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Synthesis and Characterization of CZTS and CZTSe Quaternary Compounds for Solar Cells Applications

A Dissertation

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بِسْمِ اللَّهِ الرَّحْمَٰنِ الرَّحِيمِ

﴿هُوَ الَّذِي بَعَثَ فِي الْأُمِّيِّينَ رَسُولًا مِّنْهُمْ يَتْلُو عَلَيْهِمْ آيَاتِهِ وَيُزَكِّيهِمْ وَيُعَلِّمُهُمُ الْكِتَابَ وَالْحِكْمَةَ وَإِن كَانُوا مِن قَبْلُ لَفِي ضَلَالٍ مُّبِينٍ﴾

(سورة الجمعة: الآية 2)

DEDICATION

To the one who encouraged me to persevere all my life, to the most prominent man in my life

(dear father)

To the giving heart

(My beloved mother)

To those who made an effort to help me and were the best support

(My family and my friends)

To everyone who contributed even a letter to my academic life .....

To all of them: I dedicate this work, which I ask God Almighty to accept sincerely

Ali

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ABSTRACT

Cu_2ZnSnS_4(CZTS) and $Cu_2ZnSnSe_4$(CZTSe), are copper zinc tin sulfide, and selenide materials. They are developing as promising new long-term light absorption materials for photovoltaic (PV) systems. The materials are abundant on the planet, non-toxic, and inexpensive. In this work**,** CZTS and CZTSe were synthesized by using two techniques. Firstly, copper zinc tin sulfide and selenide CZTS and CZTSe thin films have been prepared using two-step procedure. The initial step started with the preparation of Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ powder using the melt quenching technique, and the second step is the fabrication of CZTS and CZTSe thin films using the thermal evaporation deposition process. The obtained films were heat-treated at annealing temperatures of 50, 150, and 300°C. UV. Vis spectroscopy, Atomic force microscopy (AFM), Field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), and Fourier transform infrared (FTIR) spectroscopy were used to characterize the samples. The XRD result showed that crystal structure of all of the films were polycrystalline kesterite phase. At 300 °C, CZTS film crystallite size was (9.8 nm) and for CZTSe film was (10.9 nm). The direct band gaps for CZTS and CZTSe estimated by Tauc's equation were (1.95 and 1.89 eV); (1.90 and 1.79 eV); (1.87 and 1.71 eV) at 50, 150, and 300°C. The energy gap of CZTS and CZTSe materials is not far off the optimum value for the greatest solar cell efficiency. According to AFM findings, particle size and root-mean-square (RMS) of CZTS and CZTSe film increased with increasing annealing temperature when grain size is directly related to temperature. In addition, the surface morphological characteristics showed smooth, compact and uniform film formation at highest annealing temperature. The functional groups are analyzed by using FTIR spectroscopy. Hall measurements revealed that all of the samples were p-type. The highest carrier concentrations were found 9.75×10^6 cm^{-3} for CZTS at 300°C and 6.72×10^6 cm^{-3} for CZTSe at the same temperature. The

maximum open-circuit voltage (V_{OC}) was 0.23 mV, the highest short-current density (J_{SC}) was 7.41 mA/cm^2, and the highest efficiency (η) was 14.8%, according to measurements of heterojunction for ITO/CZTS/CdS/ZnO/Al solar cell devices' (J-V) curves; as for ITO/CZTSe/CdS/ZnO/Al solar cell devices, were the highest open-circuit voltage (V_{OC}) 0.38 mV and short-current density (J_{SC}) 4.9 mA/ cm^2, and the device highest efficiency (η) was 15.6 %, therefore, both devices went through an annealing process at 300 °C

Secondly CZTS and CZTSe thin films have been prepared using a two-step procedure. The initial step started with the preparation of CZTS and CZTSe powder using the hydrothermal technique which was heat-treated at annealing temperatures of 400, 600, and 800°C, whereas the second step is the fabrication of CZTS and CZTSe thin films using a spin coating process. AFM, FE-SEM, XRD, and FTIR were used to characterize the samples. The XRD result showed that the crystal structure of all films was polycrystalline kesterite phase. At 800 °C, CZTS film crystallite size was (15.47nm) and for CZTSe film was (25.4nm). The morphological properties using FE-SEM showed that the CZTS and CZTSe thin films shape were compact with more densely packed grains at the highest annealing temperature. According to AFM results, particle size and (RMS) of CZTS and CZTSe film increased with increasing annealing temperature when grain size is directly associated with temperature. The direct band gaps for CZTS and CZTSe estimated by Tauc's equation were (1.73 and 1.68) eV; (1.66 and 1.59) eV; (1.56 and 1.53) eV at 400°C, 600°C, and 800°, the energy gap of CZTS and CZTSe materials is not far off the optimum value for greatest solar cell efficiency. Hall measurements revealed that all of the samples were p-type. The lowest value of resistivity was found to be 0.031 Ω.cm for CZTS at 800°C and 0.0191 Ω.cm for CZTSe at the same temperature. The maximum open-circuit voltage (V_{OC}) was 0.39 mV, the highest short-current density (J_{SC}) was 4.81 mA /cm^2, and the highest

efficiency (η) was 13.3%, according to measurements of heterojunction for ITO/CZTS/CdS/ZnO/Al solar cell devices' (J-V) curves; as for ITO/CZTSe/CdS/ZnO/Al solar cell devices, were the highest open-circuit voltage (V_{OC}) 0.42 mV and short-current density (J_{SC}) 5.12 mA/ cm^2, and the device highest efficiency (η) was 15.1 %, therefore, both devices went through an annealing process at 800 °C.

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List of Abbreviations

Abbreviation	Definition
AM	Air Mass
AM0	The solar radiation spectrum outside of the earth's Atmosphere
AM1	The distance of the solar radiation spectrum required to reach the earth's surface when the sun is directly at an overhead position relative to the earth
AM1.5	Solar radiation at the earth's surface when the solar rays make an angle of 48.2^{o} with the vertical
4GSCs	Fourth Generation Solar Cells
CZTS	Copper zinc tin sulfide
CZTSe	Copper zinc tin selenide
a-Si	Amorphous Silicon
CB	Conduction Band
CIGS	Copper Indium Gallium Selenide
c-Si	Crystalline Silicon
LEDs	light emitting diodes
DIW	Deionized water
CdTe	Cadmium Telluride
DSSCs	Dye Sensitized Solar Sells
FESEM	Field Emission Scanning Electron Microscopy

ITO	Indium Tin Oxide
FWHM	Full Width at Half Maximum
I-V	Current-Voltage
J-V	Current density–Voltage
MA	Methyl amine
MPP	Maximum Power Point
PCE	Power Conversion Efficiency
PV	Photovoltaic
TCO	Transparent Conductive Oxide
UV-Vis	Ultraviolet-Visible
XRD	X-Ray Diffraction
ICDD	International Center for Diffraction Data

List of Symbols

Symbol	Meaning	Units
A	Absorbance	-
a,b and *c*	Lattice constants	Å
c	Speed of light	m/s
D	The crystallite size	nm
d_{hkl}	Interplanar spacing	Å
E	Energy of the photon	eV
E_g	Optical Energy Gap	eV

F F	Fill Factor	-
hkl	Miller indices	-
I_{ph}	The light-generated current density	mA
I_{SC}	Short circuit current	mA
I_{Sh}	Shunt current	mA
J_{max}	Current density at maximum power point	mA/cm^2
J_{SC}	Short−circuit current density	mA/cm^2
K_B	Boltzmann constant	J/K
B	Constant	-
η	Efficiency	-
P_{in}	The incident power	mW/cm^2
P_{max}	Maximum power	mW/cm^2
q	The electron charge	-
T	The temperature	K
V_{max}	Maximum voltage	V
V_{OC}	Open-circuit voltage	V
α	Optical absorption coefficient	cm^{-1}
θ_z	Solar zenith angle	Degree
λ	Wavelength of the photon	nm
n	Integer number	-
A	The active surface area of the cell	cm^2
K	Scherrer's constant	-

θ	Bragg's angle	degree
β	Full width at half maximum	rad
R_s	Series resistance	$\Omega.cm^2$
R_{Sh}	Shunt resistance	$\Omega.cm^2$

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Chapter One

Introduction &

Literature review

1.1 Introduction

More than 80% of the world's energy is currently produced from fossil fuels like coal, oil, and natural gas. These fuels produce greenhouse gases when they are consumed. In addition, the cost of the energy generated by these sources is rising. All of the world's energy needs can be met by photovoltaic (PV) energy, which is abundant, clean, and non-polluting. Electronic devices that convert sunlight into power are known as solar cells. To supply the world's energy needs, we only need to cover 0.1 percent of the earth's surface with 10 percent power conversion efficiency (PCE) solar cells [1]. At the moment, the high costs of solar cell production and construction are preventing widespread use of the technology [2]. The most common type of solar cell is made from crystalline silicon, which is extremely pure. The cost of solar panel production is pushed up by the high cost of silicon fabrication. As a feasible alternative to silicon-based solar cells, thin-film solar cells are rising in popularity. When it comes to absorption, a 100 times thinner layer of thin film absorber materials may absorb the same amount of energy as crystallized silicon, which has a 100 times greater absorption coefficient. Because the grain boundaries in thin film materials make it easier to separate charges and convey them while also allowing for less recombination, they are less critical in film solar cell materials than they are in crystalline silicon solar cells [3]. To put it another way, thin-film solar cells are less expensive to produce than silicon solar cells.

Thin-film solar cells are catching on as a practical replacement for silicon-based solar cells. Instead of using thin semiconductor films like cadmium telluride (CdTe) or copper indium gallium diselenide, these devices utilize thick silicon wafers (CIGS). Because of the toxic or scarce nature of many of the semiconductor elements commonly used in their production (such as cadmium), film solar cells

made from CIGS and CdTe have already achieved astounding laboratory efficiency of around 15-20 percent (like, indium, tellurium). Cost and availability of various materials are shown in Figure 1.1. These solar cells are only viable if they use non-toxic and abundant materials that can be found on Earth.

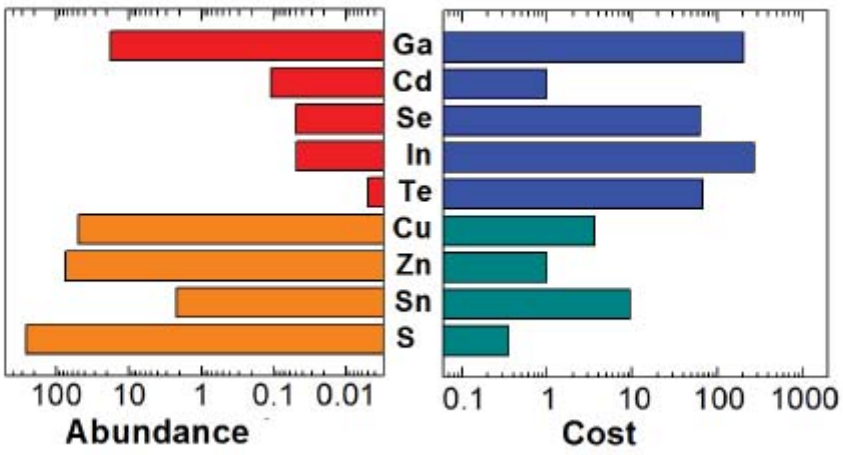

Figure 1.1: Comparison of the costs and availability of major components used in the production of thin film solar cells [4].

By the way, the quaternary compounds such as Cu_2ZnSnS_4 (CZTS) and $Cu_2ZnSnSe_4$ (CZTSe), due to their appropriate optical characteristics, elemental availability, and nontoxicity of their elements, are emerging as viable active-layer semiconductor for low-cost thin-film solar cell applications [5]. In the literature, CZTS refers usually to the selenide, sulfide, or sulfide-selenide form of the compound. CZTS and CZTSe compounds are p-type semiconductors with a direct bandgap of nearly 1.5 (eV) for selenide (CZTSe) [6] and about 1.6 eV for sulfide (CZTS) [7].

There have been numerous published research on the production of CZTS even though it is a relatively new material. This includes both vacuum and non-vacuum procedures. CZTS and CZTSe devices with an active layer manufactured using solution-based methods have the highest PCE of 8.4%, while CZTS devices

with a thermally evaporated CZTS absorbent layer have the highest PCE of 12.6 percent [9]. However, despite significant progress toward improved PCEs for CZTS-based solar cells, the best-reported device's performance remains far below the theoretically predicted efficiency of roughly 30% [10].

1.2 Generations of solar cells

1.2.1 First-generation solar cells

The photovoltaic effect was discovered in 1839 [11], despite this, the first silicon (Si) p-n junction structured PV device was invented by Bell laboratories in 1954 [12]. Crystalline silicon was the primary material used in the first wave of solar cell development because of its ubiquitous availability. Based on the degree of crystallization, first-generation solar cells can be split into two groups. A monocrystalline solar cell has only one crystal, and a polycrystalline solar cell which has several crystals in it. Other absorber materials for PV devices, notwithstanding Si market dominance, are also being researched. Device manufacturing requires an enormous amount of silicon, which has a wide range of pricing, as well as significant material processing expenses [13].

1.2.2 Second-generation solar cell

The light absorber in second-generation solar cells is more effective at absorbing light than in first-generation solar cells, therefore they utilize less material. Because they are substantially thinner than crystalline silicon solar cells, second - generation solar cells are often referred to as thin film solar cells. Cu(In, Ga)Se_2 (CIGS), CdTe, and amorphous silicon (a-Si) are the most commonly utilized thin film light absorber materials. Compared to the absorber layers of silicon-based solar cells, the CdTe and CIGS absorber layers are typically 10 μm and 2.5 μm in thickness, respectively [14,15]. Cell efficiencies of 20.4% and 19.6%, have been obtained in CIGS and CdTe respectively [16], edging closer to

monocrystalline silicon's all-time high (25.0 percent) [17,18]. However, the scarcity of In, Ga, and Te rare metals has resulted in a higher production cost because of their limited availability. CIGS and CdTe-based PV devices currently account for 10 to 15 percent of the market, following Si solar cells [19].

1.2.3 Third-generation solar cells

A high power conversion efficiency and low cost make third-generation solar cells ideal. As a result, the production cost is heavily influenced by the amount, accessibility, and ease with which materials used in device creation may be processed. A wide range of cutting-edge technologies and materials have been employed in the development of 3rd generation solar cells. Solution-processed photovoltaic devices, such as sensitized solar cells, Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$, and polymer organic solar cells, have numerous applications due to their low manufacturing costs. CZTS and CZTSe are the most promising light absorber materials for next-generation thin-film PV because of its low raw material cost and toxicity [20]. Figure (1.2) shows the classification of solar cells.

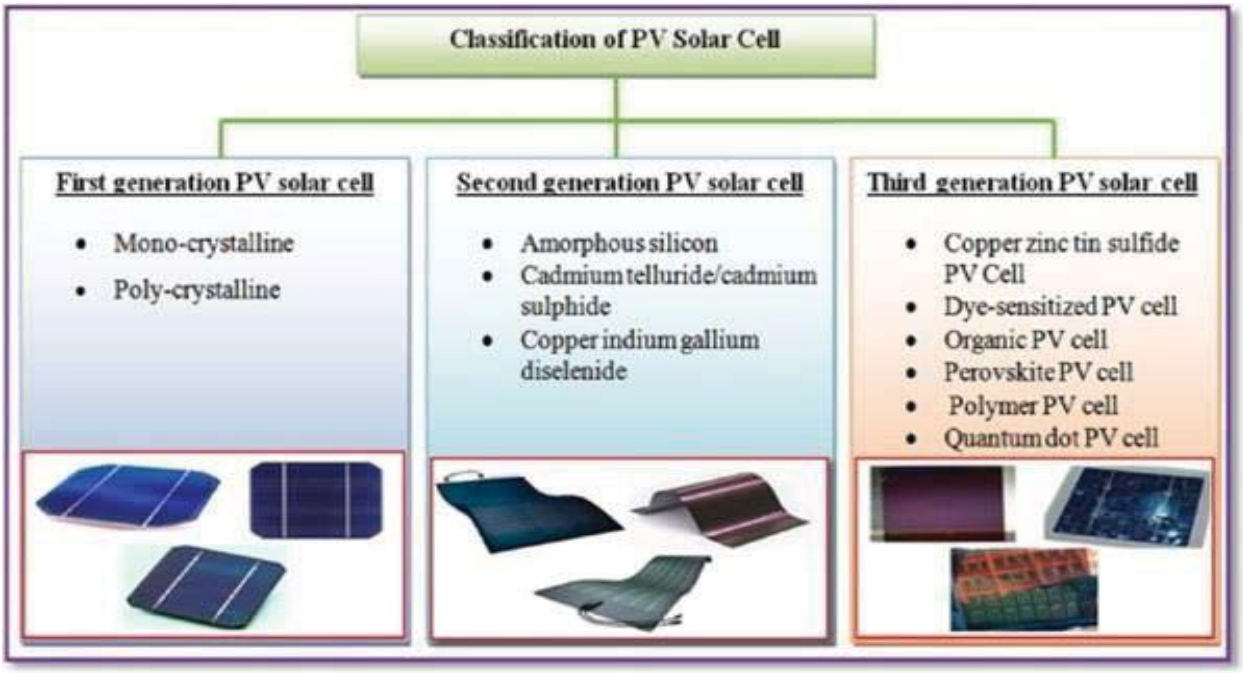

Figure 1.2: The classification of solar cells [21].

1. 3 The Novel Material: CZTS and CZTSe

The potential uses of copper chalcogenide semiconductors in photovoltaics (PV), photocatalysis, solid-state light-emitting diodes (LEDs), and biomedicine have sparked a lot of interest in the past [22]. Due to their optical absorption coefficient, photo stability, low cost, and desirable direct bandgaps, CZTS and CZTSe copper-based quaternary compounds have attracted attention. CZTS and CZTSe are being researched as an alternative light absorption material to CIGS and CdTe [23] because the production cost can be further reduced and production scale restrictions can be overcome. Copper (Cu), zinc (Zn), tin (Sn), sulphur (S), and selenium (Se) are the only elements in CZTS and CZTSe that are readily available [24], inexpensive, and kind to the environment. For example, zinc and tin are all more abundant than indium and gallium [25].

1.4 Literature Review

Tiwari et al. (2014) deposited CZTS thin film by using sol–gel by spin-coating technique. The replacement reaction route is used to prepare the CZTS thin film. The soda lime glass substrate was coated with a ZnS layer using chemical Bath deposition (CBD) in this procedure. Once this was done, it was submerged in a metal solution containing cupric chloride, zinc chloride, and stannous chloride for 10 minutes, and then the glycerol solution was added. Sol-gel spin coating was used to deposit ZnO onto an ITO coating on SLG for use in solar cells. CBD was then used to deposit CdS. Colloid graphite served as a top contact after the CZTS was deposited using the replacement reaction route. AFM indications the films to be homogeneous and compact with RMS roughness of 6 nm. The direct band gap of CZTS films was 1.45 eV. The CZTS films exhibit p-type conduction, the hole concentration and hole mobility is determined to be 3.6×10^{17} cm^{-3} and 1.4 cm^2V^{-1}

s^{-1} respectively. With a superstrate configuration of graphite/ CZTS/ CdS/ ZnO/ ITO/ SLG, the solar cells produced V_{oc} = 521 mV, J_{sc} =19.13 $mAcm^{-2}$, FF = 62%, and 6.17 percent efficiency [26].

Bakr et al. in 2015 prepared copper zinc tin sulfide (CZTS) films by using chemical spray pyrolysis technique at temperatures ranging from 200°C to 450°C on clean, preheated glass substrates. Scherrer's formula was used to calculate the crystallite size. The XRD results showed that all films are polycrystalline in nature with tetragonal structure and preferred orientation along (112) plane. AFM results showed homogenous and smooth thin films. The absorbance and transmittance spectra have been recorded in the wavelength range of (300- 900) nm. And Tauc's equation was used to calculate the optical energy gap for direct electronic transition. This study found that as the substrate temperature increases, the band gap decreases and the optical allowed energy gap for the direct electronic transitions ranged from (2.3 -1.85) eV [27].

Mrzog in 2015 investigated how changing the electrochemical deposition parameters affected the characteristics and development of CZTS thin films. When the triangle wave pulse affects the characteristics of CZTS thin films. It was found that the energy band gap (Eg) about 1.48 eV, the concentration and the mobility of CZTS films were 4.5×10^{20} cm^{-3} and 3.79 cm^2 $V^{-1}S^{-1}$, The efficiency of the solar cell with a device glass/Mo/CZTS/CdS/ZnO/Al:ZnO/ was 2.94% [28].

Bakr et al. in 2016 deposited Cu_2ZnSnS_4 (CZTS) thin films by using chemical spray pyrolysis (CSP) technique at substrate temperature of (400) °C and of about (300) nm thickness at different thiourea concentrations of (0.14,0.16, 0.18, 0.20, 0.22 and 0.24) M. It was found that the energy band gap (Eg) decreases as the

thiourea concentration increases and it was in the range of (2.22 - 1.75) eV. The XRD results showed that all films are polycrystalline in nature with tetragonal structure and preferred orientation along (112) plane. The AFM results showed smooth and homogenous thin films [29].

Qu et al. in 2016 synthesized Cu_2ZnSnS_4 (CZTS) nanoparticle inks and the influence on the performance of thin film solar cells made by converting the nanoparticles to large CZTSSe grains in selenium has been investigated. The reaction time, temperature and cooling rate of the nanoparticle fabrication process are found to affect doping level, secondary phases and crystal structure respectively [30].

Das et al. in 2018 investigated Cu_2ZnSnS_4 (CZTS) thin films as their non-toxicity, earth-abundant nature, and ideal band gap matched with solar spectrum(1.45- 1.65eV), thin films are a viable absorber for inorganic photovoltaic device application, high absorption coefficient ($10^4 cm^{-1}$).Structure, phase, and shape of produced CZTS nanocrystals have been verified by XRD, SEM, and other characterization techniques. The crystalline phase of synthesized CZTS has been confirmed by X-ray diffraction analysis. Nanocrystals of CZTS are typically around 4 nm in size. In a photovoltaic device, the synthetic CZTS nanocrystals could serve as the absorber layer. Here, a low cost, environment friendly facile hydrothermal route to synthesize phase pure CZTS nanoparticles [31].

Fouad et al. in 2018 Using a low-cost chemical bath deposition process, generated high-quality Cu_2ZnSnS_4 thin films of various thicknesses (240-418) nm were deposited on previously cleaned glass substrates. The impact of the deposition circumstances on the variation of the CZTS films' structural, optical, optoelectrical, and electrical properties has been studied. The XRD shows CZTS

thin films exhibited a polycrystalline the kieserite crystal structure. The difference of the DC conductivity with temperature for the CZTS thin films. An Al/n-Si/P-CZTS/Au hetero-junction has been created. The substrate for the device was a 0.5 mm thick, 1-10 Ω.cm resistive, phosphorus-doped Si wafer. Photovoltaic behavior was observed for the fabricated device which had a solar conversion efficiency of 3.37% [32].

Chang et al. in 2018 studied the effects of heat treatment on the efficiency of Cu_2ZnSnS_4 solar cell. Solar cells with an (V_{oc} = 730 mV) and PCE of 11% were found using heat treatment to decrease heterojunction recombination. When Cd atoms are exposed to this heat treatment, they are more easily moved into Zn or Cu lattice sites, the performance improvement of CZTS photovoltaic is achieved by using a simple heterojunction heat treatment process. This approach enables elemental inter diffusion, leading to a Zn gradient within CdS and a Cd gradient within CZTS, as well as a Na accumulation and local Cu-depletion at the heterojunction. The approach also leads to the formation of new phases: Cd diffusion into the lattice of CZTS surface forms a thin layer of $Cu_2Cd_xZn_{1-x}SnS_4$ while Zn diffusion into the CdS likely forms ultrathin Zn_xCd_{1-x} S; and likely formation of a new phase of $Cu_{2-x}Na_xZnSnS_4$ (average x ~ 0.07) nanoclusters are revealed. The allowing for greater elemental inter-diffusion. This, in turn, promotes Na accumulation and local Cu deficiency within the heterojunction region. A better alignment of the conduction bands is obtained near the hetero-interface, resulting in new phases forming and reducing non-radiative recombination. The first kesterite cell (including selenium-containing) of standard centimeter-size to surpass 10% efficiency was demonstrated using this approach, and it was certified at a centimeter-scale (1.11 cm^2) of 10 percent Cu_2ZnSnS_4 [33].

Cui et al. in 2018 created a variety of $Zn_{1-x}Sn_xO$ (ZTO, $0 \leq x \leq 1$)films using atomic layer deposition for use as a buffer layer in CZTS photovoltaic cells. A 10 nm $Zn_{0.77}Sn_{0.23}O$ buffer layer is used to establish a good band alignment, which led to an astonishing 10% rise in the V_{oc} of the CZTS solar cell. The existence of an incredibly thin Zn(S, O) layer is proven by meticulous examination of the microstructure and chemical makeup of the CZTS/ZTO interface. The large improvement in open circuit voltage is explained by the lowered interfacial defects resulting from the slight lattice mismatch at the CZTS/Zn(S,O)/ZTO heterointerface, as well as the passivation given by a greater sodium concentration throughout the CZTS/ZTO device. They concluded by demonstrating a CZTS solar cell efficiency of 9.3%, the best efficiency for a Cd-free pure sulphide CZTS solar cell [34].

Zhang et al. in 2019 fabricated CZTS nanocrystal inks by a wet ball milling method. The as-fabricated CZTS nanocrystal inks were used to deposit CZTS precursors with precisely controlled CZTS films by a spin-coating method followed by a rapid high pressure sulfur annealing method. XRD and Raman characterization showed no secondary phases in the annealed film, the absence of the detrimental phases. A solar cell efficiency of 6.2% (V_{oc} = 633.3 mV, J_{sc} = 17.6 mA/cm^2, and FF = 55.8%) with an area of 0.2 cm^2 was achieved based on the annealed CZTS film as the absorber layer [35].

Mkawi et al. in 2019 studied the effects of morphological, structural and electrical characteristics of the synthesized structures. Analytical methods were used to determine the composition of the samples. These nanoparticles have a kesterite structure according to XRD patterns and Raman measurements. Spherical CZTS nanoparticles can be seen forming using transmission electron microscopy in oleylamine (OLM) of 6 mL. Examination of the nanocrystal thin films by

scanning electron microscopy reveals a perfect, uniform-grain structure with particle sizes between 1 and 2 μm. The direct band gap measured in UV-Vis-NIR spectra was 1.47 eV, putting it on the cusp of the ideal value needed for photovoltaic applications. There is commercial potential for the synthetic method because of its speed and ease of use. The conversion efficiency of solar cells constructed from glass/Mo/CZTS/CdS/i-ZnO/AZO/Ag was determined to be around 2% [36].

Mkawi in 2020 examined how several metals (Li, Na, Sb, and Cr) affected the characteristics of CZTS thin films. The structural, morphological, electrical, and optical properties of the films were examined. Using electrodeposited thin films, he showed the spin coating process for the deposition of four distinct metals. After doping, the crystallinity of the kesterite phase improved, and X-ray diffraction (XRD) corroborated this. The major intensity peaks of the kesterite phase correspond to the (112), (200), (312), and (332) planes. The Na-doped CZTS thin film contained a pure kesterite phase with just a small quantity of contaminants, according to Raman spectroscopy. Based on the absorption measurements, an energy gap absorption edge with a range of (1.56 - 1.71) eV was estimated, and depending on the doping metal, improvements in the energy gap were seen. In the visible spectrum of light, the absorption coefficient exceeded 10^4 cm^{-1}. Under simulated AM1.5, the solar cell's performance was 2% when its device configuration was Glass/ITo/CZTS/CdS/i-ZnO/ZnO: Al/Ag [37].

Mkawi et al. in 2020 studied the effects material properties while controlling the size of Cu_2ZnSnS_4 nanoparticles by means of XRD (X-ray diffraction), UV–Vis (spectroscopy), electron microscopy (FE-SEM), and Raman spectroscopy, as well as by means of TEM (electron microscopy). The high crystallinity of the kesterite phase was confirmed by XRD and Raman spectroscopy. An obvious

preferential orientation of the nanoparticles was found to be along a crystallographic axis (112). It was found that CZTS nanoparticles have a bandgap between 1.59 eV and 1.82 eV, which is close to the optimum bandgap value for solar cell conversion devices, according to UV–Vis absorption measurements. CZTS nanoparticle crystals with diameters ranging from 10 to 40 nm were found in the TEM study, depending on the concentration of the stabilizing agent. In solar cell devices utilizing Al/ZnO: Al/ZnO/CdS/CZTS/Mo, the CZTS synthesized with PVP stabilizer at a concentration of 9 mg/mL had a maximum J_{sc} = 9.83 mA per cm^2, V_{oc} = 0. 453 V, F.F = 61.1 percent, and an efficiency of 2.7% for Al/ZnO [38].

Chamekh et al. in 2020 Cu_2ZnSnS_4 (CZTS) thin films' structural and optical properties were studied, where the films were annealed at different temperatures. Vacuum thermal evaporation was used to deposit thin films onto regular glass substrates. CZTS film structure was analyzed by means of the Diffraction by X-rays. The spectra demonstrated that the crystalline quality of CZTS films was improved by heat treatments. In all annealed films, it was discovered that the (112) direction was the favored orientation. features of optoelectronics CZTS thin films were investigated using UV-Vis spectrophotometry. Optical analysis of annealed specimens showed a coefficient of absorption greater than 10^4 cm^{-1} band gap between 1.48 and 1.56 eV [39].

Tikote et al. in 2020 studied a simple hydrothermal synthesis route for quaternary kesterite CZTS powder without any post annealing treatment. The effect of reaction temperature on the properties of CZTS was investigated. The sample obtained at high reaction temperature 200ºC revealed the formation of pure CZTS, tetragonal structure with (112), (220) and (312) reflections, while for low

reaction temperature various secondary and ternary phases were observed. The Raman result agreed well with the structural analysis reported using XRD. The energy band gap ~1.50eV was estimated for the sample prepared at higher reaction temperatures. Stoichiometric chemical composition of CZTS sample (2:1:1:4) was determined for the sample synthesized at 200°C [40].

Ozdal et al. (2020) examined the influence of annealing temperature on CZTS thin films using the sol-gel spin coating process, they looked at the morphology and optoelectronics properties. The achieved results for X-ray diffraction (XRD) indicated a polycrystalline structure of CZTS thin film, the SEM and AFM micrographs showed a uniform and dense texture of the samples, besides the effect of annealing temperatures on CTZS morphology and surface was discussed. Eg of the films annealed at 300, 500 and 550 °C was found to be 1.58 eV and 1.63 eV for film annealing 400°C [41].

Vishvas et al. in 2021 examined thermal evaporation-deposited CZTSe films. After deposition, the films underwent a 10 min annealing process at 450 °C. After being deposited and annealed, the films were treated with thiourea solution to add sulphur and partially replace the Se (1 Molar). The films were additionally annealed for 10 minutes at 450 °C following the thiourea treatment. The films were characterized for phase analysis using XRD, and crystallite size was discovered (11.7 – 16.74) nm. EDX was used to analyze the composition. The thin films band gap changes (1.16–1.28) eV depending on the S/Se ratio in the region where it was discovered. The ratio of sulphur to selenium had an impact on the thin films conductivity and mobility. After thiourea treatment, the CZTSe absorber layer's obtained electrical and optical properties were sufficient for device fabrication [42].

Saha et al. (2021) used a CdS(n)/$(Ag_xCu_{1-x})_2ZnSnSe_4$ (p) /$Cu_2ZnSnSe_4$ (p+) structure to improve the efficiency of a CZTSe solar cell. Due to its low manufacturing cost and environmentally friendly ingredients, the direct bandgap of $Cu_2ZnSnSe_4$ (CZTSe) material is a suitable absorber for thin film photovoltaics. They set the carrier density of each layer so that CZTSe is depleted and the produced minority is efficiently collected. they CZTSe as the back surface absorbent layer to prevent surface recombination and ITO as the back electrode to avoid band bending and increase the open-circuit voltage. They also tune the thicknesses of different layers, resulting in an efficiency of 18.63 % [43].

Karbassi et al. (2021) showed CZTS is an ideal absorbent layer for solar cell manufacturing because of its bandgap of 1.4 to 1.5 eV and low cost of manufacture, making it an effective absorbent layer for solar cells. Cu_2ZnSnS_4 (CZTS) was synthesized using a simple hydrothermal process. According to X-ray diffraction spectroscopy (XRD), the nanoparticles produced by CZTS have a Kesterite structure, the grain size was between 125 and 477 nm. As could be seen in the FESEM image, the annealing process improved the morphology of CZTS thin films, making them more compact [44].

Ghosh et al. (2022) The effects of molybdenum disulfide (MoS_2) as a buffer layer on the various parameters of CZTS-based solar cell devices have been researched in high-efficiency sunlight devices. The CZTS film's band gap was 1.52 eV, and the absorber layer thickness was tuned, ranging from 0.5 µm to 4 µm. Improving upon certain aspects of solar cells' performance: the open circuit voltage is 0.8521 V, and the short circuit current was 25.3 mA /cm^2, the fill factor was 84.76%, and the efficiency was 18.27% [45].

1.5 Aim of the Work

The aim of this work can be summarized in the following points:

1. Preparation and characteristics study of CZTS and CZTSe powders by Melt quenching and Hydrothermal techniques.
2. Preparation and characteristics study of CZTS and CZTSe thin films using thermal evaporation and spin coating techniques at different annealing temperatures.
3. Fabrication and study I-V properties of CZTS and CZTSe quaternary heterojunction solar cells structure compositions [ITO / CZTS / CdS / ZnO/Al] and [ITO / CZTSe / CdS / ZnO/Al]