

Review Article

A Review on Development Prospect of CZTS Based Thin Film Solar Cells

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$\text{Cu}_2\text{ZnSnS}_4$ is considered as the ideal absorption layer material in next generation thin film solar cells due to the abundant component elements in the crust being nontoxic and environmentally friendly. This paper summarized the development situation of $\text{Cu}_2\text{ZnSnS}_4$ thin film solar cells and the manufacturing technologies, as well as problems in the manufacturing process. The difficulties for the raw material's preparation, the manufacturing process, and the manufacturing equipment were illustrated and discussed. At last, the development prospect of $\text{Cu}_2\text{ZnSnS}_4$ thin film solar cells was commented.

1. Introduction

With the increasing consumption of conventional energy and the gradually serious environmental crisis, the research and application of solar cells attracted a worldwide attention. In the past ten years, the progress of the thin film preparation technology promoted the technology of the second generation solar cells based on semiconductor thin film materials to flourish. Due to the demand for less material, the thin film solar cell technology can effectively reduce the cost of materials. Moreover, the thin film materials can flexibly deposit on substrates such as glass, stainless steel, and plastic, especially suitable for solar building integration.

Currently, the main thin film solar cells include the amorphous silicon thin film, cadmium telluride (CdTe), copper indium selenium (CIS), copper indium gallium selenium (CIGS), the gallium arsenide, and the copper zinc tin sulfur ($\text{Cu}_2\text{ZnSnS}_4$ is hereafter referred to as CZTS), and, so forth, the gallium arsenide and cadmium telluride contain toxic elements (cadmium and arsenic) and copper indium gallium selenide system contains rare indium elements; thus, these two types of solar cells cannot meet the future development of solar cells. The CZTS is quaternary compounds of stannite structure; its band gap is about 1.50 eV, which is very close to the best band gap required by semiconductor solar cells (1.35 eV). CZTS is the direct band gap semiconductor

material with a high absorption coefficient and a multi-layer structure; thus, it can be employed in the absorption layer of thin film solar cells. Compared with the currently commercialized crystalline silicon CdTe CIGS, due to its abundant component elements in the earth crust, nontoxic and environmentally friendly CZTS thin film solar cells are one of the best candidate materials for solar absorbing layer [1–3], which is expected to become the ideal absorption layer material of next generation thin film solar cells.

In 1977, the $\text{Cu}_2\text{CdSnS}_4$ based monocrystalline solar cells were successfully fabricated and reached the efficiency of 1.6% in Bell Lab [4]. Ito and Nakazawa in Japan Shinshu University utilized the synthesized $\text{Cu}_2\text{CdSnS}_4$ monocrystal to achieve an open circuit voltage of 165 mV in 1988 [5]. In 1997, Katagiri et al. synthesized p-type conductivity with a band gap of 1.45 eV and the absorption coefficient over 10^4 cm^{-1} and obtained the conversion efficiency of 0.66% [6, 7]. However, the existence range of single-phase based CZTS is small and quaternary synthesis is difficult, so it is no new breakthrough for quite a long time, such as the band structure, defect type, and so on. It is still under investigation.

In recent years, the CuInSe_2 cells have reached more than 10% components efficiency and obtained a certain amount of industry expectation. Indium resources were increasingly scarce with the expansion of the tablet display area, and people have strengthened the study on CZTS. With Veeco

of CIGS equipment manufacturers quitting from the CIGS in August 2011 for a too long period of commercialization and cost reduction, the United States CIGS PV module supplier Solyndra Company applied for bankruptcy, and the CZTS attracted more attention.

The mature vacuum coating technology in CIGS solar cells has been successfully employed in the CZTS thin film solar cells. Nagaoka University of Technology in Japan utilized the atomic-beam evaporation and sputtering method to achieve a conversion efficiency of around 6%. But vacuum lines were still unable to avoid expensive equipment. In search of lower cost cells, people began experimenting with different liquid nonvacuum deposition methods in the recent two years and achieved a conversion efficiency of 11.2% in small scale CZTS solar cells. Hereafter the CZTS had aroused the latent commercial interests. For example, IBM and the subsidiary of Showa Shell-Solar Frontier joined hands to exploit nonvacuum deposition technology for CZTS. Solar Frontier had extensive experience in CIS thin film PV technology development and industry. Moreover, IBM announced that it would also work with DelSolar to develop CZTS technology. The AQT Solar of U.S. announced that its conversion efficiency of CZTS film solar was close to 10% by vacuum sputtering method and began the commercialization process of products. On November 21, 2012, Korea DGIST developed a vacuum deposition coating craft which can be applied in the common production, and they had successfully fabricated the CZTS thin film solar cells with a photoelectric conversion efficiency of 8% higher than the world's highest conversion efficiency at that time. DGIST announced that this would be a huge boost for the expansion of solar cell market.

2. Materials and Methods

2.1. Chemical and Physical Properties of CZTS

2.1.1. Crystal Structure of CZTS. $\text{Cu}_2\text{ZnSnS}_4$ is the quaternary compound semiconductor of stannite structure, and its main ingredient is the mixture of $\text{Cu}_2\text{FeSnS}_4$ and $\text{Cu}_2\text{ZnSnS}_4$. Generally, stannite presents steel gray with slight olive green metallic luster, usually in the form of grain bulk. It mainly occurs in hydrothermal deposits in Cornwall and Bolivia, UK.

In 1960, Pamplin had proposed stannite ($\text{Cu}_2\text{FeSnS}_4$) quaternary compound semiconductor structures [8] of ultracrystal pack in *Nature*. It was not until 1974 that Schäfer and Nitsche had fabricated $\text{Cu}_2\text{ZnSnS}_4$ for the first time [9]. Parasyuk et al. presented that there was only one phase ($\text{Cu}_2\text{ZnGeS}_4$) existing in the Cu_2S -ZnS- GeS_2 system and two quaternary intermediate phases, $\text{Cu}_2\text{CdGeS}_4$ and $\sim\text{Cu}_8\text{CdGeS}_7$, existed in the Cu_2S -CdS- GeS_2 system, when the isothermal section of the Cu_2S -Zn(Cd)S- GeS_2 systems was constructed using X-ray diffraction analysis at 670 K [10]. $\text{Cu}_2\text{ZnSnS}_4$ in quaternary Group I_2 -II-IV- VI_4 is obtained through indium of Group III being replaced by the Zn of Group II and Sn of Group IV in CuInS_2 in the evolution [11-13]. The evolutionary relationship is shown in Figure 1.

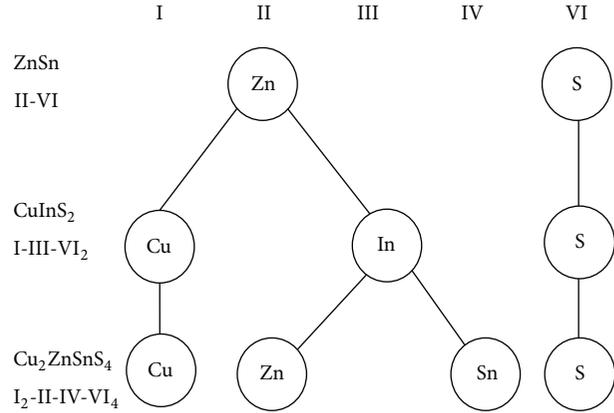


FIGURE 1: The evolution graph of quaternary CZTS (adapted from [12]).

CuInS_2 and $\text{Cu}_2\text{ZnSnS}_4$ are just a representation of I-III-VI_2 and I_2 -II-IV- VI_4 .

$\text{Cu}_2\text{ZnSnS}_4$ can be divided into two structures, stannite and kesterite, according to the different locations of Cu and Zn, as shown in Figure 2. It can be seen that stannite evolves from (001) oriented CuAu and kesterite from (201) oriented Chalcopyrite [14]. In addition, people presented a PMCA-primitive-mixed CuAu structure in the theoretical simulations, and it was obtained by rotating the ZnSn layer in stannite 90 degrees. This structure currently had not yet been reported in the experiment [8].

There are still a lot of controversies about the structure of $\text{Cu}_2\text{ZnSnS}_4$. First principles proved that I_2 -II-IV- VI_4 compounds are the most stable in kesterite, while Olekseyuk et al. found that the monocrystal $\text{Cu}_2\text{ZnSnSe}_4$ was of the stannite structure [16]. Nateprov et al. had determined the crystal structure of $\text{Cu}_2\text{ZnSnSe}_4$ using the single crystal X-ray diffraction and found that the best refinement was obtained for the model in the space group $I-42m$, which suggested that copper and zinc atoms alternate in the d Wickoff position of the space group and statistically occupy it with equal probability [17]. Schorr et al. observed the partial disorder of Zn and Cu produced by CuZn layer in kesterite structure through neutron scattering [18]. CuZn layer partial disordering made kesterite structure exhibit the same space group with stannite. It was more difficult for X-ray diffraction spectroscopy to distinguish the two structures. Schorr had proved that $\text{Cu}_2\text{ZnSnS}_4$ was of the kesterite structure by neutron scattering and Rietveld analysis [19]. Persson proposed that its structure could be judged by utilizing the anisotropy of stannite and kesterite to measure the dielectric constant of parallel to axis c and perpendicular to the axis c [20].

People have made a lot of researches on the lattice constants of $\text{Cu}_2\text{ZnSnS}_4$ by X-ray diffraction and neutron scattering. As shown in Table 1, the theoretical calculations also showed that the lattice constant of sulfide is less than that of selenide. There are still some differences between stannite and kesterite, but there is no unified conclusion till today.

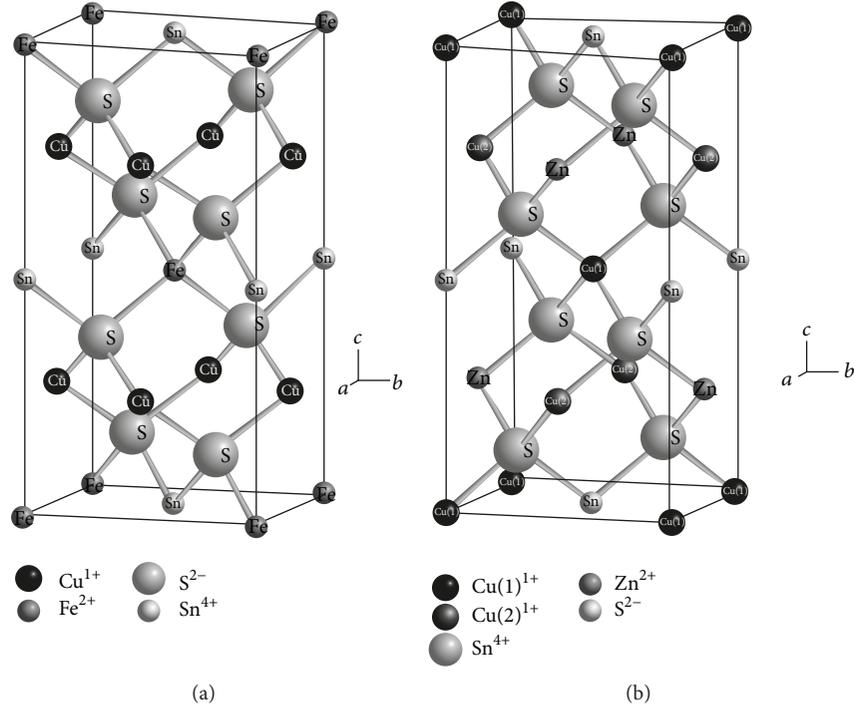


FIGURE 2: Crystal structures of (a) stannite and (b) kesterite (modified from [3, 15]).

TABLE 1: Lattice constants and band gap of Cu₂ZnSnS₄ and Cu₂ZnSnSe₄.

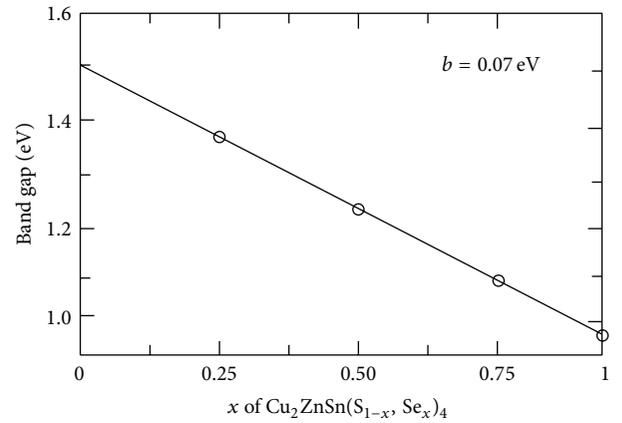
	$a/\text{\AA}$	$b/\text{\AA}$	$c/2a$	E_g/eV
Sulphide	5.419	10.854	1.0015	1.5
Selenide	5.695	11.345	0.9960	1.0

TABLE 2: Theoretical calculating value of the band gap of Cu₂ZnSnS₄ and Cu₂ZnSnSe₄.

	Chen et al. [11]	Vidal et al. [21]	Paier et al. [22]	Persson [20]
Se kesterite	0.96	1.02		1.05
Se stannite	0.82	0.87		0.89
S kesterite	1.50	1.64	1.49	1.56
S stannite	1.38	1.33	1.30	1.42

2.1.2. Energy Band Structure of CZTS. The uncertainty of basic composition and crystal structure leads to the research difficulties of electrical, optical properties, and so on. For the solar cell materials, electrical properties, such as width of energy band, density of states, doping behavior, and transport properties, are very important. For the energy gap of Cu₂ZnSnS₄ and Cu₂ZnSnSe₄, although there are some nuances in a lot of theoretical results, they all reflect that the band gap of sulfide is wider than that of selenide, as shown in Table 2.

For CZTS doped with selenium, if the proportion of Se in Se and S is recorded as X , it may be represented as

FIGURE 3: Varying diagram of Cu₂ZnSn(S_{1-x}, Se_x)₄ band gap with x (adapted from [23]).

Cu₂ZnSn(S_{1-x}, Se_x)₄, and its band gap can be adjusted from 1.0 eV to 1.5 eV:

$$E_g(X) = (1-x)E_g(\text{CZTS}) + xE_g(\text{CZTSe}) - bx(1-x). \quad (1)$$

When b is equal to 0.07, we can obtain the varying diagram of band gap of Cu₂ZnSn(S_{1-x}, Se_x)₄ with x , as shown in Figure 3.

2.1.3. Research into Phase of CZTS. The addition of elements has increased the degrees of freedom of chemical composition and structure. The researches for quaternary

semiconductor are more complex relative to the unary, binary simple semiconductors. When synthesizing quaternary semiconductor, it is noteworthy how to obtain quaternary semiconductor with specific composition and avoid the generation of binary, ternary impurity phase. $\text{Cu}_2\text{ZnSnS}_4$ contains four kinds of elements, which can be combined to form many other binary, ternary compounds such as CuS, Cu₂S, ZnS, SnS, SnS₂, and Cu₂SnS₃. In the process of synthesizing $\text{Cu}_2\text{ZnSnS}_4$, when the composition proportion of some uncertain elements shows higher or the growth environment changes, these heterocyclic compounds will be generated.

At present, there is no clear idea about the growth mechanism of $\text{Cu}_2\text{ZnSnS}_4$. It is found very difficult to fabricate single-phase $\text{Cu}_2\text{ZnSnS}_4$ in the experiment. Olekseyuk et al. had studied the phase equilibrium of $\text{Cu}_2\text{S}-\text{ZnS}-\text{SnS}_2$ system in the earlier time [24], and Dudchak and Piskach also studied the phase equilibrium of $\text{Cu}_2\text{SnSe}_3-\text{SnSe}_2-\text{ZnSe}$ [25] and found that single-phase stannite $\text{Cu}_2\text{ZnSnS}_4$ or $\text{Cu}_2\text{ZnSnSe}_4$ exists only in a very small field; the tolerability of component deviation was only 1%-2% below 550°C, which was far less than the tolerability range of chalcopyrite to Cu-poor, which is 4%. In addition, Olekseyuk had investigated the phase equilibrium in the quaternary system $\text{Cu}_2\text{Se}-\text{ZnSe}-\text{Cu}_2\text{SnSe}_3$ and found that the quaternary compound $\text{Cu}_2\text{ZnSnSe}_4$, which melted incongruently at 1061 K, was formed in the system. The compound crystallized in the tetragonal structure with the lattice parameters $a = 0,5855 \text{ nm}$ and $c = 1,1379 \text{ nm}$ [26].

Nagoya et al. has introduced the element chemical potential U_x to describe the element content in artificial atmosphere. $U_x = 0$ indicates that the element content is higher and pure elemental material can be formed. The lower U_x is, the less element composition is. Therefore, in order to avoid the simple substance of residual constituent elements in the synthetic sample, we require that $U_x < 0$. In Cu-rich condition ($\Delta U_{\text{Cu}} = 0$), it can get the phase boundary of CZTS ZnS, SnS, CuS, and Cu_2SnS_3 through different combinations of ΔU_{Sn} and ΔU_{S} [27, 28].

As shown in Figure 4, the scope of chemical potential which is in favour of synthesizing quaternary semiconductor phase of $\text{Cu}_2\text{ZnSnS}_4$ is very narrow. Stable region is only 1 eV long and 0.1 eV wide. At present, the maximum efficiency of $\text{Cu}_2\text{ZnSnS}_4$ solar cells is obtained in Zn-rich and Cu-poor material, $\text{Cu}/(\text{Zn} + \text{Sn}) = 0.8$, $\text{Zn}/\text{Sn} = 1.22$, and for viewing the statistics of different components cells efficiency, the cells tending to deviate the requirement have a low efficiency [29]. Nagoya et al. calculated the chemical potential phase diagram of $\text{Cu}_2\text{ZnSnS}_4$ in the Cu-poor condition and found that the stable regions of $\text{Cu}_2\text{ZnSnS}_4$ were smaller than the those of the Cu-rich [27]. From the phase diagrams of Figure 4 and the theoretical calculation, it can be seen that ZnS impurity phase is likely to exist in the $\text{Cu}_2\text{ZnSnS}_4$ material of Zn-rich and Cu-poor. At least, the fact that there is ZnSe in the thin film materials of $\text{Cu}_2\text{ZnSnSe}_4$ has been already confirmed by SIMS and the means of AES depth analysing in the Lab [30–32]. The Cu_2SnS_3 band gap is smaller than CZTS, only with 1.0 eV [33], which will reduce the open-circuit voltage of cells. In addition, CZTS also has a high temperature phase

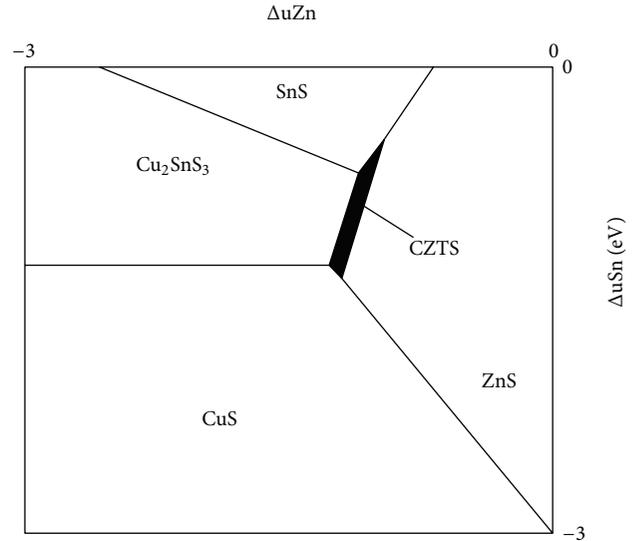


FIGURE 4: The chemical potential phase diagram of $\text{Cu}_2\text{ZnSnS}_4$ under Cu-rich conditions (adapted from [27]).

transition similar to CuInSe_2 , and CuInSe_2 will transit from tetragonal chalcopyrite to cubic sphalerite structure at 806°C [13, 34, 35], which is similar to the inversion of Cu-In cation. The structure of CZTS will transit from tetragonal kesterite to cubic sphalerite [36] at 876°C due to the inversion of Cu_{Sn} and Zn_{Sn} .

2.2. Preparation Method of CZTS Thin Film

2.2.1. Electrochemical Deposition Method.

Electrochemical deposition is a coating method to reduce the cations in the aqueous solution, organic solution, or hot-dip fluid in the cathode by supplying potential difference with external circuit power. In the 1970s, people began to try the electrochemical deposition of semiconductor materials [37, 38].

Nowadays, the electrodeposition technique has been widely employed in the fabrication of solar cells, such as the CIGS solar cells researched by France CISEL [39] and the CdTe cells produced by BP plc. [40]. Although CdS in the electrodeposition had used the thiourea as precursors [41], it was very difficult to find such a stable sulfur source in the electrodeposition CZTS. In 2008, the Bath University in Britain employed the method of laminating and vulcanizing electrodeposition Cu/Sn/Zn to obtain the CZTS solar cells with a conversion efficiency of 0.8% [42–44]. In 2010, by annealing for 2 hours at 575°C in an atmosphere of N_2 carrier gas containing S powder and 10% H_2 , they obtained the cells device with a conversion efficiency of 3.2% through improved technology [45].

In 2009, Nagaoka University of Technology obtained a conversion efficiency of 0.98% by using electrodeposition of Cu/Sn/Zn laminate and then annealing it for 2 hours at 600°C in the carrier gas containing sulfur powder. Before electrodeposition, they plated a Pb layer on the Mo to increase the adhesion of substrate [46]. Later, they gained the solar

cells with a conversion efficiency of 3.16% through the one-step codeposited CuZnSn alloy and then annealing for 2 hours at 600°C in the carrier gas containing sulfur powder [47].

In the same year, Ennaoui in Germany HZB obtained the CZTS solar cells with a photovoltaic conversion efficiency of 3.4% through one-step codeposition CuZnSn in the solution containing 3 mM Cu²⁺, 3 mM Zn²⁺, 30 mM Sn²⁺, and some complexing agent and then annealing it for 2 hours at 550°C in an atmosphere of Ar gas containing 5% H₂S and then made CZTS films with Cu-poor etching the Cu_xS in the KCN solution with 3.5% density. After light treatment for 10 minutes, its efficiency was increased to 3.6% [48, 49].

In 2012, IBM utilized the commercially plating solution to sequentially deposit Cu/Zn/Sn laminate and annealed it for 30 minutes in N₂ at 350°C, made CuZnSn alloying, and then annealed for 12 minutes at 585°C in the N₂ containing sulfur powder and finally deposited CdS and ZnO to obtain the CZTS solar cells with an efficiency of 7.3% [50].

More recently, Shinde et al. [51] reported a novel chemical successive ionic layer adsorption and reaction (SILAR) technique for CZTS thin films formation by sequential reaction on SLG substrate surface. CZTS thin films were formed by sequential immersion of the substrate into the beakers containing the cationic precursor solutions of 0.1 M CuSO₄, 0.05 M ZnSO₄, and 0.05 M SnSO₄ (1:1:1) and the anionic precursor solution of 0.2 M thioacetamide. The films obtained were then annealed at 400°C for 4 h. The photoelectrochemical solar cell (PEC) cell was constructed using the annealed CZTS thin film and exhibited an efficiency of 0.12%.

Mali et al. [52] reported fabrication of CZTS thin film based solar cells using similar approach obtained a conversion efficiency of 0.396%. This low efficiency of the device was due to the high contact resistance, which was not reported by the authors. The same group of researchers later on improved the efficiency of CZTS thin films based solar cell using similar approach to 1.85% [53]. This is the highest efficiency so far obtained for CZTS thin film based solar cell using wet chemistry (SILAR) technique.

Recently, Washio et al. [54] reported a novel approach for CZTS thin film based solar cell using oxide precursors by an open atmosphere chemical vapour deposition (OACVD). CZTS thin films were prepared on SLG and Mo coated SLG substrates by the sulphurisation of oxide precursor thin films (Cu–Zn–Sn–O) in N₂ + H₂S (5%) atmosphere at 520–560°C for 3 h. The best solar cell yielded an efficiency of 6.03%.

The merits of thin film preparation by electrodeposition are deposition process with low temperature, no residual thermal stress between coating and substrate, and well interface bonding; the uniform thin film can be prepared on various surfaces in complex shapes and porous surface; coating thickness, chemical composition, structure and porosity can be precisely controlled, and simple equipment and low investment are other merits.

2.2.2. Vacuum Deposition Method. Vacuum deposition method is a physical deposition method that puts the film raw 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 form a solid film.

In 1997, Katagiri in Nagaoka University of Technology utilized the electron beam evaporation to fabricate the Cu₂ZnSnS₄ thin film solar cells with an efficiency of 0.66% for the first time [8, 9]. Later, through improving technology with employing ZnS as evaporation source, they obtained the photoelectric conversion efficiency of 2.62% in 2001 [55]. In 2003, through adding NaS and improving the vacuum background of annealing with a stainless steel chamber, they and obtained an efficiency of 5.45% [56].

In 1998, ZSW Company of Germany cooperated with Germany Stuttgart University and obtained the CZTS solar cells with efficiency of 2.3% by coevaporation method [57, 58]. ZSW is currently the record-holder of CIGS solar cell with an efficiency of 20.3% [59]. When employing the quaternary coevaporation method of Cu, ZnS, SnS₂, and S, Weber et al. found that the temperature of substrate is at 300–600°C; once the substrate temperature was above 400°C, Sn would have a severe loss [60] and it was difficult to control the process.

In 2009, Schock turned from ZSW Company of Germany to Germany HZB (Helmholtz-Zentrum Berlin) to continue the research of CZTS coevaporation. HZB had obtained more than 10% efficiency in preparing large-area (125 cm * 65 cm) Cu(In,Ga)S₂ module by magnetron sputtering and made many researches in the n-doped, Ga gradient distribution and surface defects and other aspects [61–68]; meanwhile, they also made some researches about the preparation technology of electrochemical deposition and magnetron sputtering in CZTS aspects as well as KCN impacting on the band offset [14, 69–73]. Schubert et al. and Bär et al. obtained Cu-rich CZTS by using quaternary coevaporation ZnS, Cu, Sn, and S technology and then removed the impurity phase of Cu_xS by KCN and had obtained the conversion efficiency of 4.1% [73, 74].

In 2010, IBM obtained the CZTS solar cell with an efficiency of 6.8% by coevaporation [75]. In 2011, 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 increased from 110°C to 150°C, and the annealing temperature increased from 540°C to 570°C; the annealing time was also 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 [76].

Saga University of Japan [77] also carried out some researches on the vacuum deposition preparing CZTS film, but there were no reports related devices. In addition, Moriya et al. from Nagaoka University of Technology employed pulsed laser deposition (PLD) sputtering from the quaternary CZTS targets to fabricate CZTS solar cells and obtained a conversion efficiency of 1.7%; the CZTS target was made of incurring Cu₂S, ZnS, and SnS₂ powder into targets before annealing for 24 hours at 750°C under vacuum [78, 79].

CZTS films prepared by vacuum evaporation method are simple in principle and better in quality. However, it is difficult to control the ratio of element chemistry, thus the yield is lower. In addition, the preparation method of vacuum deposition wastes film materials, and the cost is relatively high.

2.2.3. 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 make the material 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/cm², and fill factor of 0.277, and the conversion efficiency was only 0.66%. In order to improve the conversion efficiency, Hironori and Katagiri et al. employed Cu, Sn (or SnS₂), and ZnS as vapor deposition material by electron beam evaporation method, changing the order of deposition from an evaporation to multiple cycles evaporation, using soda lime glass instead of the ordinary glass, using ZnO:Al instead of ZnO as a window layer, and finally the cells efficiency was increased to 5.45% [80].

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 study in the laboratory, and the surface morphology, phase matching, and optical performance of thin film are better.

2.2.4. Magnetron Sputtering Method. Magnetron sputtering is that the electrons crash with Ar atom in the electric field with ionizing abundant argon ions and electrons, and the 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 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 optical band gap of 1.45 eV and hole mobility of 1 cm²/V.S. After forming a heterojunction with CdZnO, they obtained the solar cells with open-circuit voltage of 165 mV [11]. In 2011, Ito in Shinshu University and Momose in Japan Nagano National College of Technology studied the method of sputtering Cu–Sn–Zn metal precursor and then vulcanized to fabricate CZTS and obtained the CZTS cells with an efficiency of 3.7% [81].

In 2007, Nagaoka University of Technology in Japan, after having successfully fabricated the CZTS solar cells with an efficiency of 5.45% by electron beam evaporation, had successfully obtained the CZTS cells with an efficiency of 5.74% by RF sputtering [82]. Experimental procedure was to

sputter Cu, ZnS, and SnS firstly, then anneal in an atmosphere of N₂ gas containing 20% H₂S for three hours at 580°C, finally 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 increased the cells efficiency to 6.77% [83].

In 2010, Salome and Fernandes 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 S powder for 10 minutes at 525°C under the N₂ carrier gas. Katagiri et al. in Japan fabricated the CZTS thin film solar cells with the highest photoelectric conversion efficiency of 6.8% by vacuum sputtering.

Muhunthan et al. [84] performed study on cosputtering from the metal targets and sulfurization in ambient H₂S for the first time. He used metal targets to help in controlling the composition of the film.

Khalkar et al. [85] studied the formation and properties of CZTS thin films deposited using cosputtering from the Cu, SnS, and ZnS targets. The effect of working pressure, target power, and annealing conditions were also studied. The optimized parameters were applied for the deposition of CZTS thin film and films were used for postannealing.

Compared with the conventional vacuum deposition, sputter coating has many merits, such as precisely controlling the stoichiometry of elements, obtaining the film with high density, full use of raw materials, freely choosing the deposition site, reducing the contamination for vacuum chamber, the higher uniformity degree of film, and suitability for the preparation of larger scale CZTS thin film solar cells. It is now one of the most promising methods to prepare CZTS thin film.

However, there are also some shortcomings for balanced magnetron sputtering. Due to the effect of electric field, the effective coating area is shorter, which limits the geometry dimension of the work pieces to be coated. It is not suitable for larger parts or installed furnace capacity; in the balanced magnetron sputtering, the energy of flying target ion is lower, and the migration rate of low-energy deposited atoms on the substrate surface is low, so it is easy to produce a porous coarse columnar structure film. The appearance of unbalanced magnetron sputtering has partly overcome the shortcomings above, which leads the plasma on the cathode target surface to the range of 200–300 mm in front of sputtering target, so that the substrate can immerse in the plasma, which greatly improves the quality of the film.

2.2.5. Spray Pyrolysis Method. Spray pyrolysis method is to heat the surface of substrate to about 600°C and then spray one or more metal salt solutions onto the substrate surface; high temperature will cause pyrolysis of the spray coating, which will form a coat on 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 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 $(\text{NH}_2)_2$ solution by spray pyrolysis method. The substances reacted for 1 hour at the substrate temperature of 340°C and were 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 [86].

2.2.6. 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 directional local area and deposits the substrate to form a thin film.

Moholkar et al. obtained the Cu_2S , ZnS , and SnS_2 powder by grinding method, and the powder is made to CZTS target through the solid state reaction; they used an excimer laser beam to bombard the target, and CZTS thin film was deposited in a vacuum chamber, followed by annealing in $\text{N}_2 + \text{H}_2\text{S}$ gas environment. The thin film cells based on this method have open circuit voltage of 585 mV, short-circuit current density of 6.74 mA/cm² and fill factor of 0.51, conversion efficiency of 2.02%, and band gap of 1.52 eV. The study found that when the laser pulse frequency was in the range of 2–10 Hz, the grain size increased with the increase of pulse frequency. Due to the high energy density of the laser and the effect of enhanced crystallization, we obtained uniform, single, and dense crystal grains [87].

Compared with other methods, this process is simple and it can deposit the film with ideal stoichiometric ratio through controlling the composition of ceramic target and the oxygen pressure, especially suitable for depositing the metal oxide thin films and multicomponent heteroepitaxial films. Furthermore, due to the bombardment of high energy laser beam, the atoms or molecules which are sputtered by target have high energy, which contributes to the deposition of high quality thin films at low temperature.

2.2.7. Sol-Gel Method. Sol-gel method is to make the readily hydrolyzable metal compound (inorganic salts or alkoxides) react with water in certain solvents, forming Sol through the process of hydrolysis and polycondensation and make Sol form liquid film on substrate by dipping or spin-coating method; after gelatinization, it can be transformed into amorphous form (or crystalline) films by heat treatment.

Thin film fabricated by spin-coating method usually involves in three steps: first, preparing precursor solution containing specific ion; second, spin-coating precursor solution on the glass substrate to form film; and third, annealing thin films in a proper atmosphere.

In 2007, Tanaka et al. in Nagaoka University of Technology used the dimethyl alcohol as solvent and the ethanalamine

as stabilizer to make sol gelatin with cupric acetate, zinc acetate, and tin chloride and coated it on the Mo glass. In order to obtain the appropriate thickness, spin coating needed to be repeated for 5 times and then they burned it at 300°C for 5 minutes in the air and annealed it at 500°C for 1 hour in an atmosphere of N_2 gas containing 5% H_2S again. Finally, they obtained the CZTS thin film with better component and the crystallinity [84]. In 2009, through improving the technology, firstly, spin-coat and dry the 0.35 M sol for three times; then, spin-coat and dry the 1.76 M sol for 5 times; finally obtain the CZTS film with uniform surface and the efficiency of 1.01% [88]. In 2011, they obtained a conversion efficiency of 2.03% by optimizing film components [89].

In 2009, Guo et al. 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% [49]. In 2010, they obtained a conversion efficiency of 7.2% by knife coating [90], 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 [91], which were the highest CZTS cells at that time [92, 93]. After adding the MgF_2 antireflection layer, the conversion efficiency reached 10.1% [94].

Compared with other methods, it has many unique advantages: simple process equipment and without vacuum conditions or expensive equipment; large area of thin films can be prepared on substrate with different shapes and different materials. It is easy to obtain homogeneous and multicomponent oxide film and has easily quantitative doping; the film composition and microstructure can be effectively controlled. But there are also some problems: the price of raw materials is high, and some raw materials are organic, which is harmful to health; usually, the entire process requires a longer time (mainly referring to the aging time); there is a large number of micro-gel holes in the gelatin, a lot of gas and organics will escape from the drying process and lead to contraction.

3. Results and Discussion

Since the CZTS film is a kind of multicomponent semiconductor which needs high demands in the accurate atomic ratio and the process conditions of lattice matching, the process has poor reproducibility and the yield of high efficient cells is low. Meanwhile, the crystalline state and the basic characteristics of the CZTS film have not been clearly figured and the relationship between material properties and device performance of CZTS cannot be accurately explained [95]. All these factors have increased the industrialization costs of CZTS solar cells and limited the long-term development of CZTS solar cells.

At present, most preparation methods of CZTS are in fabricating alloy precursor under the conditions of heating or high temperature then heating and vulcanizing in a sulfur source environment. Quaternary compounds film can be

directly synthesized by one-step at room temperature, which eliminates the vulcanizing process so that it greatly reduces the complexity of production process. Meanwhile, it also reduces the carbon emission, which is a manufacturing process that is environmentally friendly. Physical deposition methods require a vacuum device, which makes the system more complex and production costs higher. The device structure of electrochemical method is simpler, to a large extent, and cost saving, and the electrochemical deposition is also a safe, controllable, energy-saving and environment-friendly preparation technology, with low cost and easy operation. Therefore, deposition of the CZTS thin film solar cells directly by electrochemical method under the normal temperature is a promising material preparation technique [96].

Experiment shows that it will produce secondary species in the manufacturing process of CZTS thin film, such as metal sulfide and intermetallic compound. The secondary species in thin film will become the impurity scattering electrons that will reduce the degree of freedom of the electron and seriously affect the performance of thin film. The grain size also affects the performance of films. The smaller the grain is, the more the grains per unit area are, and the more the grain boundaries are. However, the grain boundaries are the recombination centers, which will reduce the minority carrier lifetime and drift length. CZTS thin film will have cracks after annealing. Although the number of cracks can be reduced by adding polymer adhesive, it will indirectly bring in the carbon impurities, and the gap between the CZTS film and the substrate will increase the resistivity. It will also cause the tin gasifying in the annealing and sulfide process and the place where the film in contact with the substrate is vulcanized uniformly and insufficiently. Judged from the electrical properties, currently, due to the lower shunt resistance, the short circuit current density of CZTS thin film prepared is lower. The ideal cell requires a higher shunt resistance and a lower series resistance. Oxides will be introduced in the process of preparation of CZTS films, which increases the resistance of thin layer, thereby increasing the series resistance. Further, the internal defects and impurities introduced during manufacture also significantly affect the electrical properties of the films. In addition to above problems, the certain drugs used are highly toxic, explosive, and flammable chemicals and require a harsh environment for transport and storage, which increases the cost of industrial production.

4. Conclusions

In the field of CZTS films, Mitzi et al. in IBM have fabricated the CuZnSnSSe thin film solar cells with the photoelectric conversion efficiency of 9.66% by using thin film deposition method-based on solution particle. It is currently the highest conversion efficiency using the preparation vacuum method. At present, people in China have carried out the simulation of CZTS materials structure and material preparation. In 2010, Shanghai Jiaotong University fabricated the CZTS thin film solar cells by grinding printing method. Although the

conversion efficiency was only 0.49%, it had the merits of low cost, simple operation, and suitability for the preparation of large area thin film field emission cathode. Therefore, it is a promising method in the future. CZTS thin film solar cells have become the hot spot of thin film solar cell research in recent year due to the unique features. But we have to say that no matter what methods we take, the conversion efficiency of CZTS thin film cells is not ideal, with the highest less than 12%, a large gap between CZTS thin film cells and silicon solar cells, expensive manufacturing equipment, complex process steps, high cost, and low yield. Although the current efficiency of electrochemical deposition is general, the low cost is suitable for large-scale manufacturing. The efficiency of new CZTSSe thin-film cells is higher and it can be used as a substitute for CZTS thin films before technology in large-scale production for CZTS thin films is mature. However, the Se is a rare element and has a higher price. If the introduction of impurities and internal defects can be limited during the process of electrochemical deposition film and the chemical proportion in each element can be controlled effectively (Usually the ideal $\text{Cu}/(\text{zinc} + \text{Sn})$ and zinc/Sn ratio of CZTS film is between 0.85 to 0.96 and 1.05 to 1.30 resp. [97]), meanwhile fabricating the crystal grain of large size, reducing the grain boundary, increasing the minority carrier lifetime and mean free path, the absorption layer meeting the requirements of the thin-film cells can be obtained. To achieve the above requirements, it is necessary for us to understand the formation mechanism of CZTS thoroughly.

In short, with the further development of the preparation technology and equipment, as well as the mature theoretical research about basic features and crystallization condition of CZTS thin film, with its environmentally friendly features, rich content in the earth crust, and good photoelectric performance, CZTS thin film will certainly become a promising photovoltaic material after the CIGS thin film.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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