

Research on Copper Indium Gallium Selenide (CIGS) Thin-Film Solar Cells

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Abstract. As a new-style solar cell, copper indium gallium selenide (CIGS) thin-film solar cell owns excellent characteristics of solar energy absorption, and it is one of the widely used thin-film solar cells. This paper mainly focuses on the research progress of this type of solar cell. Firstly, its theoretical principles are briefly described. Then, its cell materials, configuration and fabrication procedure are introduced. Subsequently, the remarkable research work about CIGS solar cell are reviewed. Finally, its commercial status is illustrated, followed by the critical issues and future perspectives.

1 Introduction

The copper indium gallium selenide (CIGS) thin-film solar cell is a new type of solar cell developed in the late 1980s [1,2], which has been confirmed in laboratory research to obtain a theoretical photoelectric conversion efficiency of more than 20% [3]. This type of solar cell has high stability and excellent solar absorption characteristics, and has been commercialized, and it is one of the currently most widely commercialized thin-film solar cells [4].

2 Theoretical principle

Solar cell is a kind of photovoltaic device that can directly convert solar energy into electric current by absorbing photo-generated carriers in a semiconductor. In solar cells, three main processes are involved: generating charge carriers by absorbing photons, separating carriers, and collecting carriers. A semiconductor material often absorbs photons with energy greater than its band gap. The absorbed photons excite an electron to move from the valence band to the conduction band in the absorbing material, which creates an electron-hole pair. The generated charge carrier pairs are either recombined or separated and then collected. The absorbed photons depend on the thickness and absorption coefficient of the absorber material. The key part of the solar cell is the formation of the p-n junction, which consists of two semiconductor materials connected together, one of which is n-type doped and the other one is p-type doped. In CIGS solar cells, a variety of different semiconductor materials are used for the formation of p-n junctions, so such structures are called heterojunctions. Using heterojunctions allows batteries to be provided with a wide band gap window layer, thereby reducing surface recombination. The valence band and conduction band

have discontinuities and device structures that can be observed in the band diagram of the p-n heterojunction. This kind of junction represents the possibility of the formation of energy barriers in the phenomenon of charge carrier transport. The conversion of minority carriers in the p-type absorber layer can decouple the physical and electronic junctions by the formation of buried junctions, thereby becoming majority carriers located on the adjacent interface zone, which also reduces the feasibility of recombination [4].

3 Battery material, structure configuration and manufacturing process

The active material of CIGS solar cells is composed of a direct band gap, tetrahedral bonded compound element semiconductor, which has a chalcopyrite crystal structure. By casting any proportion of CuInSe₂ and CuGaSe₂ into alloys, CIGS solar cells can be formed. However, most high-performance devices maintain the Ga/(In+Ga) ratio between 0.25 and 0.35, and adjust the band gap of CuInSe₂ and CuGaSe₂ to 1.04eV and 1.68eV respectively by changing the capacity of gallium (Ga). At the beginning, CuInSe₂ solar cell was just a simple p-CuInSe₂/n-CdS heterojunction. However, modern CIGS solar cells have been developed to have the following configurations: substrate, molybdenum electrode, CIGS, CdS, i-ZnO, AZO, aluminum metal electrode [5].

Under normal circumstances, CIGS solar cells will use soda lime glass to make a rigid substrate. However, flexible substrates (such as polyimide or metal foil) have also been widely used in this method. In CIGS solar cells, a sputtered Mo electrode layer will be used as the back contact layer and reflective layer to reflect the least absorbed light into the absorption layer; and a P-type CIGS absorbing layer is formed above the sputtered Mo

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electrode layer. In the state-of-the-art high-efficiency CIGS solar cell, the absorber layer is formed by physical vapor deposition (for example, thermal co-evaporation at a high temperature of 600 °C) and a two-stage process (for example, first the sputtering of the precursor layer, followed by the selenization of selenium vapor or H₂Se gas).

A thin n-type buffer layer is placed above the absorber layer. This buffer layer is usually CdS deposited using a chemical bath. However, considering the environment and harmful effects, scholars have carried out a lot of research to develop a cadmium-free buffer layer [6,7]. In these studies, ZnSe, ZnS, ZnO, (Zn, Mg) O, In(OH)₃, In₂S₃, In₂Se₃, InZnSex, SnS₂, SnO₂, etc. were used as buffer layers, and these buffer layers use various preparation methods (for example, metal organic chemical vapor deposition, chemical bath deposition, electrodeposition, sputtering, thermal evaporation, atomic layer deposition, ion layer gas reaction, pulsed laser deposition, etc.) to be deposited [7]. To avoid surface damage of the CdS layer, an i-ZnO layer was added above the buffer layer, and a relatively thick AZO (specifically Al: ZnO) layer was used to cover the i-ZnO layer. The ZnO layer is deposited using only chemical vapor deposition. The AZO layer acts as a transparent conductive oxide layer to collect and transport electrons to the outside of the battery and emit as much light as possible.

4 Research progress

To show the development of CIGS thin-film solar cells, the following section mainly reviews some key research work done by domestic and foreign researchers in this field.

The history of CIGS thin-film solar cells can be traced back to the first CuInSe₂ (CIS) thin film synthesized by Hahn in 1953 [8]. Bell Labs nominated this material as a photovoltaic material in 1974. In 1974, a researcher coated an evaporated n-type CdS on top of a p-CuInSe₂ single crystal, thereby developing the first CuInSe₂/CdS heterojunction photovoltaic device [9]. In 1976, the University of Maine developed a p-CuInSe₂/n-CdS photovoltaic cell with a rigid substrate, and made the first significant progress in the efficiency of CIGS thin-film solar cells, with a reported efficiency of 4.5% [10]. In 1981, Boeing developed the first high-efficiency CuInSe₂ thin-film solar cell by vacuum-depositing an evaporated n-type CdS on the crystalline p-CuInSe₂, with a reported efficiency of 9.4% [11]. Since then, CIS solar cells have received widespread attention from researchers.

In 1993, the Advanced Industrial Science and Technology Institute (AIST) in Japan adopted an electron beam evaporation process followed by selenization to achieve the purpose of depositing an absorber layer on a flexible molybdenum foil, and the developed flexible solar cell has an efficiency of 8.3% [12]. In 1995, the National Renewable Energy Laboratory (NREL) embedded gallium into the CIS matrix to increase the band gap, open circuit voltage and fill factor of the absorber, thereby a highly efficient CIGS cell based on molybdenum coated alkali lime glass substrate was developed, and the reported efficiency is 17.1% [13]. In 1996, the International Solar Electricity Technology Corporation (ISET) used polyimide as a flexible substrate for the first time, and developed a CIGS cell through a two-stage process of sputtering metal presets, with a reported efficiency of 8.7 % [14]. In 1999, NREL deposited a ZnO/CdS/Cu (In, Ga) Se₂/Mo polycrystalline thin film solar cell on a glass substrate, further increasing the efficiency to 18.8% [15]. Then, in 2008, NREL increased the efficiency to 19.9% again by reducing the recombination during the CIGS deposition process [16]. It can be seen that NREL researchers often report what significant improvement in efficiency of CIGS solar cells built on a rigid glass substrate has been achieved. In fact, so far, NREL is also a leading research institution in the field of CIGS solar cell development.

In 2010, AIST used a three-stage co-evaporation process to deposit the CIGS absorber layer on the molybdenum flexible substrate, thus achieving the highest efficiency (14.6%) of the CIGS battery using the molybdenum substrate [17]. In 2011, Nanosolar and the Swiss Federal Institute of Materials Science and Technology (EMPA) adopted a non-vacuum low-cost printing setting and achieved the highest efficiency (17.1%) of CIGS cells using aluminum foil substrates [18]. In 2012, EMPA achieved the highest efficiency (17.7%) of CIGS cells using Mo/Ti-coated stainless-steel substrates [19]. In 2013, EMPA developed the most advanced flexible CIGS solar cell with the highest efficiency (20.4%) built on polymer foil [20]. In 2017, AIST adopted a co-evaporation process on a rigid glass substrate and developed a new CIGS solar cell with an efficiency of 22.5% [21]. In 2019, Solar Frontier used vacuum deposition technology to develop CIGS solar cells with the highest efficiency (23.4%) [22].

To show more clearly the development of CIGS thin-film solar cells using rigid or flexible substrates, this paper specifically classifies and summarizes some key research work done by domestic and foreign researchers in the field of CIGS thin-film solar cells. The specific situations are shown in Table 1 and Table 2.

Table1. Development of CIGS thin-film solar cells with rigid substrates.

Year	Substrate type	Efficiency value	Research institute	References
1976	Rigid	4.5%	University of Maine	[10]
1981	Rigid	9.4%	Boeing	[11]
1995	Rigid	17.1%	NREL	[13]
1999	Rigid	18.8%	NREL	[15]
2008	Rigid	19.9%	NREL	[16]
2017	Rigid	22.5%	AIST	[21]
2019	Rigid	23.4%	Solar Frontier	[22]

Table2. Development of CIGS thin-film solar cells using flexible substrates.

Year	Substrate Type	Efficiency Value	Research Institute	References
1993	Flexible	8.3%	AIST	[12]
1996	Flexible	8.7%	ISET	[14]
2010	Flexible	14.6%	AIST	[17]
2011	Flexible	17.1%	Nanosolar & EMPA	[18]
2012	Flexible	17.7%	EMPA	[19]
2013	Flexible	20.4%	EMPA	[20]

It can be seen from the above-mentioned development process of CIGS thin-film solar cells that rigid glass substrates have become the most widely used substrates for the deposition of absorber layers. Among many research institutions, NREL, a leading institution, has invested a lot of energy in the research of CIGS thin-film solar cells using rigid substrates. The most advanced CIGS battery with a rigid substrate currently available has an efficiency of up to 23.4% [22]. However, the current trend is to develop flexible solar cells built on flexible substrates of metal foil [23-25] and polyimide [14,23,26], and EMPA has spent a lot of thought on this aspect of research. Since the first attempt to develop flexible solar cells using molybdenum, titanium, and aluminum in 1992, the most advanced CIGS solar cell using a flexible substrate is built on a polymer foil with an efficiency of 20.4% [20].

5 Commercial application

At present, the preparation method of CIGS solar cells has been developed to a stage of industrial production for the purpose of commercialization. Some prestigious companies are already mass-producing CIGS modules built on glass substrates. These heavy rigid substrates are mainly used for grid-connected or stand-alone off-grid public facilities installed on roofs and land. Meanwhile, CIGS modules built on flexible substrates (such as polymers and stainless steel) are also currently produced. These CIGS modules built on flexible substrates are also used in roof installation and photovoltaic building integration. In transportation systems and charging applications. The existence of precision winding alignment technology improves the production potential of flexible substrates, and at the same time can reduce the size of the equipment required for different graded layers. However, so far, the development of standardized precision winding alignment deposition systems still cannot keep up with the development of CIGS solar cells, which is one of the most important reasons why the development of flexible substrates is not comparable to the development of rigid substrates.

Due to the difference in the generation kinetics in a large-scale environment, the current commercialized CIGS module can achieve a maximum efficiency of 17.4% [27], and there is still a large gap with the theoretical maximum efficiency (23.4%) achieved in the laboratory scale.

6 Key problems of CIGS solar cells

In the existing CIGS solar cell research, there are still the following key issues that limit cell performance that require attention:

(1) The existing CIGS solar cells have a relatively complicated production process and need to go through a tedious production process. Moreover, the good rate of industrially produced CIGS solar cells is not high.

(2) There is an urgent need to develop and design a deposition process that can be performed under lower temperature and can be applied to flexible substrates.

(3) The CdS buffer layer deposited by chemical bath deposition method usually uses carcinogenic cadmium, so it poses a serious threat to health and hygiene. Although selenium does not exhibit high toxicity, selenium compounds (such as H₂Se) are quite toxic. Therefore, how to find more environmentally friendly materials to manufacture CIGS solar cells is still a subject to be further studied.

(4) Material availability is also an issue that needs to be focused on in CIGS solar cell research. Most of the components in this type of solar cell are abundant in the earth's crust, except for the rare metal's indium and gallium. Moreover, these two rare metals have expensive prices.

The above several resource restrictions and ecological problems have had a considerable negative impact on the practical value of CIGS solar cells, and to a certain extent they have restricted their promotion and application in real life and business, and have led to our current failure to deploy CIGS solar cells on a terawatt scale. Therefore, in the future research of CIGS thin-film solar cells, it is necessary to start from the two aspects of material optimization and interface performance research to further improve the efficiency of CIGS thin-film solar cells.

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