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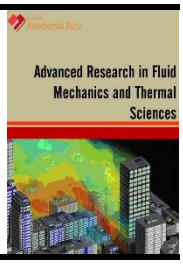

A Review of CZTS Thin Film Solar Cell Technology

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ABSTRACT

Copper Zinc Tin Sulfide (CZTS) solar cells have recently attracted attention as a potential low-cost earth abundant replacement for CIGS cells. This is due to their constituent's Zn and Sn are non-toxic and earth-abundant compare to the elements of In and Ga in CIGS. Thus, aiming to analyse solar cells free from the environmental contaminant, CZTS is viewed as a potential candidate as the absorber for the next generation thin film solar cells. However, the conversion efficiency of CZTS based solar cells reported which is relatively low (highest conversion efficiency recorded is 12.5%) from the theoretical conversion efficiency limit of 32.2%. This is due to the low fill factor (FF), open circuit voltage (V_{oc}) and current density (J_{sc}). In this study analysis of the different CZTS based solar cells and its synthesis methods will be reviewed. The effect of the compositional change and various structure in the CZTS, different buffer layers with their interfaces are thoroughly studied. The challenges regarding improving the conversion efficiency of CZTS solar cells and their future in the thin film solar cell application are discussed.

1. Introduction

CZTS is a compound semiconductor made of copper, zinc, tin, and sulfur, which are in each case for the time being sufficiently abundant elements, none of them harmful to the environment in the used amounts. Although it is comparatively new material, there are already promising results that indicate that CZTS could be used as a solar cell absorber material.

Ternary semiconductors evolved from chalcopyrite have been explored widely since the 1980s, and commercially available solar cells have already existed. Thin film solar cells based on polycrystalline cadmium telluride (CdTe), copper indium selenide (CIS), and copper indium gallium selenide (CIGS) have attracted considerable interests in the past few decades [1]. Though the power conversion efficiencies (PCE) of CIGS and CdTe based solar cells are over 11% in module production and 20% in the laboratory, the limitations are apparent due to the scarcity of In, Ga and Te and the environmental issues associated with the toxicity of Cd and Se [2]. To solve these issues, it is necessary to search nontoxic and element abundant light absorber materials [3]. Cu_2–II-IV–VI_4

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quaternary compounds, such as Cu_2ZnSnS_4 (CZTS) and $Cu_2ZnSnSe_4$ (CZTSe) have attracted considerable attention and been considered as one of the most promising 'next generation' photovoltaic materials due to their near-optimum direct band gap energy of 1.4~1.6 eV, large absorption coefficient (>10^4 cm^{-1}) and theoretical limit power conversion efficiency of 32.2%. Meanwhile, their constituents, Zn and Sn, are nontoxic and earth-abundant (Cu: 50 ppm, Zn: 75 ppm, Sn: 2.2 ppm, S:260 ppm) compared to the elements of In and Ga in CIGS [4]. Thus, aiming to develop solar cells free from the environmental contaminants, CZTS is viewed as a potential candidate as the absorber for the next generation thin film solar cells.

The solar cell development is moving into an efficient solar cell at low cost using thin film technology. Study on thin film has been made from GaAs technology. Since thin film GaAs efficiency is low, Mostofa *et al.,* manage to increase its efficiency from 14.89% to 27.16% by implement Si_3N_4 anti-reflecting coating (ARC) on the front surface of GaAs thin film solar cell [5] whereas M. Aboul-Dahab *et al.,* showed theoretically that GaAs tapered with metal nanoantenna in the absorption structures [6] could increase its absorption more than 20%. However, the main problem need to overcome for this GaAs-based solar cells related to toxic elements (As) and rare element Ga. Another solar cells research based on $Cu(In,Ga)Se_2$ (CIGS) are expanded to include alternative materials like Cu_2ZnSnS_4 (CZTS). The research deals both with fabrication as well as analysis of thin film solar cells and solar cell modules. The group has obtained solar cells with 18.5% efficiency, which is among the highest reported efficiencies for CIGS-based solar cells in the world. Although other research in solar cells focus on organic solar cells such as DSSC [73], perovskite and quantum dots, the efficiencies is still low compared to inorganic solar cells. To increase the efficiencies, study also has move on into hybrid system solar cells such as with thermoelectric material [74, 75] and phase change material (PCM) [76] as one of promising area in solar cells. However, this review will focus on development of CZTS-based as an alternative material for thin film solar cells aim at different fabrication method, characterization of thin film as well as other promising dopant for solar cell materials which not containing rare or hazardous elements. Film characterization will be reviewed from optical, electrical, chemical and structural studies. Complete solar cell devices will be discussed where the new material will replace the CIGS layer.

2. Fabrication Method

2.1 Physical Vapor Deposition

2.1.1 Electrochemical deposition method

The electrochemical deposition of semiconductor materials has been studied since 1970. Nowadays, the fabrication of solar cell has been widely used this technique such as the CIGS solar cells researched by France CISEL [5] and CdTe cells produced by BP Plc [6]. In 2012, IBM utilized the commercially plating solution to sequentially deposit Cu/Zn/Sn laminate and annealed it for 30 minutes in N_2 at 350°C, made CuZnSn alloying, and then annealed for 12 minutes at 585°C in the N_2 containing sulfur powder and finally deposited CdS and ZnO to obtain the CZTS solar cells with an efficiency of 7.3% [7]. In 2012, Washio *et al.,* [8] reported a novel approach for CZTS thin film based solar cell using oxide precursors by an open atmosphere chemical vapor deposition (OACVD). CZTS thin films were prepared on SLG and Mo-coated SLG substrates by the sulphurization of oxide precursor thin films (Cu–Zn–Sn–O) in N_2+H_2S (5 %) atmosphere at 520–560°C for 3 hours. The best solar cell yielded an efficiency of 6.03% [8]. In another studies, CZTS thin films were obtained by one-step electrochemical deposition at room temperature [9]. The alloy precursors co-plated under the optimized conditions from a mixed thiosulfate-sulfite electrolyte bath show uniform, smooth, and compact film morphology as well as uniform distribution of composition, well suited for efficient

kesterite absorbers, using electrochemical method finally delivering a Cu_2ZnSnS_4 (CZTS) thin-film solar cell with 7.4% efficiency based on a configuration Mo/CZTS/CdS/ZnO/aluminum-doped ZnO [10].

2.1.2 Vacuum deposition method

Vacuum deposition method is a physical deposition method that puts the raw film material into the vacuum chamber and heats it to high temperature to make the atoms or molecules escape from the surface then form a vapor stream entering the surface of the plated substrate. Due to the low temperature of substrate, it condenses to build a solid film.

In 2010, IBM obtained the CZTS solar cell with an efficiency of 6.8% by co evaporation [12]. In 2013, they further improved equipment and craft, employing the Cu, Zn, and Sn evaporation source of Knudsen type and Veeco S source box in metal tantalum with valves; the substrate temperature were increased from 110°C to 150°C, and the annealing temperature were increased from 540°C to 570°C while maintain the annealing time for 5 minutes. Although the film was only 600 nm, they still obtained the CZTS solar cells with an efficiency of 8.4%, which is currently the highest CZTS cells efficiency without Se [13].

2.1.3 Electron beam evaporation method

Electron beam evaporation method is to employ electric field to make electron getting kinetic energy to bombard the evaporation material of anode, which can cause the material to vaporize to achieve evaporation coating. In 1996, Nagaoka National College of Technology Research Group utilized the electron beam evaporation and curing method to fabricate the solar cells of ZnO: Al/CdS/CZTS/Mo/SLG structure with the open circuit voltage of 400 mV, short circuit current of 6.0 mA/cm^2, and fill factor of 0.277, and the conversion efficiency was only 0.66%.

Electron beam evaporation method overcomes many defects of the resistance heating evaporation, especially suitable for the production of high-melting-point material and high purity thin film material. At present, preparation of the CZTS thin film with electron beam evaporation method is the most widely studied in the laboratory, and the surface morphology, phase matching, and optical performance of thin film are better. In 1997, Katagiri in Nagaoka University of Technology utilized the electron beam evaporation to fabricate the Cu_2ZnSnS_4 thin film solar cells with an efficiency of 0.66% for the first time. According to [14] reported that $Cu_2ZnSnSe_4$ (CZTSe) thin film has been grown by e-beam evaporation from a pre-synthesized bulk source.

2.1.4 Magnetron sputtering method

Magnetron sputtering is that the electrons crash with Ar atom in the electric field with ionizing abundant argon ions and electrons fly to the substrate. The Ar ions are accelerated in the electric field to bombard the target with sputtering a lot of target atoms, and the neutral target atoms (or molecules) are deposited on the substrate to form a film. In 1988, Ito and Nakazawa in Shinshu University of Japan utilized the sputtering method to fabricate the CZTS for the first time. They sputtered the CZTS film from target material by employing the method of atomic beam sputtering and obtained the CZTS film with an optical band gap of 1.45 eV and hole mobility of 1 $cm^2/V.s$.

In 2007, the Nagaoka University of Technology in Japan has successfully fabricated the CZTS solar cells with an efficiency of 5.45% by electron beam evaporation, and has successfully obtained the CZTS cells with an efficiency of 5.74% by RF sputtering [15]. The experimental procedure was to

sputter Cu, ZnS, and SnS before annealing at atmosphere of N_2 gas containing 20% H_2S for three hours at 580°C, to obtain the CZTS thin film of Zn-rich and Cu-poor. Later the CZTS thin film was immersed in deionized water for 10 minutes, which removed the metal oxides of surface and further increase the efficiency of the cells to 6.77% [16]. In 2010, Salome and Femandes *et al.,* in University of Aveiro, Portugal cooperated with Germany HZB to fabricate the CZTS solar cells with conversion efficiencies of 0.68% by utilizing the sputtering Zn/Sn/Cu and annealing with Powder for 10 minutes at 525°C under the N_2 carrier gas. Katagiri *et al.,* [16] in Japan fabricated the CZTS thin film solar cells with the highest photoelectric conversion efficiency of 6.8% by vacuum sputtering. Moreover, Sun *et al.,* [17] investigated that selenizing CZTS precursor prepared Cd-alloying CZTSSe (sulfur about 1%) film with CdS on the top and the highest efficiency of 11.2% for CZTSSe solar cells was achieved.

2.1.5 Spray pyrolysis method

Spray pyrolysis method is to heat the surface of a substrate to about 600°C and then spray one or more metal salt solutions onto the substrate surface; the high temperature will cause pyrolysis of the spray coating, which will form a coat on the substrate surface. The quality and performance of thin film fabricated by spray pyrolysis relate to substrate temperature. If the substrate temperature is too high, it will be uneasy for the film to be adsorbed on the substrate; when the substrate temperature is too low, the crystallization of the film will be deteriorated. According to experiment results, the CZTS thin film will have better optical property if the substrate temperature is controlled within the range of 500°C–650°C in pyrolysis. Kamoun made a reaction in $CuCl_2$, $ZnCl_2$, and $SnCl_2$ and vulcanized them in SC $(NH_2)_2$ solution by spray pyrolysis method. The substance reacted for1hour at the substrate temperature of 340°C and was annealed for 120 minutes at 550°C. Finally, the CZTS thin films with a band gap of 1.5 eV were fabricated. The spray pyrolysis device is simple and easy to operate; the experimental procedure is simple, and no vacuum and gas protection devices are needed, so the cost is low, and the thin-film materials have good performance [18]. In another, a silver (Ag) incorporated kesterite Cu_2ZnSnS_4 (CZTS) thin film was fabricated by a facile spray pyrolysis method, and the device achieved a reduction in the amounts of unfavourable copper on zinc antisite defects in comparison with those in the bare CZTS film [19].

2.1.6 Pulsed laser deposition method

Pulsed laser deposition method is a physical vacuum deposition process that makes the high-power pulsed laser focus on the target surface to produce high temperature and cauterization and then produce high pressure and high-temperature plasma; the plasma emission expands in a local directional area and deposits the substrate to form a thin film [20].

In another study was reported the fabrication of Cu_2ZnSnS_4 (CZTS) solar cell efficiency 5.2% using PLD method in ultra-thin absorber layer (less than 450nm) [21]. In another way, [22] investigated that Ge doping with CZTS significantly enhances crystalline and microstructural quality of the absorber films by its liquid phase assisted growth mechanism. The solar cell fabricated with Ge/Ge+Sn ratio of 0.124 having 1.21 eV band gap exhibits best PCE of 3.82% due to improved microstructural properties using Pulse Laser Deposition (PLD) method. Furthermore, the pulsed laser deposition technique was applied for the preparation and characterization of $Cu_2(ZnMg)SnS_4$ (CZTS) thin films for solar cell applications. The effect of various zinc/magnesium compositional ratios on the properties of the CZMTS thin film was investigated [23].

2.2 Chemical Vapor Deposition (CVD)
2.2.1 Sol-gel method

In 2009, Guo *et al.,* [4] in Purdue University fabricated the 16 nm CZTS nanoparticles by a hot infusion method, prepared the CZTS films by dropping coating method, and obtained the conversion efficiency of 0.8%. In 2010, they obtained a conversion efficiency of 7.2% by knife coating [24], and the cells had no significant recession after lighting for a month. In 2010, IBM obtained a conversion efficiency of 9.6% by spin-coating the hydrazine solution [25], which were the highest CZTS cells at that time. After adding the MgF_2 antireflection layer, the conversion efficiency reached 10.1% [26]. But there also some problems: Some raw materials are organic, which is harmful to health, the raw material price is high, and the entire processes need more extended time.

2.2.2 Thermal deposition

Hydrazine is highly toxic and reactive and must be handled using appropriate protective equipment to prevent physical contact with either vapor or liquid. Solution-based deposition techniques have also received a great deal of attention because of their potential for lower cost processing. A hydrazine-based route recently led to a record 9.7% power conversion efficiency for the mixed sulphide – selenide CZTSSe materials [25], whereas colloidal nanocrystal-based CZTSSe deposition has led to cells with 7.2% power conversion efficiency [24]. These early results show substantial commercial promise for the kesterite - based class of thin-film photovoltaic materials, especially if the power conversion efficiency could be pushed above 10% [25]. Wang *et al.,* [27] manage to fabricate CZTSSe thin film solar cell using hydrazine-based real solution approach getting 12.5% efficiency. Table 1 below summarizes materials, method, and efficiency obtained from the different method.

Table 1
Material, method and efficiency

Material	Method	Efficiency, %	Reference
CZTS	Hydrazine	12.5	[27]
CZTS	Hydrazine	10.1	[26]
CZTS	Thermal Co-evaporation	11.6	[28]
CZTS	PVD	8.4	[13]
CZTS using Cd alloy	Sputtering	11.2	[17]

3. Effect of the Buffer Layer in Device Architecture

The typical composition of CZTS thin film solar cell is similar to that of a CIGS device. A heterojunction is created at the interface between p-type CZTS absorber and n-type CdS buffer layer. Kaiwen Sun *et al.,* showed that incorporating sodium into CZTS induces the redistribution of the metal element, facilitates recrystallization of the CZTS film, and encourages the phase's evolution. Appropriate sodium quantities have been shown to increase power conversion efficiency from 3.07% to 4.10%, while further sodium increases tend to deteriorate the device's efficiency [29]. Ericson's Tove *et al.,* investigated using the $Zn_{1x}Sn_xO_y$ (ZTO) buffer for CZTS solar cells to replace the standard CdS-buffer. ALD has deposited the ZTO-buffer, and the band alignment with the absorber can be adjusted by varying the process temperature. However, it is again clear that ZTO is an auspicious buffer material for solar cells from CZTS, continually surpassing its references to CdS. The highest efficiency presented in this paper was 9.0%. (ZTO with AR). This is the highest efficiency reported for

Cd-free CZTS full-sulfur [31]. Changwoo Hong *et al.,* reported that CdS buffer/CZTS heterojunction solar cells had been successfully fabricated using the relationship between device performance and device parameters and device performance as different CdS buffer thicknesses, the CdS buffer was added 70 nm thick with the CZTSSe absorber layer, which is 8.8 percent efficiency [32]. Mehmet Eray in Erkan *et al.,* investigated that the absorber/buffer interface passivation in CZTSSe thin-film solar cells deposition of 1 nm-thick Al_2O_3 layers ALD near room temperature. The passivation of ALD-Al_2O_3 decreases the density of acceptor-like defects at the interface of the CZTSSe/CdS and recombination at that interface. They show that the elevated VOC is caused by reduced recombination at the CZTSSe/CdS interface and wider depletion distance, resulting in a comparatively narrower quasineutral area and thus lower deeper recombination in the absorber layer [33]. Khaled Ben Messaoud *et al.,* investigated that the standard CdS buffer layer was replaced by (Cd, Zn)S processed by chemical bath deposition for the outputs of $Cu_2ZnSnSe_4$ (CZTSe) based solar cells. The morphology and composition of (Cd, Zn)S thin films were analyzed as a function of the ratio of [Zn]/([Zn]+[Cd]) in the chemical bath (80, 85, and 90 percent). The resulting CZTSe/(Cd, Zn)S devices show a substantial reduction of the hetero-interface barrier due to the lower density of O contamination in (Cd, Zn)S compared to CdS, resulting in a lower deep p-type recombinant density [35]. Jianjun Li *et al.,* reported Zn(O, S)/CZTSe hetero-junction interfaces using CBD. ZnO and $Zn(OH)_2$ secondary phases were eliminated from the Zn(O, S) layer by concentrated ammonium etching and soft annealing therapy, thereby limiting the band fluctuation induced by secondary phases and significantly improving the consistency of the hetero-junction junction. The Zn(O, S)/CZTSe devices displayed a relatively small series resistance of 0.23 V cm^2 and a relatively large fill factor of about 60%, benefiting from the absence of a high resistance i-ZnO sheet. As a result, with an antireflection coating, a 7.2% efficiency Zn(O, S)/CZTSe solar cell was acquired. The system analysis results suggest that the Zn(O, S) layer may have a defect level and serves as a shortcut for transporting the negative charge carrier across the Zn(O, S) layer. These encouraging findings suggest that low-cost and environmentally friendly CBD Zn(O, S) films promise to be used as the Cd-free buffer layer for solar cells with kesterite thin film [36]. Table 2 below summarize optical band alignment of different buffer/absorber interfaces below:

Table 2
Details information about optical band alignment of different buffer/absorber interfaces.

Mat.	Buffer	CBO (eV)	VBO (eV)	E_g Buffer	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	η (%)	Ref.
CZTS	ZnCdS	0.37	-.83	2.7	747.8	19.5	63.2	9.2	[29]
CZTS	CdS			2.32	666.7	19.47	67.51	8.76	[30]
CZTSe	Cds	0.55	+.09	-	-	-	-	-	
CZTS	ZnSnO				679	21.6	61.4	9.0	[31]
CZTS	CdS	+0.6 to -0.40	-1.6	3.3-2.3	494	34.054	51	8.77	[32]
CZTSe	CdS	0.1	-	2.4	582	27.72	69.7	11.23	[33]
CZTS	CeO2	-0.12	+1.92	3.3	621	19.0	55.8	6.6	[34]
CZTSe	(Cd, Zn) S	-	-	3.6	390	35.4	61.5	8.7	[35]
CZTSe	Zn (O, S)	1.2	+1.47	3.53	358	33.5	60.03	7.21	[36]

CdS are widely used as a buffer layer in CZTS-based solar cells [37]. However, the carrier recombination at the interface between CZTS absorber and Cds buffer results in a decrease of V_{oc}. The recombination at the interface can be caused by the 7% lattice misfit between CZTS and Cds which favors formation of defects that deteriorate device performance [21]. The ZnS could in effect passivate the interface owing to tiny misfit of about 0.5% between CZTS and ZnS. This could shrink interface recombination thus increasing V_{oc}. However, the presence of ZnS improved series resistance (Rs) of the device due to spike like CBO of 0.86 eV at CZTS/ZnS interface. Kim *et al.,* [38]

fabricated a CZTS PV device with ZnS buffer layer. ZnS buffer layer was deposited on top of CZTS absorber by RF sputtering method. It has been reported that optimized sputtering power and thickness of the buffer were 95 W and 30 nm in that order. CZTS / ZnS-based PV device with a η of 2.11% was reported while η of the reference device with CdS buffer prepared by chemical bath deposition (CBD) technique was 4.97%. The low η of the CZTS / ZnS-based solar cell can be attributed to the large spike-like CBO at the interface between CZTS and ZnS which limits electron transport through the heterojunction. Ericson *et al.,* [39] prepared CZTS solar cell with Zn(O, S) substitute buffer having a η of 4.6%. Taking into account large positive CBO between CZTS and ZnS, large negative CBO between CZTS and ZnO, it has been supposed that implementation of Zn(O, S) alternative buffer could result in optimal band alignment. It has also been shown that CBO between buffer and absorber could be varied by adjusting O/S ratio. The buffer layer was grown by atomic layer deposition (ALD) at 120°C. The best Zn(O, S) - based PV device showing η of 4.6% had 6:1 Zn(O, S) buffer layer composition while the orientation solar cell with CdS buffer had a measured η of 7.3%. An alternative $Zn_{0.35}Cd_{0.65}S$ buffer layer was used to fabricate CZTS PV device by Sun *et al.,* [40]. The buffer layer was grown by the successive ionic layer adsorption and reaction (SILAR) method. The composition of the buffer was adjusted to get optimum CBO which was directly measured by X-ray photoelectron spectroscopy (XPS) technique. CZTS solar cell based on this alternative buffer layer had η of 9.2% while a η of 7.8% was obtained by the reference solar cell with CdS buffer. Moreover, implementation of the alternative buffer layer with a band gap of 2.7 eV enabled to improve V_{oc} an FF compared to the reference device. Bras *et al.,* [37] reported CZTS solar cell with sputter-grown In_2S_3 buffer. Flexible stainless-steel substrates were used instead of SLG to withstand fast temperature changes. Sodium precursor layer was deposited before Mo back contact deposition to increase the re-crystallization of the CZTS absorber. The single quaternary target of Cu-poor Zn rich composition was used to fabricate the absorbers. The device fabrication procedure was performed without breaking vacuum and took less than 40 min. This approach prevented contamination of the CZTS absorber. The solar cell with In_2S_3 buffer had a measured η of 4.2 % while the η of the solar cell with CdS buffer was only 2%. This progress was attributed to improve hetero junction quality of CZTS/ In_2S_3. Hiroi *et al.,* [43] used a composite buffer layer based on a combination of CdS and In_2S_3 layers to suppress carrier recombination at the interface. As a result, a V_{oc} of 758 mV was achieved, and a solar cell showed a η of 9.19%. Besides, reduction of recombination at both absorber/ buffer and buffer/i-ZnO interfaces was obtained. Moreover, it has been suggested that small CBO at absorber/buffer layer interface (0 – 0.1eV) could cause a reduce of R_{sh}. Yan *et al.,* [41] also investigated effect of hybrid In_2S_3/CdS on a performance of CZTS solar cells. A V_{oc} of 714 mV and η of 6.62% were achieved for the most excellent device. Development in V_{oc} compared to CdS reference device was explained by higher carrier concentration in CZTS due to in doping (In diffuses from buffer layer to CZTS absorber layer) and more favorable band alignment at buffer/absorber interface. Platzer-Bjorkman *et al.,* [42] implemented $Zn_{1-x}Sn_xO_y$ (ZTO) buffer layer instead of CdS to decrease the interface recombination. ZTO buffer was created using the ALD technique. The device with ZTO buffer exhibited activation energy of 1.36 eV while that value of the CZTS device with CdS buffer was only 1 eV. Such an increase in activation energy was explained by the decline of recombination at the buffer/absorber interface as a result of enhanced band alignment at the interface between CZTS and ZTO. It has been shown that the implementation of ZTO buffer caused an increase of V_{oc} compared to CdS reference devices. As a result, a η of 7.4% was achieved. Table 3 summarizes reported information regarding the impact of the buffer layers on photovoltaic properties of sputter-grown CZTS solar cells.

Table 3
Properties of buffer layer with CZTS

Types of the buffer layer	Buffer layer growth method	J_{sc} (mA/cm3)	V_{oc} (mV)	FF (%)	H (%)	Substrate	Ref.
ZnCdS	SILAR	19.5	0.7478	0.632	9.2	SLG	[40]
CdS	CBD	20.4	0.665	0.574	7.4	SLG	[40]
In2S3	CBD	21.6	0.708	0.601	9.19	Glass	[43]
In2S3	Sputtering	13.9	0.531	0.508	4.2	Stainless steel	[37]
CdS	CBD	18.4	0.561	0.482	4.97	SLG	[38]
Zn (OS)	ALD	17.2	0.482	0.555	4.6	SLG	[39]
CdS	CBD	17.5	0.652	0.638	7.3	SLG	[39]
In2s3/CdS	CBD	17.6	0.714	0.527	6.62	SLG	[41]
$Zn_{1-x}Sn_xO_y$	ALD	17.9	0.682	0.602	7.4	SLG	[42]

4. Effect of Back Electrode Interface Quality on Solar Cell Performance

Decomposition of CZTS in the existence of Mo during sulfurization at a temperature upper than 500°C is an important problem for the fabrication of high-quality interface between the absorber layer and Mo back electrode [44].

It can be seen that further inquiry of absorber/back contact interface is required to get better FF and overall device performance. Several methods to inhibit chemical reaction at the interface between CZTS absorber and Mo back electrode was reported. Yang *et al.,* [45] revealed that thermal pretreatment of Mo layer in N_2 atmosphere before deposition of CZTS layer could slow down the formation of the resistive MoS_2 layer at the interface between CZTS and Mo. Moreover, it has been stated that high-temperature treatment of Mo-coated SLG substrate improved diffusion of Na atoms to the Mo layer. According to the paper, Na could passivate defects at the interfaces and grain boundaries within CZTS absorber. Scragg *et al.,* [46] fabricated a CZTS solar cell with a thin inert TiN intermediate layer (IL) to suppress chemical reactions at the absorber/back interface. A η of 5.5% was obtained for CZTS device with TiN IL, while a η of reference device was 7.9%. The decrease of η was recognized to enhance R_s of TiN-based device.

Zhou *et al.,* [47] used a thin carbon layer to decrease chemical reactions at the interface. It has been revealed that the carbon IL refilled voids at the interface and reconnected absorber to the back-contact layer. A solar cell with a η of 5.2% was obtained. In another study, Liu *et al.,* [48] fabricated sputter-grown CZTS device with 10 nm ZnO IL providing η of 4.3%. The device exhibited R_{sh} of 1630 Ωcm^2 which is the highest for CZTS solar cells made by sputtering to the best of our knowledge. Table 4 summarizes reported information regarding the impact of the IL on CZTS device performance.

Table 4
Photovoltaic properties of sputter-deposited CZTS solar cells with IL

Intermediate layer	Fabrication Method	Thickness (nm)	V_{oc} (v)	FF	Rs (Ohm cm^2)	η (%)	J_{sc} (mA/cm^2)	Substrate	Ref.
Tin	Reactive Sputtering	20	0.621	0.471	6.9	5.5	18.2	SLG	[46]
Ref. device			0.667	0.6	2	7.9	19.6	SLG	[46]
Carbon	Evaporation	25	0.6	0.42	-	5.2	20.5	SLG	[47]
Ref. Device			0.59	0.4	-	4.1	17.5	SLG	[47]
ZnO	Sputtering	10	0.641	0.42	15.1	4.3	15.97	SLG	[48]
Ref. device			0.324	0.32	19.7	1.113	10.8	SLG	[48]

CZTS solar cells prepared using single target sputtering move toward typically exhibit lower FF compared to the solar cells fabricated using other sputtering methods. This may be caused by a deviation of CZTS composition in the back contact area due to out-diffusion of elements during high-temperature conduct [48]. Thus, study of absorber/back contact interface is required to provide new pathways to get better FF of the solar cells further. Therefore, further investigations are required to find alternative pathways owing to described limitations of Mo for CZTS solar cell application. Execution of metal stacked back electrode may permit to provide an effective way to overcome disadvantages of solo layer Mo back contact and increase FF of CZTS-based photovoltaic devices.

5. CZTS on Different Substrates

CZTS based photovoltaic devices were fabricated on different substrates depending on the availability and research ideas. Efficiency of the fabricated device will depend on various factors, which includes the substrates used. Adhesion of the deposited layers and its conductive nature is considerable for good device performance. Band alignment if the devices have impact in the performance due to its heterointerfaces. The band alignment of the layers and its substrates are essential in defining the device characteristics. Charge trapping and the interstate bands should be analyzed well before fabricating the device.

Investigation of the experimental and theoretical investigation was carried out for $Ag_2ZnSnSe_4$ (AZTSe)/CdS heterojunction. Results reveal that the CdS had higher conduction band minimum than the AZTS interface which results in an ideal band alignment for photovoltaic application [49]. Device properties of the solar cell are analyzed with the detection of the defects involved in the layers and the type of bands [50]. To identify the device property with the band alignment of the layers and substrates of the solar cells its performance on various substrates has been studied in the following sections.

5.1 Fabrication of CZTS Solar Cell on Molybdenum (Mo) Foil

Molybdenum (Mo) is the tremendous preference as material for back contact electrode of CIGS-based photovoltaic. This is because of its stability at processing temperature is improved after contact resistance to CIGS-based photovoltaic. Molybdenum (Mo) is silver like appearance, and it has the 6th highest melting point of all elements. The resistivity value of Molybdenum (Mo) is nearly 5×10^{-5} Ωcm [51]. The Molybdenum (Mo) is deposited on soda lime glass (SLG) throughout vacuum techniques such as electron gun approach and sputtering technique with an inexpensively [52]. $CuInS_2$ (CIS) based photovoltaic device also use Molybdenum (Mo) as back contact electrode [53]. CIGS/Mo interface had ohmic contact perform with $MoSe_2$. Raud and Nicolet work on the Mo/Se, Mo/In, and a Mo/Cu diffusion pair has shown Se to react with Mo to form $MoSe_2$ with lesser quantity at an annealing temperature of nearly 600°C [54].

Tong *et al.,* [55] investigated the vacuum thermal annealing approach based on Molybdenum (Mo) back contacts to increase the crystalline properties of Molybdenum (Mo) films and $CuInS_2$ (CIS) absorber which leads to strengthening the photovoltaic efficiency. CZTS based thin film photovoltaic was fabricated using Molybdenum (Mo) as a back-contact electrode. Rapid thermal annealing technique based on Molybdenum (Mo) back contact electrode has enhanced the crystalline properties of evaporated CZTS absorber with better efficiency [56]. The primary choice is Molybdenum (Mo) foil substrate as a back contact because of its well-matched coefficient of linear expansion is 5.2×10^{-6} K^{-1}, which is a better expansion range compare to other metal foil substrate [57]. The purity of Molybdenum (Mo) foil will be high, so no need for barrier layer at the photovoltaic

device configuration and high purity level Molybdenum (Mo) foil to enhance the electrical properties of the absorbers of the photovoltaic [58].

5.2 CZTS on Si Substrate

The first-generation photovoltaic is likewise known as conventional, traditional or wafer-based cells are crafted from crystalline silicon. Commercially to be had and fabricated photovoltaic devices include substances inclusive of polysilicon and monocrystalline silicon. The maximum commonplace bulk fabric for photovoltaic is crystalline silicon (c-Si), which is likewise known as solar grade silicon. Bulk silicon is separated into the multiple categories in step with crystallinity and crystal length within the ensuring ingot, ribbon or wafer. These cells are functionally primarily based on the concept of p-n junction photovoltaics. Epitaxial wafers of crystalline silicon may be grown-up a monocrystalline silicon "seed" wafer through chemical vapor deposition (CVD). Then the wafers may be in different as self-supporting wafers of some standard thickness (e.g., 250 µm) and manipulated through a hand. Then the wafers are instantly substituted for wafer cells cut from monocrystalline silicon ingots [59]. Photovoltaic made with this "kerfless" have efficiencies drawing close one of the wafer-cut cells. Instead, reduced cost of fabrication was accomplished when the chemical vapor deposition (CVD) can be performed at atmospheric pressure in a high-throughput inline manner. The surface of epitaxial wafers is textured to improved light absorption [60]. Silicon thin-film cells were mainly deposited throughout chemical vapor deposition (CVD) from silane gas and hydrogen gas. Deposition parameters resolve the form of silicon inclusive of amorphous, polycrystalline, nanocrystalline and microcrystalline silicon [61]. Amorphous silicon is the most well-advanced thin film technology until now utilized in the fabrication of devices. Amorphous based silicon (a-Si) photovoltaics is made upon non-crystalline or microcrystalline silicon. Amorphous based silicon has a greater band gap (1.7 eV) than crystalline silicon (c-Si) (1.1 eV), because of it absorbs the visible part of the solar spectrum more strongly than the high-energy density infrared segment of the spectrum. The manufacturing of amorphous silicon (a-Si) thin film photovoltaics uses glass as a substrate and deposits the thin layer of silicon during the deposition process. Procrystalline silicon with a low quantity fraction of nanocrystalline silicon is most beneficial for high open circuit voltage [62]. CZTS thin film changed into deposited on the n-type silicon substrate through spin-coating to fabricate a Mo/p-CZTS/n-Si/Al heterostructure based photovoltaic. The p-CZTS/ n-Si heterostructure based photovoltaic and suggest a conversion efficiency of 1.13% with V_{oc} = 520 mV, J_{sc} = 3.28 mA/cm^2, and fill-factor (FF) = 66% [63].

5.3 CZTS on ZnO Substrate

ZnO changed into one of the metal oxides used in photovoltaics which exhibits fascinating properties such as high bulk electron mobility, wide band gap and transparent. ZnO based nanostructures were manufactured with a huge range of the synthesis routes. Efficiencies of the ZnO based photovoltaics are better while as compared to TiO_2 based solar cells. Advanced performance must be analyzed and mentioned with the perspective of future applications of the ZnO in dye-sensitized photovoltaics [64]. CZTS devices are likely to CIGS based devices. The structural design is usually SLG/Mo/CZTS/CdS/i-ZnO/ZnO: Al. Commonly CZTS based ZnO substrate is encompass Molybdenum (Mo) coated soda lime glass (SLG) as the electrical contact, a thin CZTS based light absorber layer which is in contact with an n-type CdS layer to generate a p-n junction, and the thin i-ZnO/Al: ZnO layer on top of the CdS layer performing as a window layer and electrical contact [65]. In 1997, Friedlmeier *et al.,* [66] produce thin film photovoltaics using a CZTS layer as the light absorber

in contact with an n-CdS/ZnO window layer. Unique architecture for liquid junction-based photovoltaics made from ZnO/Al: ZnO/ZnS or ZnS/CZTS core/shell vertically aligned nanorods array have been reported. Over fluorine-doped tin oxide (FTO) coated glass, vertically aligned Al-doped ZnO nanorod had been grown over ZnO seed layer and it turned into followed with the resource of the surface transformation of the ZnO based nanorods to ZnS or ZnSe via solubility constant (Ksp) distinction prompted anion trade in an S_2- or Se_2-solution to produce ZnO/ZnS and ZnO/ZnSe core-shell (CS) structures. One after the other, CZTS nanoparticles are synthesized from the excessive temperature arrested precipitation and subsequently used for sensitization of ZnO/ZnS CS-VANR nanostructures.

Basically, used device configuration of SLG/Mo/CZTS/ CdS/Al: ZnO/Al/Ni for CZTS thin film-based photovoltaics to have a look at the solar cell performance. The device consists of Molybdenum (Mo) coated soda lime glass (SLG), an electrical contact, a layer of CZTS as a light absorber layer in contact with n-type CdS to form p–n junction, a thin layer of Al: ZnO as a window layer on top of the CdS layer, and finally an Al/Ni layer as an electrical contact [67].

6. Conclusions & Challenges and Future

Non-hazardous, earth-abundant and cost-effective CZTS is an excellent alternative material to the CIGS solar cells. There are more than a few ways to synthesize CZTS thin films and also nanocrystals or nanoparticles, along with them vacuum-based and nonvacuum-based physical methods and several solution-based chemical methods. The more devotion is required towards the structure related properties, such as crystal structure, secondary phases, impurities, defects, and their concentrations, vacancies, dislocations, etc. The precise tuning of the band gap should be more critical for the CZTS absorber material and that can be done by ensemble the defect by adding some impurities in the host material [68] such as Na, Ag, and Sb and by partial replacement of Cu-sites by Cd and of S-sites by Se. The buffer layer with appropriate properties and their proper interface with the absorber is needed otherwise the open circuit voltage, and the short circuit current density cannot achieve more important value. To develop the photoelectric conversion efficiency, the following conditions should be satisfied by the cell

i. Novel growth and characterization techniques.
ii. Deeper theoretical understanding of the defects and secondary phase formation.
iii. An Ohmic back electrical contact which could result in a low recombination velocity.
iv. A strongly optimized interface between the absorber and buffer layer, which could also result in slow electron-hole recombination.
v. Tiny amounts of defects and disorder in the bulk of the absorber layer, enhancing minority charge carrier lifetimes and limiting recombination processes.

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