



Preparation and Study of $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) Thin Film and Application of Solar Cell

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Abstract

Global energy consumption (primary energy) continues to increase in parallel with economic growth, but due to issues such as the limited availability of fossil fuels and the need to reduce carbon dioxide emissions, there is a demand for safe, stable and environmentally friendly energy sources. Solar cells are expected to use solar energy, a natural and sustainable energy source.



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Introduction:

Global energy consumption (primary energy) continues to increase in parallel with economic growth, but due to issues such as the limited availability of fossil fuels and the need to reduce carbon dioxide emissions, there is a demand for safe, stable and environmentally friendly energy sources. Solar cells are expected to use solar energy, a natural and sustainable energy source.

Crystalline silicon cells are currently the dominant type of solar cell, achieving a high photovoltaic conversion efficiency of 25.6%. 1) While technological advancements are contributing to cost reductions, However, the raw material, ultra-pure silicon, remains expensive. Furthermore, long-term operation is challenging due to photodegradation. Semiconductor composite solar cells have been developed to address these issues. Solar cells made from composite semiconductors do not require ultra-pure materials and are less susceptible to light-induced damage. However, Generally, solar cells are made from composite semiconductors of groups II-IV or III-V.

Solar cells made of CdTe and $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$ (CIGSe) have achieved remarkable efficiencies exceeding 20%. Because elements like indium and tellurium are scarce and rare, and cadmium is highly toxic, the use of these devices on a terawatt scale may be limited. In recent years, $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) compounds appeared as alternative materials membranes thin solar cells. This is thanks to its distinctive photovoltaic features and its use of non-toxic materials that are

abundant in nature. It is a polycrystalline CZTS compound with a structure derived from the copper indium gallium selenium CIGSe compound. Continued research and development of the CIGS compound resulted in the replacement of indium and gallium, considered rare and scarce elements, with zinc and tin, leading to the development of the new compound CZTS. In addition, Some of the formulas that CZTS contains are:. Structure of stannite exhibits the tetragonal arrangement, but the alternation of cation positions in the crystal lattice results in a difference in symmetry. The installation of the CZTS system is based on Wurtziten, which is a strongly bonded hexagonal compound. All elements are measured in proportions in the compound Cu_2ZnSnS_4 , although the kistrite structure is the most commonly used in solar cells[1].

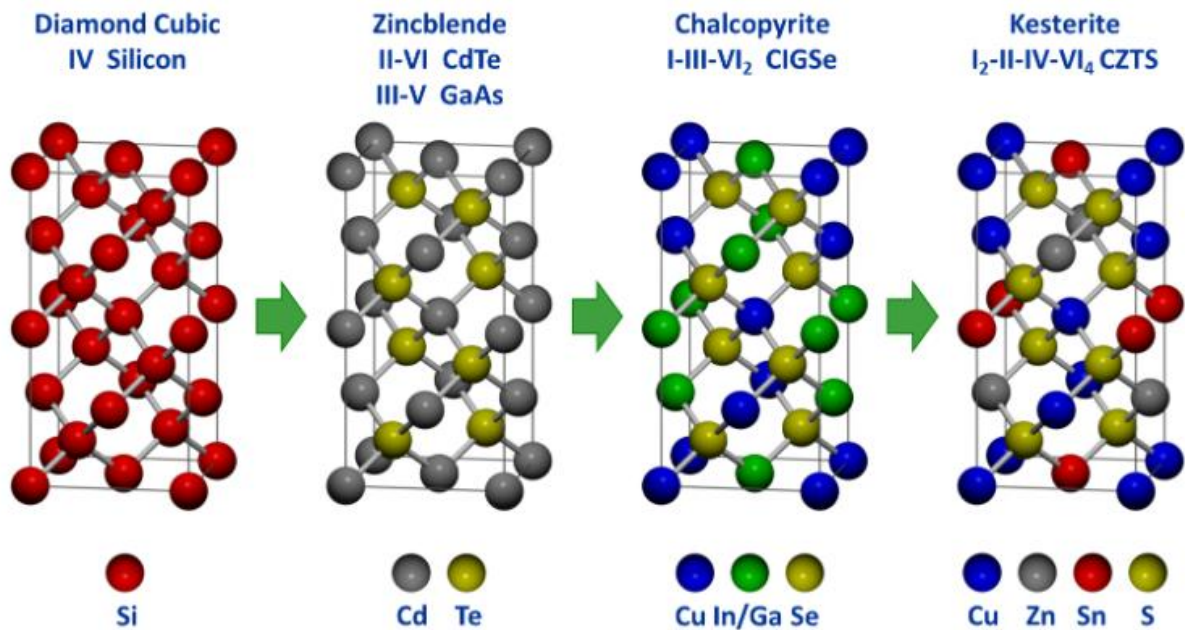


Fig.1 Crystal structures of semiconductor materials.

CZTSe Solar Cell Development

At Shinshu University in Japan in 1988, CZTS material was first studied as a solar cell material. The researchers prepared CZTS thin films in the laboratory using spray deposition technology and measured their electrical conductivity. The results showed that holes are the majority charge carriers in this compound (p-type), and that the blocked energy gap was 1.45 electron volts. This compound also has an absorption coefficient greater than 10^4 cm^{-1} Within the visible light spectrum. [2]. Research on this topic continued, and in 2009 improvements were made to the CZTSe cell by treating the cztse compound with solutions and also by selecting window layers, resulting in efficiencies of approximately 7%. [3,4]. In 2013, using a hydrazine-based solution method, IBM researchers were able to prepare the CZTS compound and achieve an optimal conversion efficiency of 12.6%. [5]. In 2022, researcher Ersan Y. Muslih and his team prepared thin films of the $Cu_2ZnSnSe_4$ compound using the solution method. Optical and structural tests of the compound were performed, and the results showed that the prepared films were of high quality. Regarding the electrical properties, the cell conversion efficiency was approximately 18.5%, and the short-circuit current was 30 mA/cm^2 [6].

Fabrection of CZTSe solar Cell.

The methods for preparing CZTSe thin films and applying them as solar cells are classified into two main approaches: 1- Vacuum method 2- Solution method. The vacuum method includes atomization, atomic layer deposition, and evaporation, while solution-based processes include nanocrystal "inks," electro-deposition, solid gel molecular precursors, and spray thermal

decomposition[7]. Using one of the methods mentioned above to prepare multilayer solar cells, including a CZTSe absorber layer, It is a process of depositing materials onto conductive wafers. Soda-glass coated with Mo is commonly used.

Which acts as a back-end connection point. It is often annealed at high temperatures (around 500-600 degrees Celsius) With the presence of gases such as hydrogen, argon, Sulfur(S), selenium(Se), and sulfides. Adaptation layer, which is an n-type semiconductor material, is deposited on top of the absorption layer. The Window layer is a transition metal oxide such as ZnO or In₂O₃, is deposited. This layer has a large energy gap of approximately 3.2 eV and is used as a transparent electrode, allowing the maximum amount of light to pass through to the cell, which stimulates the transfer of electrons to the absorption layer. Finally, the patterned metal electrodes (such as nickel/aluminum) It is evaporated to obtain the cell in its final form, as illustrate in Figure 4.

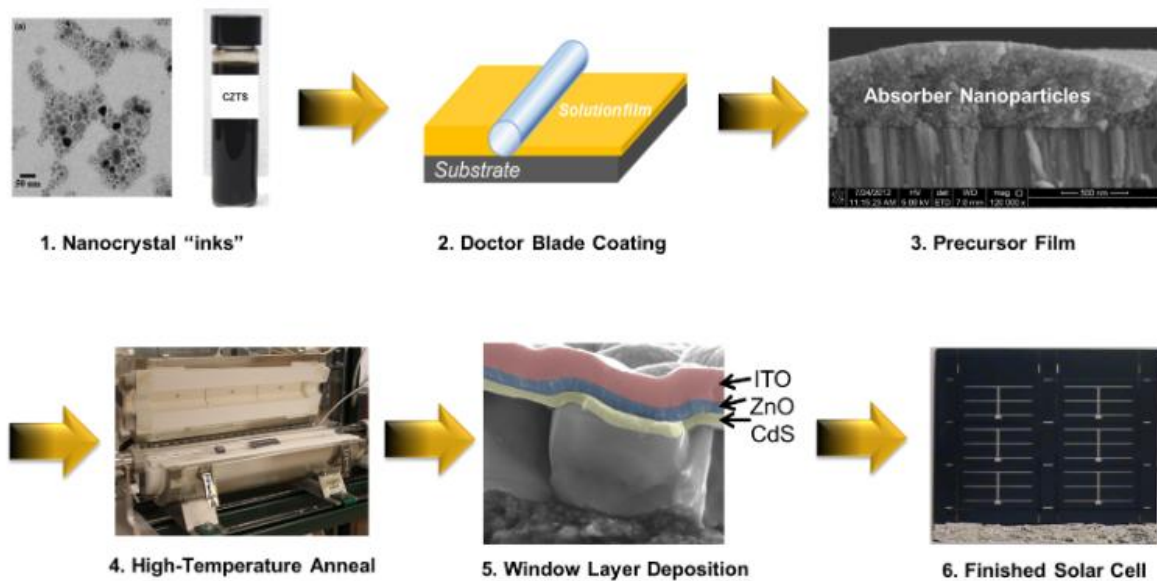


Fig.4 Typical diagram of the production of solar cells made from (CZTS): nanoparticle-based processing

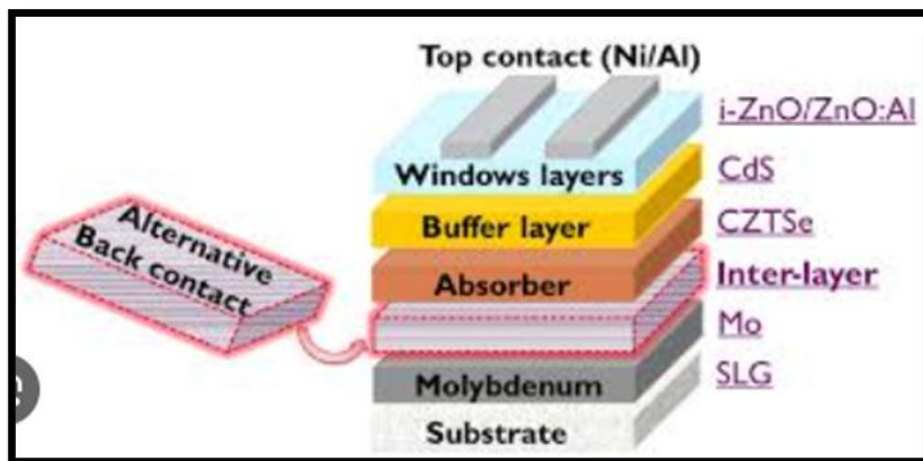


Fig.2 Typical structure of solar cells based on CZTSSe materials.

CZTSe material properties

The charge vectors concentrations and absorption factor in Cu₂ZnSn(S,Se)₄ are comparable to those in copper indium gallium selenium compound. Also, the lifetime of these carriers (and the

associated diffusion length) is very short (less than 9 nanoseconds) for CZTS. The formation of defects in the compound and the process of Re-union at the grain limites may cause a shortened charge carrier lifetime. Appearance of defects in $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ is common because to the decrease energies, resulting from defects in zinc and copper anti-sites and copper voids[8]. The presence of defects leads to a reduction in the electrical characteristics of the CZTSe cell, including a reduction in open-circuit voltage and energy conversion efficiency in the zinc-tin sulfide solar cell. There are also other secondary phases in CZTSe quaternary compounds that negatively affect the performance of the solar cell. Published studies indicate that all secondary phases negatively affect the performance of zinc-tin sulfide (CZTS) crystals, and a lot of these are difficult to discovery and quite widespread. Common phases include zinc sulfide (ZnS), tin sulfide (SnS), copper sulfide (CuS), and copper-tin(III) sulfide (Cu_2SnS_3). It is not easy to identify these phases using conventional methods such as X-ray diffraction (XRD) due to the overlap of the ZnS and Cu_2SnS_3 peaks with CZTS. While some impurities such as ZnS can be eclectic elimination from the $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ compound via adding spicy dilute hydrochloric acid.[9]. Therefore, CZTSe is considered a polycrystalline material. The band gap for the various crystalline forms has been found to extent between (1.1 - 1.5) eV. Raman dispersion is used to assistance description the multiple forms of CZTS.[10].

CZTSe Solar Cell Limitation

Preparing CZTSe in practice is difficult due to its complex structure. Achieving thermodynamic stability within the material is difficult; in fact, a pure phase material cannot be obtained.; moreover, One of the drawbacks of preparing CZTSe is that, with increasing temperature, the tin element becomes volatile and cannot be easily controlled. Furthermore, numerous If the reaction cannot be controlled during preparation, secondary phases such as ZnS Cu_2SnS_3 may appear. [11]. Furthermore, the formation energies of the stannite and cassiterite phases are similar, so a mixture of the two is likely to form during the synthesis process. Therefore, it is not possible to differentiate between two materials using Conventional XRD technology. Crystalline defects form very easily in the $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})$ compound. Because similarity in ionic radii between copper and zinc cations, antiselective site defects are generated between them. Furthermore, the defects that form cannot be completely eliminated, but they may cause band-tail states to appear - which are essentially trap states that are formed result of changes in electrostatic potential in material. These states lead to a prominent reduction in Voc and this severely limits the performance of the solar cell. In general, after identifying the defects in the crystal structure of CZTSSe, researchers focused on identifying and minimizing these defects[12]. One of the proposed modern methods is replacing the copper or zinc atom with another atom of a significantly different diameter.

Conclusion:

$\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})$ CZTSSe is considered one of the most promising absorber materials for thin-film solar cell technology due to its abundant components and non-toxicity. CZTSSe also features an ideal direct energy band gap of between 1 and 1.45 electron volts, and a high absorption coefficient ($>10^4 \text{ cm}^{-1}$) in the visible light region, which achieves the conversion of as much solar spectral energy as possible. However, the preparation of these thin-film cells faces challenges due to their tetragonal crystal structure. Defects may appear between the crystals, in addition to the emergence of undesirable secondary phases during the film growth process. Consequently, these defects lead to a decrease in conversion efficiency and open-circuit voltage.

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