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Introduction

Harvesting solar energy is the current motivation in research to meet the growing demand for energy. World energy demand is continuously increasing, and according to the 2015 World Energy Estimate, it exceeds 13,000 million tons of oil equivalent and is expected to double by 2025 (Petroleum, 2016). With the advancement in technology, the production of renewable energy has increased considerably; still, only 14.1 % of energy requirements worldwide fulfilled using renewable energy. The majority of the energy requirement is fulfilled using conventional energy sources (Petroleum, 2017). Although solar energy is available without any price on the earth's surface, still the use of solar energy in power production is limited up to only 1.3% of global power generation (Petroleum, 2017). So there is a requirement for continuous efforts to explore solar energy as an alternate energy source for possible power generation as well as other distributed applications such as heating and cooling.

1.1 Motivation

The need for alternate energy sources got attention for the first time during the 1970-1980 energy crisis. Further, due to the rapid growth of population as well as industrialization, energy demand keeps on increasing. To fulfill this growing energy demand, conventional fuel such as coal, oil, gas etc. are excessively consumed and thus, causing the fast depletion of fossil fuels. Also, upon consumption, these fossil fuels release greenhouse gases, i.e., CO_2, CH_4, SO_2, NO_2 etc., and the environment gets polluted together with global warming [Abdmouleh et al., 2015]. Due to global warming, the uneven changes in earth climate are observed, causing (i) the melting of glacier, (ii) drought, and (iii) flood [Lior, 2008]. Further, environmental degradation is also affecting the health of human beings. As per the WHO report, directly or indirectly polluted environment is causing the death stall up to 1, 60,000 annually, and more severe impact is expected in the coming years (Mekhilef et al., 2011). So these serious issues drive political leaders and scientific communities to come forward to explore alternative renewable energy sources, which must have no or minimal impact on the environment. Varieties of renewable energy sources are available, e.g., wind, geothermal, biomass, hydropower, and tidal energy. These energy sources have the potential to fulfill the global energy demand [Schnitzer et al., 2007]

Among potential renewable energy sources, solar energy is the most abundant source. The earth receives 89300 TW, which is around 7500 times global energy consumption annually [Tsao et al., 2006, Gadonneix et al., 2013]. The solar energy is usually harnessed using solar photovoltaic and solar thermal technologies. Solar photovoltaic technology is widely adopted to convert solar energy into electricity directly. Whereas, in the solar thermal process, different approaches are used to convert solar energy into thermal energy, which can later be used to generate electricity or for other distributed applications. For the conversion of solar energy into thermal energy, absorbers are used together with infrared reflector layers to minimize the probable thermal losses. An absorber with high solar absorptance and low thermal emittance is called spectrally selective coating (SSAC) [Cao et al., 2014]. Solar thermal energy has been used in numerous applications ranging from low to high-temperatures. Currently, due to high energy demand and increased pollution, solar energy is extensively being investigated and explored in various sectors to fulfill energy requirements with no pollution or say minimum pollution. Till now, CSP plants of about 3 GW capacity are installed or being installed worldwide. Further, solar thermal energy also can be used in heating or cooling application directly, and till now, 300GW of such systems are installed worldwide [Mauthner and Weiss, 2016). In low-temperature range, solar thermal energy is used for water heating applications. There are five types of solar-based water heating systems currently being used for domestic hot water supply. These are thermosyphon systems, integrated collector storage, direct circulation, indirect water heating systems, and air systems. These systems are based on mostly flat plate collectors. Also, solar thermal energy has been used for space heating and cooling application. The space heating systems are similar to that of water heating systems. In an active solar space system, collectors are used for heating the storage units, and fluid for providing thermal energy in a controlled way. Under the space heating system category, the different solar thermal technologies used for space heating are based on air systems, water systems, and heat pump systems. For the preservation of food and medicine at low temperatures and to provide cooling, the solar refrigeration system is being utilized. These distributed systems are advantageous where the source of electricity is not available for providing electricity cooling. These systems are also used for space cooling applications. Further, in low to medium temperature range (80 °C – 240 °C), solar thermal energy is used in industrial process heat applications. About 15 % of the total electrical energy is consumed in industrial heat production, which can be minimized by using solar thermal energy resources [Kalogirou, 2004]. Generally, the industrial heat is used for sterilizing, drying pasteurizing, distillation, evaporation, and hydrolysis. The other industrial heat processes, where solar thermal energy is used, are solar industrial air/water systems and solar steam generation systems. The parabolic trough collector is commonly used in steam generation systems. Here, low-temperature steam can be utilized for sterilization, desalination, and evaporation. Solar thermal energy-based desalination plants are currently explored, and showing promise for large scale water desalination with the enhanced performance [Kalogirou, 2004, Kalogirou, 1998]. In addition to such distributed solar thermal applications, the most important one is the electricity generation using concentrated solar power (CSP) technology. In such solar thermal systems, incident irradiance is collected using reflectors on absorber tubes and used to generate super-heated steam for running power blocks to generate electricity. The deferent collector systems used for this purpose are the parabolic trough, tower, and parabolic dish systems.

The solar thermal systems are based on different operating temperate ranges. These are low-temperature range i.e. ≤ 100°C, mid-temperature range i.e. 100°C < T < 400°C, and high-temperature range (> 400°C). The different solar collectors are required for different operating temperature ranges. These are responsible for absorbing the incident solar energy and converting efficiently into thermal energy and are further classified as (i) non-concentrating collector, and (ii) concentrated collectors. For low-temperatures, generally, non-concentric collectors are used, and the two most common non-concentric collectors are flat plate collectors (FPC), and evacuated tube collectors (ETC). In non-concentric collectors, both diffuse and direct solar radiation is absorbed, and thus, Sun tracking is not a constraint. Generally, FPC is installed on rooftops or high rise places. The FPC systems are easy in operation and are efficient as well as long life-time compared to other collectors. Using FPC, the maximum achievable temperature is ~ 100 °C. However, using different heat transfer fluids in place of water, higher-temperature is also possible. Further, by introducing high selective spectral coating in standard FPC, stagnation temperature can go beyond 200°C [Kalogirou, 2004]. The FPCs are classified on the basis of heat transfer fluid and are (i) liquid type FTC and (ii) air type FPC. These FPC suffer from high thermal losses. On the contrary, evacuated tube collectors may achieve much higher temperatures with respect to FPC as here, heat losses are minimized by using evacuated glass tubes. In ETC, the absorber tube is inside the evacuated glass tube, and thus convective/radiation losses are minimized. The absence of air inside the tube in ETC provides good insulation, which assists in achieving higher temperatures. The maximum temperature may go up to 200 °C in ETCs [Kalogirou, 2004]. These nonconcentric collectors are used in domestic hot water supply, and industrial process heat applications in low-temperature regions

[Selvakumar and Barshilia, 2012]. In mid-temperature range, concentric collectors such as parabolic trough collector, linear Fresnel reflector are used commonly. These collectors are useful for industrial heat process-based applications up to 240 °C or more [Kalogirou, 2004]. Further, more than 350 °C can be achieved by modifying the collectors' design. Evacuated tube collectors (ETCs), where ≥ 200°C can be achieved, also falls in this category and are mostly used for industrial heat processes.

In high-temperature (> 400 °C) range, concentric collectors are used in solar thermal power plants for electricity generation. The concentric collectors fall in this category are parabolic trough collector (PTC), Linear Fresnel collectors (LFC), central receiver, and parabolic dish collectors. Among these, parabolic trough collector technology is well matured and commonly used in solar thermal power generation plant. The PTC based largest power plant is installed in California, having 354 MW electricity generation capacity [Kennedy, 2002]. In PTC, a linear receiver tube is placed along the focal line of parabolic reflectors. The concentration ratio up to 80 is achieved in PTCs, depending upon the size of the parabolic reflector and tube [Gharbi, 2011]. The performance of PTC is improved by integrating Sun tracking mechanisms with reflectors [Kalogirou, 2004, Cope et al., 1979]. For example, single-axis tracking mechanism is developed by Industrial Solar Technology Corporation for solar collectors (Krueger and Heller, 2000). Another concentric collector similar to PTC is Linear Fresnel reflector (LFR) in which a linear array of planes or curved reflectors are placed on the ground to concentrate light on the elevated collector. The concentration ratio of LFR is 25-100, and its operating temperature may vary from 250 to 500°C [Gharbi et al., 2011].

The concentric collectors with further higher operating temperature are central tower receiver and parabolic dish collectors. In a central receiver, slightly concave mirrors or heliostats are used to reflect the incident incoming solar radiation for concentrating on to a central receiver mounted above the ground. The concentration ratio in the central tower receiver collector is very high ~ 300 - 1500. With such a high concentration at one point, the operating temperature in the central tower receiver collector goes up to 1000 °C [Schwarzbšzl et al. 2000, Chavez et al., 1993]. Another high operating temperature concentric collector is a parabolic dish collector (PDC), which is the most efficient among all collectors. With two-axis tracking system, incoming solar radiation is focused on a point receiver mounted at the focal point of the parabolic dish. The concentration ratio for a PDC is ~ 600-2000. With such a high concentration ratio and point focused receiver, the operating temperature in PDC may reach up to 1500 °C. The receiver absorbs and converts solar energy into thermal energy using a circulating fluid. This thermal energy is used directly to generate electricity by a generator attached with a receiver or transported using pipes to CSP plant for electricity generation [Kalogirou, 2004]. Also, open-air volumetric receiver (OAVR) is a high temperature solar thermal system, can be integrated for various distributed solar thermal applications [Sharma et al., 2015]

It was Tabor who proposed the idea of using SSAC on a collector to harness solar energy around in 1956 [Tabor, 1956]. Electrodeposited black chrome, nickel sulfide- zinc sulfide composite, and copper oxide were among some of the coatings developed during the first generation solar absorbers, which were employed on collectors [Tabor, 1956, Shaffer, 1958, Tabor, 1961]. Over the years, different SSAC structures are reported consisting of different materials and geometrical structures. These SSAC structures are intrinsic absorber, multilayer structure consisting of semiconductor and metal with antireflection coating on top, multilayer stack of metal and dielectric, composite of ceramic and metal as the solar absorbers. Other SSAC structures are blackbody based absorbers like black paints and textured surfaces for optical trapping of incident radiation [Kennedy, 2002]. The metal-dielectric based SSACs are common in use because of flexibility in selecting the constituent metal and dielectric to get the desired optical properties such as high solar absorptance and low emittance. Also, these structures are relatively easy to synthesize using various deposition techniques [Cao et al., 2014]. Black chrome ($Cr\text{-}Cr_2O_3$) is one of the most widely explored and used metal-dielectric based SSAC for low and mid-temperature applications. However, black chrome based SSAC structures are not in use nowadays due to the hazardous nature of chromium, which is carcinogenic [Vasudevan., 1981].

Since 1955-56, various spectrally selective coatings are developed and reported. These include (i) intrinsic or ―mass absorbers; (ii) semiconductor-metal tandems and multilayer absorbers; (iii) metal-dielectric composite (cermet) absorbers; (iv) surface texturing, and (v) selective solar-transmitting coating on a blackbody-like absorber. These structures are deposited using different synthesis routes (e.g., electrochemical, chemical conversion sol-gel, spray pyrolysis, and paint, falling under solution route deposition), PVD (e.g., sputtering) as well as CVD routes. However, limited coating structures are commercially viable, and most of the explorations are still under laboratory levels. Initially, the electrochemically deposited spectrally selective coatings were scaled for large area and also commercialized for their applications in solar thermal systems. For example, black chrome was one of the first SSAC fabricated and later commercially produced [Brunold et al., 2000]. The solution-based deposition involves simple fabrication steps, and usually require low process temperatures. However, solution route may require a large amount of chemical precursors and lead to toxic chemical wastes [Kennedy, 2002, Cao et al., 2014]. Such solution derived coatings are applicable in low-temperature range, as these coating structures exhibit chemical and thermal instability at higher temperatures. That's' why numerous SSAC structures are reported using solution route at laboratory scale, but very few coating structures are realized for large scale field applications in solar thermal systems. As an alternative, vacuum-based techniques are explored and showed promise for coatings suitable for high-temperature applications. The majority of these SSACs are fabricated using PVD (e.g., sputtering, chemical vapor deposition (CVD), plasma CVD) systems. These techniques require low material consumption and cause negligible environmental pollution. These vacuum processes assisted structures show good reproducibility. The PVD coated structures show better adhesion as well as structural and chemical stability even at higher-temperature. These PVD processes can also be used to synthesize different spectrally selective coatings, without releasing/producing environmentally hazardous materials [Selvakumar and Barshilia, 2012]. Yet, these processes are cumbersome, and costly due to the essential requirement of high vacuum (e.g. 10^{-6} mbar in case of sputtering), making such deposition systems complex and costly. Due to these associated processes and system difficulties, limited SSAC structures are realized at the commercial scale [Kennedy, 2002, Selvakumar and Barshilia, 2012]. The coating structures for low temperature solar thermal applications are established and used in a number of applications in domestic applications such as hot water supply, industrial heat process, space heating, and cooling. In contrast, there are several difficulties for high-temperature SSACs, and very few reported SSAC structures are stable at high-temperature in a vacuum and show degradation at a lower temperature in open ambient conditions [Kennedy, 200].

Thus, even after numerous reported SSACs, the majority of them are stable up to mid-temperature range, and very few could exhibit thermal stability in high-temperature range in vacuum. None of these coatings are stable in open air conditions at high-temperature. The development of high-temperature stable SSACs faces challenges in terms of both materials as well as fabrication technique. The stability of individual layer, adhesion between layers in case of multilayer structure is also very important at higher temperature. Also at higher temperatures, the chances of interdiffusion of substrate material or within interlayers will also be very high, which in turn affects the optical properties of structure and thus, the overall performance of the solar thermal system. The composite systems made of high melting point refractory metals in ceramic (i.e., dielectric) matrix may exhibit suitable solar absorber material characteristics. The SSAC structures must have structural and chemical stability against corrosion degradation. Further, the majority of reported high-temperature SSAC structures are fabricated using PVD, which is a complex synthesis route as compared to the solution route in terms of easy fabrication step and cost-effectiveness. So, there is a requirement of developing a simple and cost-effective approach to realize thermally and environmentally stable SSACs for high-temperature applications. The process should also be easily scalable to ensure coatings on large surface area structures without affecting the solar thermal properties.

1.2 Objective

This research work is focusing on the development and characterization of thin-film based spectrally selective coating structures for possible solar thermal applications. The salient objectives covered in this thesis include:

1) Optimization of black chrome as a spectrally selective coating for large scale solar thermal application.
2) Corrosion resists Ni, Co co-pigmented nanoporous anodized alumina as spectral selective coating structure for solar thermal applications.
3) W/SS thin film as high-temperature infrared reflector for solar thermal applications: Intrinsic properties and impact of residual oxygen.
4) Oxide-based $SiO_2/ZnO/(Sn\text{-}In_2O_3)_{n=4}/SS$ spectrally selective structure for solar thermal applications.
5) Intensive characterization of these coating structures to understand the microscopic origin of absorption and emittance properties of these coating structures.
6) Thermal and chemical i.e. corrosion stability of the developed coating structures.
7) Scaling the dip-coating process to realize the coating on 0.33 meter long tubes.

1.3 Outline of the thesis

The thesis presented here is describing the development of Oxide and Metal-Oxide based spectrally selective coating structures for solar thermal applications. **Chapter 1** of the thesis describes the importance of solar energy and its requirement. It also outlines the motivation behind this work, together with some solar thermal applications. Further, it also describes the conversion of solar energy into solar thermal using spectrally selective coatings and the objectives of current research. **Chapter 2** explains the solar spectrum, characteristics for an ideal spectrally selective coating for solar thermal application. This chapter also presents the state of art on spectrally selective coatings and different deposition techniques. It discusses the limitation and challenges in the development of SSAC structures. Chapter 3 covers experimental details about different synthesis and characterization methodologies, which are used in carrying out this research work. **Chapter 4** discusses the optimization of black chrome coting for large surfaces or device applications. The effect of current, thickness, and time duration of deposition is described in detail. Also, thermal and corrosion stability studies are presented. **Chapter 5** covers the microstructural and optical properties of Ni-Co co-pigmented nanoporous anodized alumina. Its' corrosion behavior and thermal stability properties are also discussed in detail. **Chapter 6** presents the optical and microstructural properties of W/SS thin films fabricated using sputtering. The impact of residual oxygen and intrinsic W electronic structure on IR reflection properties is discussed in detail. **Chapter 7** discusses the oxide-based $SiO_2/ZnO/(Sn\text{-}In_2O_3)_{n=4}/SS$ based multilayer SSAC structure fabricated using a sol-gel dip-coating route. Its long term thermal stability and corrosion behavior are also studied. The scaling of this process is demonstrated by realizing coatings on 0.33 meter long tube. **Chapter 8** summarizes and concludes the research work and provides input for future developments. The annexure discusses the detail of dip-coting system developed at IIT Jodhpur.