis techniques. Thickness sensitive and thickness independent spectrally selective surface, nanocomposite material such as carbon embedded dielectric matrices, and nickel composite based spectrally solar selective coatings are also developed for low-temperature photothermal applications. The development of such coatings is also summarized in Table 2.1.

Table 2.1 : Historical developments of low temperature solar selective coatings

S. No.	Substrate	Deposition Technique	Absorptance (α)	Emittance (ε)	References
Black Nickel (Ni- Zn-S alloy)					
1	SS	Electroplating	0.84	0.18	McDonald and Curtis, 1976
2	Nickel	Electroplating	0.96	0.007	Borzoni, 1976
3	316L SS	Electrodeposition	0.91	0.1	Lira-Cantú *et al.*, 2005
Black Copper Oxide (CuO)					
4	SS	Electroplating	0.98	0.05	Bhowmik *et al.*, 2001
5	Copper	One-step chemical conversion method	0.94	0.08	Xiao *et al.*, 2011
6	Copper	Facile Chemical oxidation	> 0.95	<0.07	Karthick Kumar *et al.*, 2013
Thickness Sensitive Spectrally Selective (TSSS) Coatings					
6	Aluminum	Coil-coating	0.92	0.38	Orel *et al.*, 1990

		processes			
7	Aluminum	Coil-coating processes	0.92	0.15	Orel *et al.*, 1991
8	Aluminum	Draw bar coater	0.90-0.92	0.2-0.25	Crnjak Orel *et al.*, 1996
9	Aluminum	Spray	0.90	0.20	Kunič *et al.*, 2011
Thickness Independent Selective Surfaces (TISS)					
10	Metal sheet	Sol-gel	0.90	0.3	Japelj *et al.*, 2008
Carbon Embedded Dielectric Matrix Based Selective Surfaces					
11	Aluminum	Sol-gel	0.71 & 0.84	0.06 & 0.04	Katumba *et al.*, 2008
12	Aluminum	Sol-gel	0.85	0.05	Roro *et al.*, 2012
13	Aluminum	Sol-gel	0.84	0.2	Roro *et al.*, 2012b
Nickel Composite Based Selective Surfaces					
14	Copper	Electrodeposition	0.94	0.08	Tharamani and Mayanna, 2007
15	FTO glass	Electrodeposition	0.83	0.14	Klochko *et al.*, 2015
Novel Black Coloured (CuCoMnO$_x$) Composite Selective Coatings					
16	Aluminum	Sol-gel	0.9	0.05	Kaluza *et al.*, 2001
Nanogold Containing Selective Coatings					
17	Copper	Solution chemical technique	0.86	0.09	Chang *et al.*, 2013

2.4.2 Mid-Temperature (200°C < T < 350°C) Spectrally Selective Absorber Materials

Mid-temperature spectrally selective absorber surfaces are employed for industrial applications such as process heat, desalination etc.. Several spectrally selective absorber materials and structures are developed and commercialized for mid-temperature applications. Black chrome (BC) is one of the most studied spectrally selective absorber surfaces for photothermal applications. MTI (Materials Technology Inc.) has commercialized the BC solar selective coatings deposited on Ni-coated Cu substrate in the United States (US). Chrome Coat in Denmark and Energie Solaire in Switzerland have also developed BC selective surface on Cu and SS substrates [Brunold *et al.*, 2000]. NASA Lewis research center has shown electroplated decorative finishing, known as BC, with desired solar selective properties. Here BC was deposited on dull nickel modified substrates or directly on rough surfaced substrates, to increase the absorptance in the visible spectral region [McDonald, 1974]. The optimum plating time with current density 180 Ams/ft^2 (0.19 A/cm^2) is around one to two minutes, which

resulted into the coating surfaces with optimal combination of the highest absorbance and the lowest radiative losses [McDonald and Curtis, 1975]. The best selectivity has been reported for 1.0 micron thick BC selective film on copper and 0.7 microns thick BC on nickel substrates. In these plated BC structure, a suspension of metallic chromium particles has been observed with particulate size ranging between 0.05 – 0.30 microns. There is no degradation in reflectivity and microstructural properties in these coatings below 300°C temperature. However, BC selective coatings degraded drastically after heat treatment in the range of 500°C – 600°C temperature even for 1 hour, both in air and vacuum [Lampart, 1978; 1979]. The optical properties of BC selective films also depend on the microstructure of electrodeposited BC films and a change in the microstructure of the absorber at elevated temperatures is the principal region for degradation of their solar thermal response [Ignatiev *et al.*, 1979]. Degradation of electrodeposited BC coatings can be understood in two ways: (i) at low temperature (< 300°C), a reduction in deposited hydroxide to oxide with desorption of H_2O and H_2, causing an upward shift of infrared response and thus, enhancement in the infrared emittance and (ii) the high-temperature oxidation of the fine chromium crystallites comprising the coatings, resulting into the optical degradation in the visible range and thus a decrease in solar absorption [Zajac *et al.*, 1980]. The thermally treated BC selective coatings showed minor changes below 300°C in air even for more than 100 hours continuous heat treatment. However, above 300°C in both air and vacuum, there is pronounced degradation. The main reason of this degradation is the diffusion of environmental oxygen, causing conversion of metallic chromium particles into Cr_2O_3 leading to poor spectral selectivity [Lampart, 1980]. Optical properties of BC coatings also change due to substrate surface topography in near–infrared reflectance. However, the visible reflectance is insensitive to these changes [Axelbaum and Brandt, 1987; Sebastian *et al.*, 1997]. The selective absorption in BC coatings is dominated by the finely distributed metallic chromium particles inside the chromium oxide matrix. Lee et al. attributed the observed optical degradation to the conversion of chromium into chromium oxide at the surface of the BC coatings [Lee *et al.*, 2000]. As deposited BC selective surfaces have trivalent chromium hydroxide and chromium in the form of chromates. However, previous studies also suggested the presence of hydroxides and metallic chromium in these BC structures. The major component, chromium hydroxide is converted to Cr_2O_3 after annealing at 400°C by losing water vapors [Anandan *et al.*, 2002]. Bayati et al. designed electrochemical bath using chromium trivalent ion instead of toxic hexavalent ions [Bayati *et al.*, 2005]. Thick BC layers (~ a micron) are successfully electroplated on stainless steel substrates form trivalent chromium salt, where BC structure consist of Cr, Cr_2O_3, CrO_3, and $Cr(OH)_3$. These structures exhibit good absorptance properties ~ 0.97 and moderate emittance ~ 0.1 [Hamid, 2009; Eugenio *et al.*, 2011]. The developments of mid-temperature spectrally selective coatings are summarized in Table 2.2.

Table 2.2 : Historical developments of mid-temperature solar selective coatings

S. No.	Substrate	Deposition Technique	Absorptance (α)	Emittance (ϵ)	References
center: **Black chrome (Cr-Cr$_2$O$_3$)**					
1	SS	RF sputtering	0.9	0.1	Fan and Spura, 1977
center: **Metal-doped Alumina (M-Al$_2$O$_3$) cermet based solar selective coatings**					
2	Al	Anodization	0.93-0.96	0.10-0.20	Andersson *et al.*, 1980
3	Al	Anodization	0.96	0.20	Li, 2000
4	Al	Anodization	0.93	0.03	Boström *et al.*, 2004
5	Al	Anodization	0.94	0.1	Blain *et al.*, 1985; Zhang and Mills, 1992; Cuevas *et al.*, 2014
6	Al	Anodization	0.85	0.1	Möller and Hönicke, 1998
center: **Metal-doped aluminum nitride (M-AlN) Cermet and AlN Multilayer Based Solar Selective Coatings**					
7	Glass	DC magnetron sputtering	0.93-0.96	0.03-0.04	Zhang *et al.*, 1998
8	Glass and Copper	Plasma enhanced chemical vapor deposition (PECVD)	0.95	0.05	Rebouta *et al.*, 2012
9	Silicon (Si)	RF/DC sputtering	0.94	0.04	Du *et al.*, 2011
10	Quartz	Reactive DC Sputtering	0.82-0.94	0.05-0.27	Wu *et al.*, 2013
11	SS	Reactive DC Sputtering	0.938	0.099	Feng *et al.*, 2015a
center: **NbTiON/SiON Selective Absorber**					
12	Copper (Cu)	Magnetron Sputtering	0.95	0.07	Liu *et al.*, 2012
center: **CrN$_x$O$_y$/SiO$_2$ Selective Absorber**					
13	Cu & Si	DC magnetron Sputtering	0.947	0.050	L. Wu *et al.*, 2013
center: **CrMoN/CrON**					
14	SS & Al	Sputtering	0.90-0.92	0.13-0.15	Selvakumar *et al.*, 2013

15	Al	Magnetron Sputtering	0.78	-	Gaouyat *et al.*, 2013
Ultrafine Chromium Particles as Selective Absorber					
16	KBr	Evaporation	0.97	0.19	Granqvist and Niklasson, 1977
Carbon-Silica Nano-composite Selective Absorber					
17	Glass	Sol-gel	0.94	0.15	Katzen *et al.*, 2005
Cr-O (Cr-CrO) Cermet Selective Coating					
18	Al	Planar DC magnetron	0.92-0.95	0.09-0.10	Lee, 2006
$Cr_xO_y/Cr/Cr_2O_3$ Selective Absorber					
19	Cu	Pulsed Sputtering	0.899-0.912	0.05-0.06	Barshilia *et al.*, 2008
20	Al	Electrochemical Process	0.923	0.06	Ding *et al.*, 2010
Cu-Co-Mn-Si-O Black Selective Surface					
21	SS	Sol-gel (dip-coating)	0.95	0.12	Joly *et al.*, 2013
TiN/TiSiN/SiN Selective Absorber					
22	SS	DC reactive Magnetron Sputtering	0.95	0.04	Feng *et al.*, 2015b
MgO/Zr/MgO Multilayered Selective Absorber					
23	SS	e-beam evaporation	0.92	0.09	Nuru *et al.*, 2015
$W-SiO_2$ and $Nb-TiO_2$ Cermets Selective Absorber					
24	SS	RF/DC Sputtering	0.91/0.93	0.08/0.09	Wäckelgård *et al.*, 2015

Among these mid-temperature spectrally selective coatings, aluminum oxide (Al_2O_3) (alumina) is another extensively studied ceramic material. This can be converted into metal-ceramic (cermet) structures using different metal particles in the host matrix. Several metals, such as Ni, V, Cr, Co, Cu, Mo, Ag, Si, and W have been investigated in conjunction with aluminum oxide (Al_2O_3) for cermet structures [Möller and Hönicke, 1998]. For example, nickel (Ni)-pigmented alumina (Al_2O_3) based selective surfaces are broadly studied and commercialized by Tekno Term Energi in Sweden and Showa in Japan for photothermal applications. Developments of Ni-pigmented aluminum oxide spectrally selective coatings are summarized in Table 2.2 (S.No. 2, 3, 4, 5, & 6). In nickel pigmentation, nickel metal nano particles are introduced electrochemically into the porous alumina structures. The optical properties of hybrid structures depend on the nickel content to get the desired optical properties. However, nickel insertion along the pores of anodized aluminum is not necessary for good optical performance [Salmi et al., 2000], because selectivity in Ni-Al_2O_3 coatings is due to the composition of Ni/alumina composite and interference effect [Galione et al., 2010]. Pigmentation with Ni acetate resulted in better emittance values as compared to Ni sulfate. However, both nickel precursors based structures are relatively insensitive to the solar absorptance values for these structures [Suzer et al., 1998]. Metal-doped aluminum nitride (M-AlN) cermet based solar selective coatings have also been extensively studied for photothermal application and developed for both mid and high-temperature applications. The progress in M-AlN cermet selective absorbers is summarized in Table 2.2 (S. No. 7 to 11). These spectrally selective coatings are commercialized by China for the mid-temperature solar thermal application.

Several coatings with tandem structures such as cermet, multilayered etc. have also been explored for mid-temperature solar thermal applications, which are summarized in Table 2.2 (S. No. 12 to 24). In multilayer metal-dielectric graded index solar selective coatings, improvement in solar absorptance is due to the destructive interference effects within the coatings [Farooq and Hutchins, 2002]. The main durability load for a solar absorber is the operating temperature and stagnation temperature [Köhl et al., 2004]. Spectrally selective coatings of carbon nanoparticles embedded in SiO_2, ZnO, and NiO matrices are fabricated by using the sol-gel technique on aluminum substrates. The NiO based absorber surface exhibited optimal solar selective behavior, followed by ZnO and then SiO_2 based coatings. The NiO-based absorbers also exceeded the solar selectivity of SOLKOTE commercial paint coatings on the aluminum substrate [Katumba et al., 2008a]. The metal-dielectric film structures exhibit good spectral selectivity with solar absorption efficiency higher than 0.95 in the 400 - 1200 nm wavelength range [Zhou et al., 2012] and can be used for mid-temperature solar thermal applications.

2.4.3 High Temperature (T > 350°C) Spectrally Selective Absorber Materials

High temperature spectrally selective absorber materials are extremely important for their potential use in concentrated solar power (CSP) system for power generation. The efficiency of CSP plants strongly depends on the optical properties and thermal stability of the spectrally selective absorbers. The spectrally selective absorber materials should have high absorptance (> 0.95), low emittance (< 0.10), not only at room temperature but also at high temperatures. These structures should also show good thermal stability above 400°C in air and vacuum. The selective absorber materials should exhibit high oxidation resistance and chemical inertness over the operating temperature range. The low emittance at high-temperature is very important as the thermal radiative losses from the absorber are proportional to the fourth power of temperature (T^4) [Duffie and Beckman, 1991]. Several high temperature spectrally selective absorber materials are developed with time and are summarized in Table 2.3 (S. No. 1 to 35). Optical properties of the high temperature spectrally selective absorber films usually starts degrading due to the diffusion of environmental oxygen into absorber layers and oxidizing the metal content inside the absorber layers. In addition, the substrate material may start diffusing into the absorber structures at higher temperatures (>400°C) [Cheng et al., 2013].

Table 2.3 : Historical developments of high-temperature solar selective coatings

S. No.	Substrate	Deposition Technique	Absorptance (α)	Emittance (ε)	References
MgO/Au Cermet Selective Absorber					
1	SS	RF sputtering	0.9	0.1	Fan and Zavracky, 1976
M-Al$_2$O$_3$ (M = Au, Ag, Cr, Cu) Cermet Selective Surfaces					
2	Glass	Co-evaporation	0.90	0.05	McKenzie, 1979
3	Quartz	Co – evaporation	0.98	-	Craighead et al., 1981
4	Cu	Co-evaporation	0.95	0.1	Niklasson and Granqvist, 1982; 1983a ; 1984c
Pt – Al$_2$O$_3$ Cermet Selective Absorber					
5	SS	RF Co-Sputtering	0.92	0.14	Vien et al., 1985
Co – Al$_2$O$_3$ Isotropic Cermet Sub-layers Selective Absorbers					
6	Cu and glass	e-beam evaporation	0.90	0.024	Zhang and Mills, 1992b; 1992c
MoSiO$_2$/Al$_2$O$_3$ and Pt/Al$_2$O$_3$ Multilayer Selective Absorber					
7	Si, quartz, and alloys	RF sputtering	0.95 and 0.92	0.08 to 0.2 and 0.14	Schön et al., 1994
Al$_2$O$_3$ Cermet Selective Absorber					
8	Glass	Co-evaporation	0.955	0.032	Zhang et al., 1996
Cr-Cr$_2$O$_3$ and Mo-Al$_2$O$_3$ Based Layered Cermet Selective Absorber					
9	Cu and Glass	DC Sputtering	0.88 to 0.94	0.15 to 0.04	Teixeira et al., 2001
Zr-ZrO$_2$ Cermet Selective Absorber					
10	Glass	DC reactive sputtering	0.96	0.05	Zhang et al., 2003
Ti-Al$_2$O$_3$ Cermet Selective Absorber					
11	Nickel	Ion beam sputter deposition	0.93	0.09	Shumway et al., 2003
Mo-SiO$_2$ Cermet Selective Absorber					
12	SS and Glass	Sputtering	0.94	0.13	Esposito et al., 2009
HfO$_x$/Mo/HfO$_2$ Multilayer Selective Absorber					
13	SS & Cu	Magnetron Sputtering	0.902-0.917	0.15-0.17	Selvakumar et al., 2010

**Ag – Al$_2$O$_3$ Nano-Cermet Spectrally Selective Absorber**					
14	Cu, Si & Glass	Magnetron Sputtering	0.93	0.04-0.05	Barshilia *et al.*, 2011
**Pt – Al$_2$O$_3$ Cermet Selective Absorber**					
15	SS	RF Sputtering	0.98	0.05	Nuru *et al.*, 2012
**Al$_x$O$_y$/Pt/Al$_x$O$_y$ Multilayer Selective Absorber**					
16	Glass, Si & Cu	e-beam vacuum evaporator	~ 0.94 ± 0.01	~ 0.06 ± 0.01	Nuru *et al.*, 2012
**Mo-SiO$_2$ Cermet Selective Absorber**					
17	Glass	Sputtering	0.95	0.15	Zheng *et al.*, 2013
**Al$_x$O$_y$/Pt/Al$_x$O$_y$ Multilayer Selective Absorber**					
18	Cu	e-beam vacuum evaporator	0.951	0.09	Nuru *et al.*, 2014
**Al$_x$O$_y$–AlN$_x$-Al Selective Absorber**					
19	Quartz glass	DC Magnetron Reactive Sputtering	0.94	0.07	Yue *et al.*, 2003
**TiAlN/TiAlON/Si$_3$N$_4$ Tandem Selective Absorber**					
20	Cu	Magnetron Sputtering	0.95	0.07	Barshilia *et al.*, 2006
**Ti$_{0.5}$Al$_{0.5}$N/Ti$_{0.25}$Al$_{0.75}$N/AlN Selective Absorber**					
21	Si	RF/DC Magnetron Co-sputtering	0.945	0.04	Du *et al.*, 2011
**TiAlN/TiAlON/SiO$_2$ tandem Selective Absorber**					
22	Cu and glass	DC Magnetron Sputtering	0.955	0.05	Rebouta *et al.*, 2012b
**HfMoN(H)/HfMoN(L)/HfOH/Al$_2$O$_3$ Tandem Selective Absorber**					
23	SS	Magnetron Sputtering	0.94-0.95	0.13-0.14	Selvakumar *et al.*, 2012
**Ti/AlTiN/AlTiON/AlTiO Multilayer Selective Absorber**					
24	SS	Magnetron Sputtering	0.933	0.16-0.17	Barshilia, 2014
**TiAlCrN/TiAlN/AlSiN Multilayer Selective Absorber**					
25	SS	Cathodic Arc	0.91	0.07	Valleti *et al.*, 2014
**SS-(Fe3O4)/Mo/TiZrN/TiZrON/SiON**					

26	SS	Reactive DC/RF Magnetron Sputtering	0.92	0.08	Liu *et al.*, 2014
Al$_2$O$_3$:W Cermet Layers and AlSiN/AlSiON Bilayer Selective Absorber					
27	SS	Magnetron Sputtering	0.93-0.95	0.07-0.01	Rebouta *et al.*, 2015
NbTiON/SiON Selective Absorber					
28	Cu	Magnetron Sputtering	0.95	0.07	Liu *et al.*, 2012
Cr-Al-O Tandem Nano-multilayer Composite Selective Absorber					
29	SS & Si	Cathodic Arc ion plating	0.924	0.21	Liu *et al.*, 2014
AlCrNO Selective Absorber					
30	SS	Cathodic Arc Plating	0.93	0.20	Gong *et al.*, 2015
CrAlO Selective Absorber					
31	SS	Cathodic Arc Ion Plating	0.918-0.924	0.154-0.170	Liu *et al.*, 2015
SS-AlN Cermet Selective Absorber					
32	Glass	Sputtering	0.94-0.95	0.04-0.05	Zhang, 1998; Zhang *et al.*, 1998
ZnO/black ZnO Selective Absorber					
33	Glass	Sputtering	0.90	0.26	Brett, *et al.*, 1986
Mo-Si$_3$N$_4$ Selective Absorber					
34	SS & Si	Sputtering	0.926	0.017	Céspedes *et al.*, 2014
Carbon Nanotube Based Selective Absorber					
35	SS, Cu, Ni & Cr	Spray	>0.92	<0.01	Abendroth *et al.*, 2015

Furthermore, an electrodeposited Co_3O_4 selective absorber coating has shown an absorptance > 0.90 and an emittance < 0.2, with enhanced thermal stability at 650°C for 1000 hours [McDonal, 1980]. A new Si–Ge selective coating structures based on multi-scaled semiconductor nanostructures are designed and fabricated, exhibiting high absorptance for short-wavelength photons and efficient reflection for long-wavelength photons [Moon *et al.*, 2014]. A black oxide structure with cobalt oxide nanoparticles, embedded in a dielectric matrix through a scalable spray coating has shown high thermal efficiency of 88.2%. These structures are thermally stable and do not show any degradation even at 700°C in the air after 1000hrs annealing [Moon *et al.*, 2015].

Large numbers of spectrally selective coatings have been developed for high temperature solar thermal applications, as discussed above. However, few of them such as Mo-SO_2, W-Al_2O_3, Mo-Al_2O_3 and M-AlN where M: SS, W, Mo cermets have been successfully commercialized and are being used in evacuated tubes for solar thermal power generation. The Mo-Al_2O_3 cermet selective coatings coated receiver tubes are produced by Luz International Ltd., USA and are used in Solar Energy Generating System power plants. The coatings exhibited an absorptance of 0.96 and emittance of 0.16 at 350°C. However, this Mo-Al_2O_3 cermet structure has limited thermal stability in the air up to 300°C [Lanxner and Elgat, 1990]. SS, W, and Mo-AlN based selective coatings are commercially developed by TurboSun, exhibiting ~ 0.92-0.94 solar absorptance and ~ 0.08-0.10 emittance at 350°C. Mo-SiO_2 and W-Al_2O_3 based spectrally selective coatings are developed by Archimede Solar Energy (ASE), Italy with relatively enhanced solar absorptance > 0.94 and emittance < 0.13 at 580°C.

2.5 IDENTIFIED GAPS

The detailed literature review has been presented on the development of spectrally selective coating for different temperature ranges. There are several coatings developed and have shown promise for enhanced solar thermal performance. However, these spectrally selective absorber materials suffer from thermal stability and show respective degradation in their thermal/optical performance at temperatures 350°C or above in air or even in vacuum/inert environments. The adhesion between the substrate and adjacent layers starts degrading with thermal cycling. In addition, the diffusion of chemical elements from the substrate and oxygen from external environment degrade the absorber composition, resulting into the poor selectivity performance such as absorptance and emittance of these coatings. The diffusion of oxygen oxidizes the metallic component in SSCs, and thus leads to the poor emissivity in the infrared wavelength region. The resistance against thermal and mechanical stresses during the thermal cycling is another reason for degrading their performance. The environmental stability factors such as corrosion may also affect the overall performance of the SSCs in long run.

Initially, selective absorber materials were developed by wet chemical methods such as electrodeposition, electroless deposition, anodization, chemical conversion, sol-gel, spray pyrolysis, thickness sensitive, and insensitive selective paints. However, spectrally selective absorbers, developed employing these wet chemical techniques, have faced the problem of higher chemical and thermal stability because of the relatively poor surface and adhesion qualities of SSCs. Also, these processes are not very environmentally friendly because of hazardous chemicals use and huge chemical waste after the process. Considering such issues, physical vapor deposition has been considered as one of the alternative techniques to developed spectrally selective absorbers. The developed SSCs are of relatively superior quality and exhibit long term thermal and environmental stability. However, the development of physical vapor deposition process for arbitrary and large surfaces is very challenging and not cost effective. The materials related challenges and associated technological issues need to be addressed for realizing the enhanced solar thermal performance of the developed spectrally selective structures. Thus, the design and development of a suitable material with desired solar thermal

performance with enhanced thermal and environmental stability are essential to meet the requirements. These challenges will be addressed by considering the following approach:

1. Development of novel materials for absorber applications exhibiting high solar absorptance > 0.95 and low thermal emittance < 0.05 with enhanced thermal and environmental stability for possible applications.

    This will include the development of multilayered and nanostructured modified thin films of metal/ceramic hybrid structures using different synthesis approaches.

2. Development of low cost deposition process, especially for low to mid temperature suitable spectrally selective coatings, basically for large scale applications with improved physical properties.

    The most widely investigated black chrome SSC suffers from corrosion and thermal instability under adverse operating conditions such as saline environment and high operating temperature > 350°C conditions. These can be mitigated by using the thermally stable additives to the coating structures without hampering the solar thermal performance.

3. High temperature spectrally selective absorber structures exhibit poor thermal stability and show degradation at a higher temperature in both inert and open ambient. Also, these SSCs exhibit poor environmental stabilities.

    These can be mitigated by using the combinations of refractory materials in both either cermet or multilayer hybrid structures with thermally stable anti-reflecting coatings.

2.6 SUMMARY

The spectrally selective absorber materials are coated on absorber tubes of the solar thermal energy conversion system. It is the essential part of the solar thermal energy conversion system and has a great impact on both the efficiency and the cost of solar thermal systems. Therefore, there is an increasing demand for spectrally selective absorber materials and coatings for low, mid- and high-temperature solar thermal applications. Here, we have presented the basic concepts and the availability of electromagnetic radiation, such as solar and thermal radiation. Furthermore, the introductory concepts of deposition techniques are presented, used for the development of spectrally selective coatings. In the final part, the historical developments of spectrally selective absorber materials are discussed for low, mid- to high-temperature applications. For low to mid-temperature applications, several selective absorber surfaces are developed. Among these, black chrome ($Cr-Cr_2O_3$) is one of the most studied selective absorber surfaces and commercially developed by MTI, in the United States, ChromeCoat of Denmark and Energie Solaire in Switzerland. However, there are several challenges with black chrome structures such as thermal degradation and environmental stabilities at a higher temperature. Similarly, for high-temperature applications, a large number of solar selective absorber materials have been developed. Several research groups across the globe have developed selective absorber materials for high-temperature applications. However, high-temperature stability is still a challenge for these structures. Transition metal carbide and carbonitride may be the good candidates for high-temperature selective surface applications, due to their high-temperature stability and good selectivity.

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