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Introduction

Solar energy harvesting through solar photovoltaics is the current edge of research to compensate the huge energy demand. The global energy consumption has gone beyond 13k million tons of oil equivalent according to 2015 global energy data and is expected to double by the year 2025 [Petroleum, 2016]. The renewable energy utilization is growing continuously, but still, only a small fraction 14.1 % of global energy requirement is met using renewables [BP, 2017]. Among renewables, solar is considered the best for energy production as the Sun shines all over the world in terrestrial or extra-terrestrial spaces, however it shares only 1.3% of global power generation [BP, 2017]. Thus, there is a need to harness the available solar energy for possible applications including both power generation and distributed energy needs in adverse conditions.

1.1 Photovoltaic technology

Enormous development has been made in the photovoltaic research and depending on the material and the technology these can be classified into three generations. The first generation PV mainly comprised with wafer based technology centered around crystalline silicon (c-Si), multi-crystalline silicon (mc-Si) and GaAs semiconductors. Reasonably good efficiency with long-term durability makes their dominance in present photovoltaic market with the most (~80% market share) of it shared by silicon wafer-based technology. However, in spite of having huge silicon reserves (second largest) on the earth crust, the fabrication cost of silicon solar cell is quite high due to its complex and energy-intensive manufacturing steps [Green, 2016]. The high cost of existing wafer based photovoltaic poses challenges for sustainable solutions and compels to explore the new photovoltaic technologies based on alternative absorber materials with high absorption coefficient suitable for thin film solar cell (TFSC) and are kept under second generation of PV technology. The motive behind the second generation is to use the material economically with less manufacturing cost. Simple deposition techniques, low cost and high throughput make TFSC technology viable for research [Chopra, Paulson, & Dutta, 2004]. Uses of high absorption coefficient material (10^4 cm^{-1}) as an absorber with preferable direct bandgap make it suitable for almost all photon absorption within a thickness of a micrometer. Low thickness requirement in TFSC further removes some constraints over material quality as the electron-hole pairs are generated close to the space charge region. Amorphous silicon (a-Si), cadmium telluride (CdTe) and chalcogenides e.g. $CuInGa(S,Se)_2$ (CIGS,Se) are the pioneers in TFSC technology. These materials have shown significant breakthrough in competing the existing costly wafer based technology and are at commercialization stage [Green, Emery, Hishikawa, Warta, & Dunlop, 2018]. However, scarcity of In, Te and toxicity of Cd possess significant challenges in terms of environmental sustainability for widespread use of these absorbers. These limitations forces researchers to come up with other alternative absorber materials that have nontoxic low cost elements [Peter, 2011]. Quaternary kesterite compound $Cu_2ZnSn(S,Se)_4$ (CZTS,Se) in recent years came up with the possibility of overcoming the efficiency barrier in TFSC with relatively environment friendly constituents and properties similar to CIGS,Se thereby acting like a close cousin. Second generation of PV technology is limited with the single homo or hetero p-n junction solar cells thereby limited with the maximum efficiency. In third generation people came up with the idea

to enhance the photo-generated charge carrier. This enhancement can be made either by enhancing the photon absorption in the cell by using tandem structure or by the concept of multi excitons generation as is proposed in the quantum dot solar cell (QDSC). In tandem or multi-junction solar cell the efficiency is enhanced merely by adding more number of cells of different bandgap in a stack. The tandem or multi-junction solar cell utilizes specific configuration of stacking of different bandgap cells where top cell absorb high energy portion of the solar spectrum equivalent to their absorber band gap and remains transparent to the lower energy photons. The remaining lower energy photons are absorbed in corresponding lower bandgap cell and so on. These single and tandem solar cells work on single Sun condition. In contrast, the concentrated photovoltaic (CPV) devices, the intensity of Sunlight is increased several orders of magnitude by concentrating it through lenses or mirrors and is allowed to fall on the efficient multijunction solar cell for high performance. Quantum dot solar cell exhibit quantum mechanical phenomena due to quantum confinement effect, leading to suitable band gap values for efficient absorption of incident photons and photogenerated electron-hole pairs. Further, there is a possibility of multi-excitons generation in QDSC, which may lead to more than 100% internal quantum efficiency. Other new technologies such as organic photovoltaic (OPV), dye-sensitized solar cell (DSSC), and perovskite solar cells use noble concept of charge carrier generation and separation and comes under the third generation of the PV technology. These third generation technologies are still under development and not yet widely commercialized. **Table 1.1** summarizes the different generation solar cell materials with their respective device parameters.

Table 1.1 Present status of achieved laboratory solar cell efficiency for different generation of photovoltaic technology

	Solar Cell	*Best cell efficiency (%)*	*Voc (V)*	*Jsc (mA/cm^2)*	*FF (%)*	*Reference*
First generation	C-Si	26.7±0.5	0.738	42.65	84.9	[Yoshikawa et al., 2017]
	mc-Si	22.3±0.4	0.6742	41.08	80.5	[Benick et al., 2017]
	GaAs	28.8±0.9	1.122	29.68	86.5	[Kayes et al., 2011]
	InP	24.2±0.5	0.939	31.15	82.6	[Green et al., 2018]
Second generation	CIGS	22.6±0.5	0.7411	37.76	80.6	[(ZSW), 2016]
	CdTe	22.1±0.5	0.8872	31.69	78.5	[Yamaguchi et al., 2017]
	a-Si	10.2±0.3	0.896	16.36	69.8	[Matsui et al., 2013]
	CZTS	10.0±0.2	0.7083	21.77	65.1	[Sun et al., 2016]
	CZTS,Se	12.6±0.3	0.5134	35.21	69.8	[W. Wang et al., 2014][Jeehwan Kim et al., 2014]
Third generation	Perovskite	22.7±0.8	1.144	24.92	79.6	[Yang et al., 2015]
	DSSC	13.0	0.91	18.1	78.0	[Mathew et al., 2014]
	Organic	12.1±0.3	0.8150	20.27	73.5	[Green et al.,

						2018]
	Tandem (GaInP/GaAs/GaInAsP/GaInAs)	46.0±2.2	4.227		85.1	508 sun[Dimroth, 2014]
	QDSC	13.43	1.1626	15.246	76.63	[Sanehira et al., 2017]

1.2 Motivation

Cu based quaternary semiconductors Cu_2-Zn-IV-VI_4 (IV: Sn, Ge VI: S, Se) are promising and have shown potential for a suitable photovoltaic response that can open the door to surpass existing efficiency limits/barriers. The crystal structure for these compounds is similar as that of chalcopyrite CIGS with half of the group III elements replaced by group II element (Zn) and other half replaced by group IV element (Sn, Ge). In this quaternary class of compounds $Cu_2ZnSn(S, Se)_4$ (CZTS, Se) has been at the top with the maximum efficiency reached up to 12.7% [Jeehwan Kim et al., 2014]. These compounds are mostly available in kesterite and stannite phase. Direct bandgap and high absorption coefficient (>10^4 cm^{-1}) made this group of compounds suitable for TFSCs. The added advantages in this group of compounds are their relatively less toxicity and high earth abundance as compared to other high performing TFSC materials. Being quaternary there is always the possibility to tune the electronic and optical properties by alloying or partial substitution of elements within the lattice. The bandgap of $Cu_2ZnSn(S_xSe_{1-x})_4$ can be tailored from 1 eV to 1.5 eV by substituting sulfur with selenium. Further, bandgap tuning can be achieved by substituting Sn with Ge. Pure Ge based quaternary $Cu_2ZnGe(S_xSe_{1-x})_4$ compound shows a bandgap variation from 1.4-2.2 eV depending on the S/Se ratio in the lattice. Thus by varying the elemental composition, the bandgap of this group of material can be tailored to make it suitable for high-efficiency single junction solar cell or as a top cell material in the tandem structure solar cells. This allows enormous possibilities for improvement in existing photovoltaic performance [Green et al., 2018].

1.3 Objective

This research work primarily focuses on development and characterization of thin film absorbers and their integration to realize complete solar cell in conjunction with the theoretical understanding of new absorber materials and related devices. The silent objective covered in this thesis includes

1) Development of CZTS thin film using low-cost solution method and effect of precursors on the film properties.
2) Fabrication of AZO/i-ZnO/CdS/CZTS/Mo/soda lime glass structure and their electrical characterization.
3) One dimensional (1-D) numerical simulation of single junction solar cell with a possibility of efficiency improvement using graded and tandem structure.
4) Density functional calculations of structural electronic and optical properties of $Cu_2ZnGe(S/Se)_4$ in their tetragonal kesterite and stannite phase.

1.4 Outline of the thesis

The thesis presented here is mainly devoted to the chalcogenide semiconductors based solar cell technology. **Chapter 1** of the thesis is an introduction to the photovoltaic technology. It describes the technological development in the solar photovoltaic through the year and discusses about all three generations of solar cell with their current maximum efficiency. The chapter also covers the motivation and the objectives for the current research presented in this thesis. **Chapter 2** explains the solar radiation, characteristics of a solar cell and the limit on the maximum efficiency that can be achieved through a single junction solar cell. This chapter also summarizes detailed literature review of commonly used deposition technique for Cu_2ZnSnS_4

absorber thin film. It discusses the factors causing the inferior performance of the kesterite devices and the possibility to overcome the barrier to realize high efficiency. At the end it covers some of the experimental characterization techniques that are used frequently in this research. **Chapter 3** explains the fabrication steps and different technique used for deposition of constituent layers of CZTS solar cell and discusses the application of different layers in the solar cell structure. **Chapter 4** discusses the sol-gel spin coating technique adopted for the synthesis of CZTS thin film. It discusses the reaction mechanism and the impact of different precursors on the morphology of prepared CZTS films. The phase purity and the quality of film are discussed in terms of its vibrational, optical and electrical characterization. **Chapter 5** covers the detail electrical and impedance characterization of prepared CZTS solar cell. Dark and illuminated current-voltage characteristics are measured to quantify the solar cell parameters. Open circuit voltage decay analysis is discussed for characterizing minority carrier life time in the system. Detailed impedance characterization of the solar cell is made and the impedance data are fitted with the resister-capacitor circuits to explain the obtained performance of the cell. **Chapter 6** gives an insight to the possible defect states that are present in the prepared CZTS absorber thin film. It discusses Mössbauer spectroscopy measurements and explains the multivalent and disordered nature of Sn in CZTS matrix. The impact of stoichiometry and defects present in the film are discussed in terms of electrical and photo-electrical behavior of the film. **Chapter 7** presents one dimensional approach of simulating CZTS/Se heterostructure solar cell. Single junction device performance is discussed in terms of different material and device parameters. A possible CZTS/CZTSe tandem structure geometry is presented for further enhancement in efficiency. **Chapter 8** discusses density functional calculations of electronic and optical properties of $CuZnGe(S/Se)_4$ semiconductor. The favorable optical bandgap and good electrical properties makes this material a potential candidate as absorber in single junction solar cell and as a high bandgap absorber in top cell in kesterite based tandem structures.