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Introduction

1.1 MOTIVATION

The fast development and industrial growth across the globe, demand energy stockpiles and the continuous high demand for energy is causing the continuous depletion of natural resources such as oil, gas, and coal etc. On the other hand, distribution, production, and use of fossil fuel energy led to environmental degradation causing global warming. The World Health Organization (WHO), has released the impact of direct and indirect effects of climate change on the society, indicating the death of 1,60,000 people per year, which is supposed to be twice to that of the present number by 2020 [Mekhilef *et al.*, 2011]. Natural disasters such as flood, drought, air pollution etc. are taking place due to the climate change and also affect the surrounding atmospheric temperature [Lior, 2008]. Conventional energy resources produce greenhouse gasses (CO_2, SO_2, CH_4, N_2O), which have contributed directly to global warming [Abdmouleh *et al.*, 2015]. The above said problems have forced the scientific community to contemplate the alternative sources of energy. An alternative energy source should have low carbon emission, and more sustainable. The solar, wind, biomass, hydropower and tidal energies are the alternative renewable energy sources, which can be explored to meet the ever increasing energy demand [Schnitzer *et al.*, 2007].

Solar energy is one of the potential renewable energy sources. It has attracted attention because of its wide availability and environmentally benign nature [Liu *et al.,* 2013]. The rate of energy emitted by the sun is ~ 3.8 x 10^{23} kW, out of which, approximately 1.8 x 10^{14} kW is the intercepted by the earth and the rest is reflected back to the atmosphere [Thirugnanasambandam *et al.*, 2010]. The intercepted energy is thousands time more than our current power requirements. However, presently 0.008 TW of solar energy is possible to use in different ways [Aman *et al.*, 2015]. Two major technologies are employed to convert the available solar energy into electricity and heat, as shown in Figure 1.1. One is the photovoltaic (PV) technology, discovered by Edmund Becquerel (a French Scientist) in 1893. In this, a semiconductor P-N junction device is used to convert solar energy into electricity directly [Solanki, 2013]. The second one is the solar thermal technology, which converts solar energy into thermal energy, which can be used to generate electricity or to provide the thermal energy for other applications such as heating of water and space and cooling of buildings, industrial processes heat requirements, solar desalination, etc [Mekhilef *et al.,* 2011]. Relatively cheaper and environment-friendly, energy storage capability for solar thermal energy technology makes it more attractive as compared to the other renewable technologies including photovoltaics, tidal, and wind etc. for large-scale energy applications. In solar thermal technology, heat can be stored during the sun hours, which can be used later on demand. This shows a higher dispatchability of electricity/power production using solar thermal as compared to the other possible renewable resources. Here, solar energy is converted into thermal energy using a solar collector/receiver. It is a major component of the solar thermal system, which absorbs incident solar energy and converts into heat. This heat is transferred into a fluid flowing through the collector for later processing [Selvakumar and Barshilia, 2012; Kalogirou, 2004]. Solar collectors can be classified as (i) non-concentrating or stationary and (ii) concentrating ones. In non-concentrating/stationary solar collectors, the intercepting area of solar radiation is same as the absorbing area and is permanently fixed in position. These stationary collectors are further classified into (i) flat-plate collectors, (ii) stationary compound parabolic collectors and (iii) evacuated tube collectors. Whereas in the case of a concentrating (sun-tracking) solar collector,

solar energy is intercepted through a concave reflecting surface and focused onto a small receiver area, thereby increasing the radiation flux [Kalogirou, 2004]. The conversion efficiency of such collectors is limited because of conduction, convection, and radiation thermal losses from the absorber tube. These losses become significant at higher temperatures. Thus, the efficient and economical utilization require the effective conversion of collected solar energy into the thermal energy, which will depend on the development of specific coatings, capable of converting the absorbed solar energy into thermal energy without any significant thermal loss. This poses materials' challenges to design spectrally selective absorbers, which may exhibit high absorbance (α) in the wavelength range of 0.3-2.5 µm (solar spectral range) and low thermal emittance (ε) in the wavelength range 2.5-25 µm (infrared region) at operating temperature ranges [Barshilia *et al.*, 2006].

The spectrally selective absorbers can be categorized based on their operating temperatures and related applications. These are (i) low-temperature absorbers (T < 100°C), (ii) mid temperature absorbers (100°C < T < 400°C), and (iii) high temperature absorbers (T > 400°C) [kennedy, 2002]. The mid-temperature absorbers are useful in low temperature applications such as process heat for metal sintering and annealing, water desalination, and hot water etc. The high-temperature absorbers are used mainly in concentrating solar power (CSP) plants for generating electricity and very few materials are available for such applications [Selvakumar and Barshilia, 2012].

The spectral selectivity concept was introduced by H. Tabor [Tabor, 1956, 1961], J. T. Gier and R. V. Dunkle [Gier and Dunkel, 1958] in the mid-1950's, for the efficient solar thermal conversion of incident solar radiation. The initial work was focused on the low cost electrodeposition process for such absorber coating structures including NiS-ZnS composite, Nickel-Nickel oxide (black nickel), Chromium-Chromium oxide (black chrome) and Copper-Copper oxide (black copper) etc. These absorber coating structures were used in flat plate collectors for water heating applications. Solar absorptance of the electroplated black nickel on bright nickel plated copper was α = 0.901 and emittance ε = 0.05 at T = 20°C [Tabor, 1956; Gier and Dunkle, 1958]. The extensive research work on solar selective absorber coatings was carried out in the late 1970s, during the oil crisis in 1973 and afterwards [Boffey, 1970]. Several reviews and research articles on commercial spectrally selective coatings are available, focusing on the development of these absorber structures and their possible applications [Agnihotri and Gupta, 1981; Seraphin, 1979; Kennedy, 2002; Bogaerts and Lampart, 1983; Lampart, 1979; Selvakumar and Barshilia, 2012; Cao *et al.*, 2014; Amri *et al.*, 2014].

Various types of spectrally selective absorber coating structure have been investigated: (i) intrinsic or "mass absorbers"; (ii) semiconductor-metal tandems and multilayer absorbers; (iii) metal-dielectric composite (cermet) absorbers; (iv) surface texturing and selective solar-transmitting coating on a blackbody-like absorber. These spectrally selective coatings are produced using numerous techniques such as wet chemical methods: electrodeposition, electrodeless deposition, anodization, chemical conversion, thickness sensitive and insensitive spectrally selective paintings, sol-gel syntheses process, solution growth, spray pyrolysis, chemical vapor deposition (CVD), and physical vapor deposition (PVD): evaporation, sputtering, pulsed laser deposition, ion plating [Kennedy, 2002; Selvakumar and Barshilia, 2012]. Chemical methods are the cost effective, easily scalable and most importantly low-temperature processes. However, these methods exhibit poor chemical and thermal stability, produce enormous waste materials and in some cases, methods are not environmental friendly [Konttinen *et al.,* 2003; Zhao and Wackelgard, 2006].
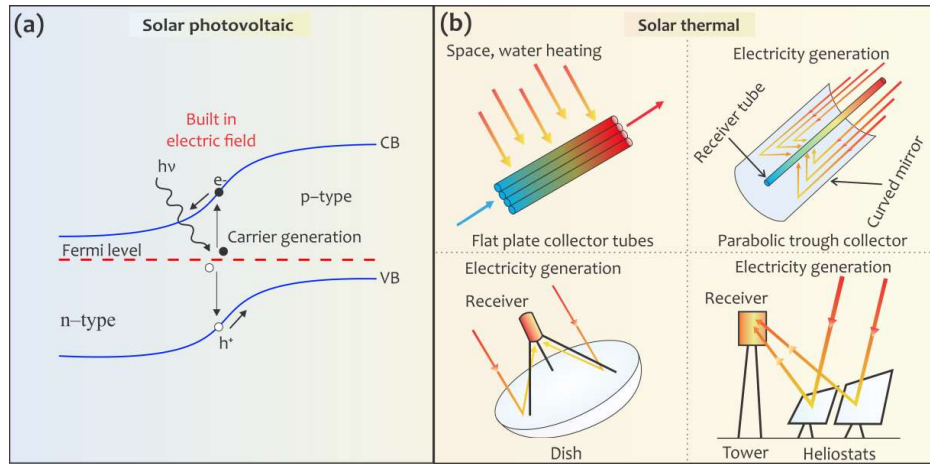
Figure 1.1 : Two prominent techniques for solar energy conversion. (Idea: http://www.volker-quaschning.de/): **(a)** solar photovoltaic process, where incident energy is absorbed to generate charge carriers for direct electricity conversion and **(b)** different solar thermal including non-concentrating (e.g. Space and water heating) and concentrating (parabolic trough, dish, and central tower receiver) technologies.

A chemical vapor deposition process can be considered as a probable choice for industrial or large scale production, but the process depends on numerous parameters and imposes difficulties in maintaining the desired stoichiometries of constituent elements in the absorber structures [Kanu and Binions, 2010]. Physical vapor deposition (PVD), such as sputtering, has shown good reproducibility, low materials consumption and lesser environmental pollution as compared to CVD processes. However, PVD is less cost effective because of its initial infrastructure related high cost requirements for large scale production of absorber coating structures, and also the high operational cost and high energy density requirements for continuous production [Barshilia $et\ al.$, 2008; Katumba $et\ al.$, 2008].

The commonly used structures are metal-dielectric composite absorbers (cermet-based), multilayer absorbers and absorber-reflector tandem structures. Various techniques and materials were used to develop a metal-dielectric composite (cermet) structures based absorber coatings for mid-to-high temperature spectrally selective absorber applications [Cao $et\ al.$, 2014]. Black chrome ($Cr-Cr_2O_3$) is one of the most studied metal-dielectric composite materials and electrodeposited black chrome is commercially developed by MTI on nickel plated copper in the USA, Chrome Coat on copper in Denmark and by Energie Solaire on stainless-steel in Switzerland [Brunold $et\ al.$, 2000]. TeKno Term Energi in Sweden and Showa in Japan have commercially developed nickel pigmented alumina based cermet selective coatings. Paint based thickness sensitive spectrally selective coatings were commercially developed by Solar etc-Z™ in Slovenia and SolKoteHI/SORB-II™ in the USA. Various types of vacuum deposited mid-temperature spectrally selective coatings are developed, but only a few of them are commercialized. For example, stainless steel-carbon (SS-C) based coating has been developed and commercialized by Nitto Kohki in Japan, SS-AlN, $CrN-Cr_2O_3$, TiNOX, a-C:H/Cr, $TiC/TiO_xN_y/AlN$ and Ni-NiO spectrally selective coatings are developed and commercialized by TurboSun in China, Alanod Solar., BlueTec, Almeco-TiNOX, IKARUS Coatings in Germany, PLASMA in Macedonia, S-Solar (Sunstrip) in Sweden. $Mo-SiO_2$, $W/W-Al_2O_3/Al_2O_3$, $Mo-Al_2O_3$, and $W-Al_2O_3$ based high-temperature spectrally selective coatings are developed by Angelantoni in Italy and Siemens (formerly Solel) in Germany [Selvakumar and Barshilia, 2012].

So far, none of the existing previous selective absorber structures employed commercially demonstrated stability in air at or above 400°C. Therefore, developing a spectrally selective absorber coatings structure, which is stable in the air beyond 400°C, is still a challenge. The high temperature stability will require the development of materials for both individual and combined layers, which should exhibit excellent adhesion between the substrate and adjacent layers, enhanced thermal and optical stability. In addition, the materials should also have high density and poor diffusion at higher temperatures to avoid the chemical degradation over the extended period at elevated temperatures. The thermal and mechanical resistances are also important for absorber materials to protect against the thermal cycling. The associated materials challenges can be avoided by considering the high melting temperature refractory metallic and ceramic materials and their composites [Kennedy, 2010].

1.2 OBJECTIVES

The thesis work has focused on the development of spectrally selective absorber materials and coatings for photothermal applications. The salient objectives covered in this thesis are:

- Enhancement of the thermal and corrosion stability of the widely used black chrome ($Cr-Cr_2O_3$) spectrally selective coatings using graphite encapsulated FeCo nanoparticles.
- Development of zirconium carbonitride as absorber and zirconium as metal reflector (ZrC-ZrN/Zr) based absorber-reflector tandem spectrally selective coatings.
- Optimization of process parameter for the desired optical, thermal, mechanical, structural, morphological, elemental and electrochemical properties of spectrally selective coatings.
- Structure-property-process correlation to understand the onset of high absorptance and low emittance in developed spectrally selective coatings

1.3 OUTLINE OF THE THESIS

The subject matter covered in this thesis is divided into six chapters and one appendix. The second chapter gives the general background of electromagnetic radiation, spectral selectivity for absorber surfaces and a review of the previous work done so far on solar (spectrally) selective absorber materials and coatings. It highlights the challenges and difficulties for spectrally selective coatings. The subject matter of the present study is to overcome some of the challenges in the development of spectrally selective coatings. The third chapter deals with the experimental methods including sample preparation and characterization used in this work for spectrally selective absorber coatings. The synthesis and characterization results for black chrome-graphite encapsulated FeCo nanoparticles composite (cremate) spectrally selective coatings are summarized in the fourth chapter. Design, experimental fabrication and characterization results of zirconium carbonitride absorber and zirconium metal reflector based absorber-reflector tandem selective coatings are summarized in the fifth chapter. Finally, chapter six summarizes and concludes the research work and provides input for future developments. The appendix discusses the experimental results on miscellaneous work, carried out during the Ph.D. work. This summarizes the experimental results on ZnO nanorod based electrodes used for hydrogen evolution & storage studies.

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