CZTS – An Expanding Horizon in the Thin Film Technology - A Review

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ABSTRACT *Looking at the global energy requirements, apart from available resources, the second dimension i.e., energy efficient materials become most burning topic for the researchers. Cu_2ZnSnS_4 (CZTS) is one of the materials in this category which provides versatile characteristics in thin film development. In the present article the advantages of the CZTS over the conventional materials are shown from various points of view. Chronological development of the CZTS synthesis technology and obtained efficiency of the material are described briefly. Characteristics of the said material and comparison with other materials in context of band gap, suitability for solar energy conversion and toxicity are discussed. Limitations those faces by current synthesis processes and possible ways to overcome them are also given at the end of the article. The study will provide a single platform to researchers and technocrats working this field as a base for further research.*

Keywords: *CZTS Material; Thin film; Energy efficient material.*

Introduction

The With the development of the industries and increase in means of the transportation the energy demand of the world is increasing with high rate. But to fulfill the tremendous requirement of energy, mainly the conventional sources of energy are used so far. These sources are also the sources of the Carbon, which create pollution and therefore environment related global problems. Thus it is the demand of today to find an efficient and eco friendly source of energy. Photovoltaic solar cell is the best option that can omit the conventional fuel operation mechanism. The Varity of materials are reported so far those can be used as deposition for on solar plate. But with all the materials, the efficiency of the solar cell is main concern of the research. Other important dimension into which researcher intended to look after is the band gap. With development in the material synthesis techniques, few very efficient materials having suitable band gap are synthesized. One of the promising material is having Copper, Zinc, Tin and Sulfur i.e., CZTS. The material having non toxic property is also one of the reasons to be very useful. Out of so many options (CdTe, CIS, CIGS, GaAs etc.) available, the manufacturers are nowadays oriented towards CZTS, because CIGS contains rare Indium and Selenium which is toxic. Therefore the problems of rare resources and environmental pollutions become troublesome [1]. To realize advantages of thin film technologies in the future, new unconventional solar cell materials that are abundant but much cheaper to produce than silicon are needed to reduce the overall cost of solar photovoltaics [2-3].

Structure of CZTS

When Indium (Group - III) is replaced by the Zn (Group- II) and Sn (Group- IV) in CuInS2 quaternary structured CZTS is obtained [4-5].There may be two possibilities of CZTS structures: (i) Stannite and (ii) Kesterite. These two structures are different from each other as they have different positions of Cu and Zn. From the so many reports over CZTS structure it can be concluded that the most commonly CZTS is available in the kesterite type of structure.

Historically, for the first time Schafer and Nitsche had fabricated Cu2ZnSnS4 [6]. It was proposed by Persson that the structure of the CZTS can be decided by utilizing anisotropy of both of the type of structures to measure the dielectric constant in different directions (i.e., parallel and perpendicular to axis) [7].

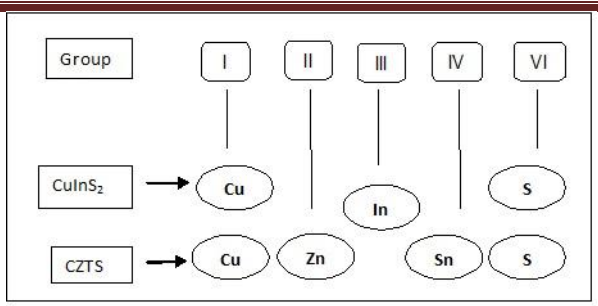

Figure 1 : Group wise elements in CuInS2 and CZTS

Energy Band Gap in kesterite and stannite phase

The energy band gap of the synthesized material varies with crystal structure. With the kesterit structure the energy band gap reported are near to 1.54 eV and with stennite those are near to 1.36 eV. Some of the calculated values of kesterite and stennite structure are shown in the Table 1.

Table 1. Band gap reported by different authors for kesterite and stennite structure.

Structure	Persson [7]	Chen et al.[8]	Pair et al. [9]	Vidal et al.[10]
Kertersite	1.56	1.50	1.49	1.64
Stennite	1.42	1.38	1.30	1.33

CZTS thin film deposition techniques

Most of the common techniques used for the deposition of other materials are also reported to be useful for the CZTS deposition. The material to be coated on the substrate is converted in the form of vapour and allow to deposit on substrate. Depending upon the way from which the vapour is created the methods are classified in two types i.e., Physical vapour deposition (in which the vapour is obtained by any physical mean without any chemical reaction) and Chemical vapour deposition technique(in which the pr oduct of the chemical reaction is deposited on substrate.)

- Physics Deposition Techniques

It is further classified into various sub categories:

- Thermal (Target heating) Process. Following are the methods those are included in this technique:
  - Pulsed Laser deposition technique

Material is subjected to a high energetic pulsed laser. The evaporated material constituent particles reach to the substrate and form a film. Only limitation is through this technique very small uniform area of deposition is obtained.

- Vacuum evaporation

Vacuum chamber is used for this type of deposition. Resistance heating, induction heating or any other out of several ways is adopted to create supply heat to the material. The atoms evaporated from the target are move toward the substrate because of vacuum.

- Epitaxy

A very accurate way for control of film deposition is epitexy or molecular beam epitaxy. Previously prepared hot substrate is cooled at growth temperature. Ultra high vacuum is required for proper deposition beam of molecules is directed towards the substrate.

- Sputtering

Instead of thermal ejection of the constituent molecules from the target, a bombardment of particles is used to pull the molecule out from the material. This technique may have different kind of variants. Depending upon varients, those are listed below,

DC/RF sputtering
DC/RF magnetron sputtering

- Chemical Deposition Techniques

In another category of the deposition technique mostly following methods are used by various researchers:

Chemical Vapour Deposition Technique (Gas Phase)

A chemical reaction is allowed between the vapour containing ingredient of complex compound to be deposited. It is used for the verity of the depositing material like metal as well as semiconductors.

Various kind of CVD has been developed by researchers that includes Plasma enhanced CVD, Metal Organic CVD, Law pressure CVD, Laser enhanced CVD Etc.

Solution based
There so many solutions based techniques which are also used to deposit CZTS.
Sol-gel
Dip Coating
Spin Coating
Spray pyrolysis
Main steps involved in this approach are shown in following box,

(i)
Preparation of precursor solution containing specific ions

(ii)
Spin coating of precursor in

(iii)
Annealing film in a controlled environment

Efficiency reported with different techniques

Previously obtained efficiency is indicated in the Table 2.

Table 2. Efficiencies for best CZTS solar cells prepared by different techniques.

Sr No.	Author	Efficiency (%)	Preparation Method
1	Katagiri et al.[11]	0.66	Physical Deposition Electron beam evaporation
2	Katagiri et al[12]	2.62	
3	Katagiri et al. [13]	5.45	
4	Friedlmeier et al.[14]	2.30	Co-evaporation
5	Wang et al.[15]	6.80	Co-evaporation
6	Shin et al.[16]	8.40	Co-evaporation
7	Schubert et al. [17]	4.10	Quaternary Co-evaporation
8	Moriyo et al.[18]	1.75	Pulsed Laser Deposition
9	Yang et al.[19]	5.45	Electron beam evaporation
10	Jimbo et al.[20]	5.74	RF Sputtering
11	Todorov et al.[21]	9.60	Spin Coating

Limitations

As material is having more than one compound, ratio of particles is difficult to maintain precisely compare to the other materials, the yield is law. Apart from that the non linear relationship between properties of material and the cell performance limits the mass production.

Conclusion

CZTS is a material that may replace the other high cost toxic and rare available material in the thin film deposition. Looking at the current scenario, an immerging scope is found to move towards this material for the solar cell field. Number of experiments reported so far shows that with the growth technology the efficiency of solar cell can be increased with this material. The above study provides wide information to researchers.

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