PROSPECTS OF CZTS SOLAR CELLS FROM THE PERSPECTIVE OF MATERIAL PROPERTIES, FABRICATION METHODS AND CURRENT RESEARCH CHALLENGES

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The quest for green energy to meet the world's ever growing energy demand has prompted the scientific community to focus their research activities on the renewable energy field. Among the candidates, thin film solar cells especially those using inexpensive, abundant and nontoxic material copper-zinc-tin-sulphide (CZTS) based solar cell is a promising type of solar which can be realized as a high efficiency and low cost solution for electricity generation. This review paper addresses the material properties, fabrication methods and current research challenges to achieve high efficiency and low cost CZTS thin film solar cells. Cu_2ZnSnS_4 (CZTS) is a prominent low cost absorber layer to be used as a substitute of CIGS absorber layer in the thin film solar cells. CZTS can lead to production of nontoxic thin film solar cells with high absorption coefficient. The scope of this review aims to evaluate the basics of CZTS solar cells fabricated by a co-evaporation technique which leads to the highest conversion efficiency so far.

1. Introduction

Currently, the major driving force in solar photovoltaics is silicon solar cell technology but currently thin film technology is gaining momentum as it offers high efficiency and low cost solar cells. Among the various thin film solar cell candidates, CZTS thin film solar cells are very promising candidate for high efficiency, low cost, non-toxic and rare metal-free solar cells for solar photovoltaic conversion purposes.

Prior to the extensive research on CZTS solar cells, chalcopyrite solar cells of copper-indium-gallium-diselenide (CIGS) thin film received much wider attention and subsequently achieved the highest cell efficiency of 20.3% after almost more than 25 years of research worldwide. CIGS solar cells have also proven to maintain high efficiency and stability in large area modules and these have prompted the commercialization of CIGS solar cells around the globe. However, the scarcity of indium and the high material cost of indium and gallium impelled researchers to look for an alternative photovoltaic material.

Copper-zinc-tin-sulphide (CZTS) is a semiconductor with excellent photovoltaic properties such as direct-band gap, high absorption coefficient, and possesses an optimal band gap energy of 1.4-1.5 eV which highly desired in photovoltaic material. Moreover, CZTS cells use abundant (rare-earth free metals), non-toxic and inexpensive material. The availability of copper, zinc, tin and sulphur on our earth's crust are 50 ppm, 75 ppm, 2.2 ppm and 260 ppm respectively. Meanwhile, the availability of indium is 0.049 ppm on the earth's crust which is relatively very low compared to zinc and tin.

In order to fabricate high quality a CZTS absorber layer, the deposition temperature and elemental fluxes are two important parameters that we must precisely control during the fabrication process and this can be achieved in a Molecular Beam Epitaxy system. In previous

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research, deposition profiles are based on the phase diagram analysis of the quaternary CZTS crystal systems. Ultimately the best deposition profile is the one which will result in α-Cu_2ZnSnS_4 crystal structure throughout the film. . The optimum Chemical Bath Deposition process was also investigated in order to fabricate high quality ZnS (O, OH) layer. The optimization of CBD processes was done by varying several important parameters such as bath temperature, molar concentration and deposition time.

In the current world of solar cells, it is necessary to fabricate low cost, high conversion efficiency solar cells without material degradation for widely used electricity generation. Thin film solar cells with a CIGS absorber have now the conversion efficiencies of 19.5% and a high optical absorption coefficient in comparison to polycrystalline Silicon solar cells [1]. In CZTS solar cells costly Indium (In) will be replaced low cost Zinc (Zn) and Gallium (Ga) with Tin (Sn). CZTS is a quaternary semiconductor of group I-II-IV-VI which has been investigated as effective light absorbing materials in solar cells recently. Figure 1 shows the periodic table of CZTS by moving from groups 12 and 14. Solar cells with this absorber layer are very a promising material because of its optical bandgap 1.4-1.56 eV and large absorption coefficient over 10^4 cm^{-1}[2]. However, in this study the bandgap has been varied between 1.4 to 1.5 eV to find out the effect on performance. In addition, CZTS does not contain toxic elements which lead to a solar cell with less environmental damage and low cost. CZTS is a direct bandgap semiconductor which can help to produce high efficiency. In a direct bandgap semiconductor, an electron making a transition from the valance band to the conduction band can do so without a change in momentum [3].

Fig. 1: Section of the periodic table showing the logic of changing from CuIn(Ga)Se2 to CuzZnSnS4 by moving from groups 12 and 14 [33].
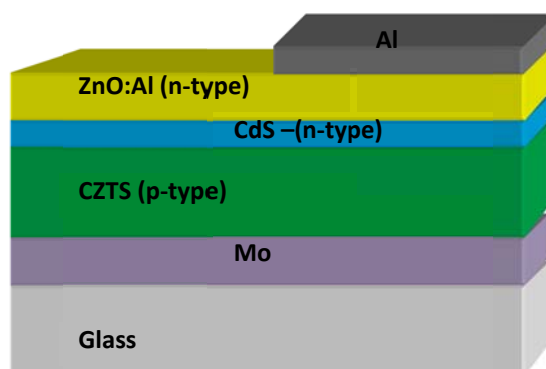

Fig. 2: Schematic Diagram of CZTS-based thin film solar cell.

Schematic Diagram of CZTS-based thin film solar cell is shown in figure 2. This consists of CdS buffer layer deposited by the chemical-bath-deposition (CBD) technique and a transparent conductive ZnO:Al film deposited by rf magnetron sputtering. However, due to the quaternary properties the structural, crystallographic, and electrical properties can be influenced by the stoichiometry composition, which will result in forming native defects [4]. In addition, in some previous work CZTS with metal rich defects have been found. The defects as well as the small grain size of CZTS cause short the diffusion length of carriers [5]. CZTS based solar cells have high series resistance, R_s = 4.25 Ω and and shunt resistance, R_{sh} = 370 Ω. The higher series

resistance and lower shunt resistance of the cells will lead to reduce a efficiency by affecting the J-V characteristics. However, light soaking can improve the performance [6]. At the same time, the temperature dependence of CZTS solar cell is very important to find out as solar cells performance generally decreases with increasing temperature. It happens due to increased carrier recombination rates, caused by thermal vibration [7]. In this paper, effects of different operating temperatures have been studied. Furthermore, the n-CdS layer which has been used as a buffer layer on top of p-CZTS is very important because of improving the interface quality with p-CZTS and improving the transmission of blue wavelength region. CdS has a bandgap of 2.53 eV [8].

2. Material properties

CZTS is a new type of an absorber and abundant materials for thin films solar cells compared to CIGS because indium and selenium in CIGS thin films are rare and cadmium is toxic. This semiconductor film can be obtained by replacing half of the indium atoms in chalcopyrite $CuInS_2$ with zinc, and by replacing the other half with tin, which is preferable for realization of a low-cost solar cell. So, when CdS forms a heterojunction with CZTS, it must be replaced with zinc sulphide (ZnS) because ZnS tunes the band gap [9]. According to photon balance calculations of Shockley-Queisser, CZTS is expected to have theoretical efficiency more than ~30% [13]. The best efficiency CZTS solar cells having Cu poor and Zn rich favour the growth of other phases during the formation of the film [14]. Due to the low Cu and high Zn ratio CZTS layer becomes more p- type semiconductor [11]. Figure 2 shows the schematic diagram of CZTS based thin film solar cell [12]. The heterojunction in the final solar cell consists of a buffer-layer and a window-layer on the CZTS film. The buffer-layers (CdS and ZnS) on top of CZTS absorber layer are deposited by the Chemical Bath Deposition (CBD) method [15].

CZTS is derived from the CIGS structure by the isoelectronic substitution of two In (or Ga, respectively) atoms by one Zn and one Sn atom. As a consequence, the CZTS layer has similar properties to the CIGS layer. One main advantage of this is that the standard device structure of the solar cells can be adopted. The crystal structure of CZTS is shown in Figure 3 which is known as the kesterite structure and can be derived from the sphalerite2 structure by duplicating the unit cell. The kesterite structure is the most stable phase of CZTS [31].
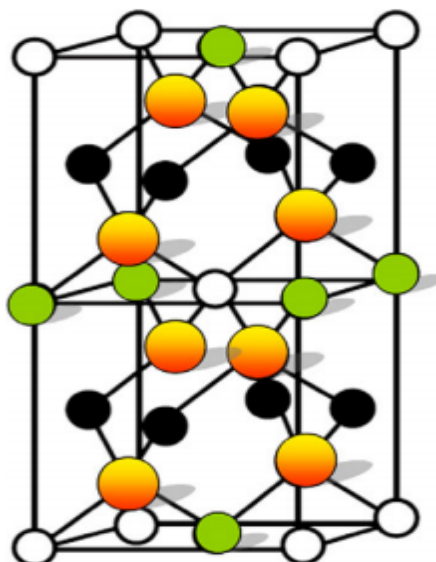

Fig. 3: Kasterite structure in which CZTS crystallizes. It is derived from the sphalerite structure by duplicating the unit cell [32].

The material CZTS, Cu_2ZnSnS_4 is quite closely related to CIGS, as shown in the Figure 1. In essence, the expensive and scarce elements indium and gallium are replaced by a 50: 50 combination of much cheaper Zn and Sn. At the same time, Se is replaced by abundant and cheap

S due to the bandgap of Cu_2ZnSnS_4 (1.45 eV). It is closer to the optimum value than the corresponding selenide compound, which has a narrower bandgap. In figure 4 all cations are ordered in the kesterite structure, and the occupation of anions is generated so that the pair-correlation function is closest to that of the random alloy.
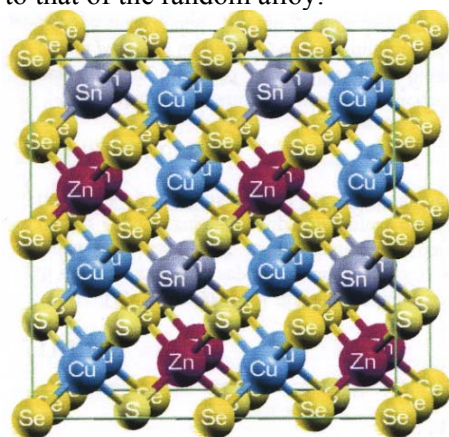

Fig. 4: The special quasirandom structure of Cu_2ZnSn (S: Se = 0.25:0.75)$_4$ with cations ordered in the kesterite structure [17].

2.1 Phase Diagram of CZTS

CZTS can be synthesized through solid state chemical reactions among ZnS, Cu_2S and SnS_2. Actually, the CZTS material usually appears in the kesterite phase because it is more stable thermodynamically compared to the stannite-type [25]. Investigation of the phase diagram of the system has shown that a single phase CZS material can be formed in a very small region which is shown in figure 5.
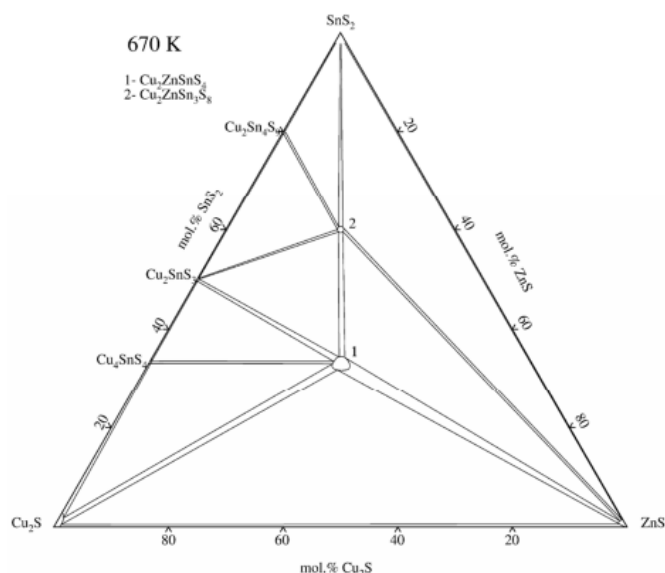

Fig. 5: Phase Diagram of SnS-Cu2S-ZnS solar cells [24].

There are ten fields drawn in the phase diagram. Each field indicates the presence of CZTS plus the one or two secondary phases. All the secondary phases contain sulphur. Due the higher sulpherzation during deposition no metallic phases will be formed [25].
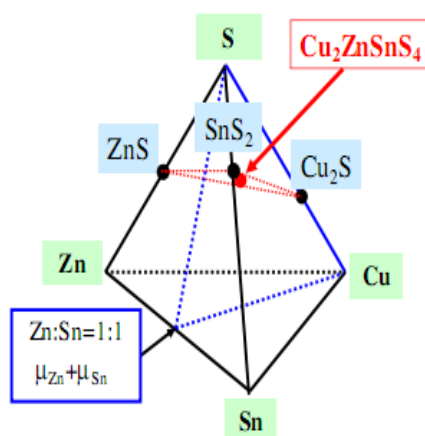
Fig. 6. Schematic phase diagram of quaternary Cu-Zn-Sn-S system.

Fig. 6 shows a schematic phase diagram of the quaternary Cu-Zn-Sn-S system. In the present study, the vacancy formation energies in CZTS in the pseudoternary system are calculated respectively, because Katagiri et al. reported that they obtained high efficiency CZTS solar cells under the Cu poor and Zn rich condition. From the pseudo-ternary phase diagram, it can be found that there are no cells in the area over 1% efficiency in the Cu-rich region. (2); even in the Cu-poor region, there are no effective cells in the area above the green (CZTS+ZnS) line. (3); even in the Cu-poor and Zn-rich region, there exists a certain limit in the Sn concentration to keep the conversion efficiency high. In order to achieve high conversion efficiency, it is necessary to fabricate CZTS thin films in the narrow region alongside the green line. If the method for removing the semi-metallic CuS from the surface of CZTS films was accomplished, the window of production condition will be widened.
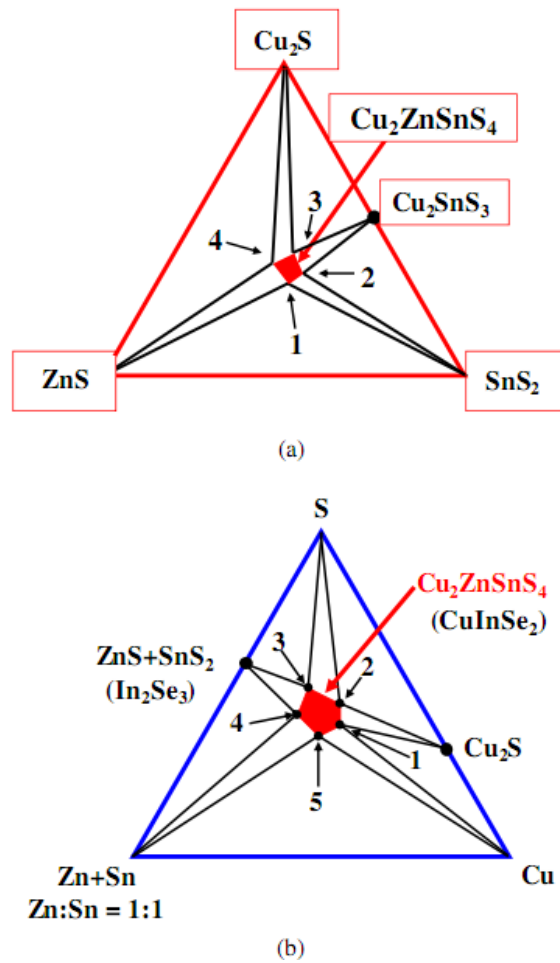
Fig. 7. Schematic phase diagram of pseudo-ternary Cu_2S-ZnS-SnS_2 system (a). Points 1 and 2 correspond to Cu-poor conditions. Points 3 and 4 correspond to Cu-rich conditions. Point 1 corresponds to Cu-poor, Zn-rich, and S-rich condition. The pseudo-ternary phase diagram of Cu-$(Zn + Sn[C : Zn = 1 : 1])$-$S$ system (b) is shown for reference. [30]

Under the Cu-poor condition such as point 1 in Figure 7, the formation energy of the Cu vacancy is smaller than those of Zn, Sn and S vacancies, as well as the result of CZTSe. In addition, the formation energy of the Zn vacancy is much smaller than those of the Cu vacancy under the Zn-poor and S-rich condition, such as point 3. The formation energy of the Sn vacancy is larger than those of Cu and Zn vacancies under the Cu-poor, Zn-rich and S-rich condition (Sn-poor condition figure second phase diagram pseudo blue colour). Therefore, the Cu vacancy is easily formed under Cu-poor, Zn-rich and S-rich condition. The phases and composition of the final thin film depend on the precursor and the sulphurization process. According to the degree of diffusion of the elements, the content of sulphur and several more aspects, the formation CZTS might be slower or faster and in doing so allow more or less loss of elements/secondary phases by evaporation as well as influence the segregation of secondary phases.

Friedlmeier et al. analyzed the structural properties of CZTS in detail with the similar pseudo-ternary ZnS-SnS_2-Cu_2S phase diagram [34]. From the figure, the Cu-poor zone is under the bold horizontal line indicating the composition of CuS of 50%. Similarly, the Zn-rich exist in a left half area separated by the bold vertical line.

2.2 Defect Physics of CZTS

According to the doping limit rules, a semiconductor is difficult to dope an n-type if the conduction band level is too high, and is difficult to dope a p-type if the valence band is too low in energy [17]. The p-type doping, or self doping, is related mainly to the electronic states near the

top of the valence band. Defect analysis for Cu_2ZnSnS_4 shown that the facile formation of defects such as Cu_{zn} antisite and Cu vacancy make it p-type intrinsically, but the ionization level of the dominant Cu_{zn} antisite is relatively deeper than that of the Cu vacancy [18].

3. Optical properties

CZTS films posess promising characteristics optical properties and aband gap energy of about 1.45 eV to 1.5 eV [10]. As a direct badgap semiconductor, CZTS has strong optical absorption (absorption coefficient is above 1 x 10^4 /cm), thus a very thin layer of film (1-2μm) can absorb over 90% of the photons over the spectrum with photon energy higher than the band gap. The optical property of the CZTS layer can be improved with a substrate temperature of 340°C [36].On the other hand, since Cu_xS has a direct optical band gap over the range of 1.7-2.16 eV that varies with the value of x. The higher band gap of the CZTS layer (1.99-2.09 eV) can be attributed to the Cu_xS phase [37]. The band gap ($E_g \sim 1.5eV$) of CZTS thin films with T_{sub}=450C is in good agreement with the experimental and theoretical values reported by other researchers. It is reported that secondary phases such as ZnS, SnS2 and Cu_2SnS_3 easily occur under lower growth temperatures during the CZTS synthesis process.
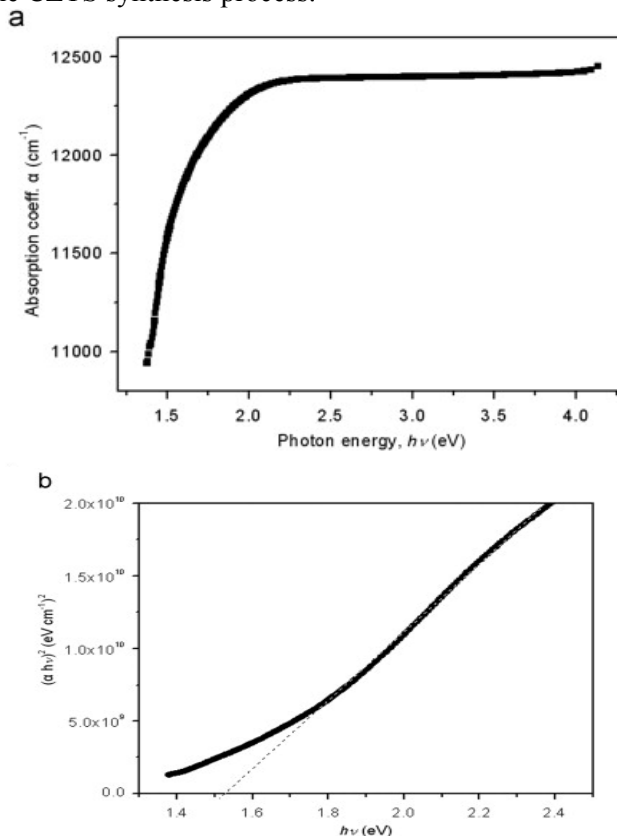

Fig. 8. (a) Optical absorption coefficient (α) of the CZTS film in situ grown by reactive magnetron co-sputtering. (b) (αhv)^2 as a function of photon energy (hv) for CZTS film in situ grown by reactive magnetron co-sputtering. [44].

The film is considered to be suitable material for photovoltaic solar energy conversion if the absorption coefficient is larger than 10^4 cm^{-1} in the visible region.

4. Latest deposition method
4.1 Sputtering
In 2003, Seol et al. prepared CZTS thin films by RF magnetron sputtering. They reported that the refractive index was 2.07, the absorption coefficient was about 10^4 cm^{-1}, and that the band

gap energy was about 1.51 eV [59]. The CZTS films were prepared by RF magnetron sputtering under argon gas. The target used in the sputtering experiments consisted of single phase Cu_2ZnSnS_4. Deposition pressure was from 0.1 to 5 Pa and sputtering power was from 20 to 50W. When Zn/Sn increases, the diffraction peak depicts the strong orientation. In the case of sputtering target with $Cu_2S:ZnS:SnS_2=1:1:1$, the Zn and Sn contents of the thin films increased but the Cu content decreased. The atomic ratio of the sputtering target was $Cu_2S:ZnS:SnS_2=2:1:5:1$ to obtain the appropriate CZTS ratio. The best atomic ratio is obtained between 50 W to 100 W. When, RF power up to 100 W and above, the Cu content of CZTS thin films was rapidly decreased, but the Sn contents with the RF power depend on the plasma density.
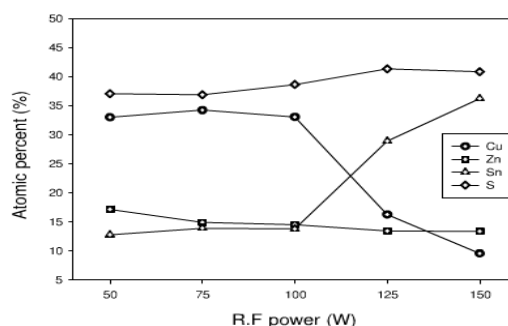

Fig. 9: Atomic percent of CZTS thin film solar cells.

Cu₂ZnSnS₄ thin films were deposited using RF magnetron sputtered at 75W (Seol,).The as-deposited films were amorphous and annealed in the atmosphere of Ar + S_2. The annealed (112), (200), (220), (312) planes were conformed to the reflection of a kesterite structure. A preferred (112) orientation was observed with an increase in annealing temperature. The intensity of the (112) diffraction peak became relatively more intense and sharp with increase in an annealing temperature. This indicates that the crystalline nature of CZTS thin films is improved with increasing the annealing temperature [60]. As the annealing temperature increases, the crystallization of the films changes into larger flat grains. The average grain size and surface flatness were increased with annealing temperature. CZTS thin films were deposited on glass substrate by RF magnetron sputtering. In the case of a sputtering target with $Cu_2S:ZnS:SnS_2 = 1:1:1$, the Zn and Sn contents of the thin films increased but the Cu content decreased.

Table (2) Experimental conditions.

Parameters	Conditions
Sputter Source	Radio frequency (13.56 MHz)
Discharge	Ar (2 sccm)
Purging method	Ar (10 sccm)
Working Pressure	25 mTorr
rf Power	50-150 W
Sputtering time	120 min
Substrate temperature	Room Temperature
Substrate	Glass

The atomic ratio of the thin films obtained at RF power between 50 and 100W was appropriate. However, at above 100 W of RF power, the Cu content of CZTS thin films was rapidly decreased, but the Sn content was significantly increased. It is believed that the abrupt change of the Cu and Sn contents with the RF power depend upon the plasma density.

4.2 MBE

MBE is a technique where a reaction of thermal gaseous beams of molecules from evaporation or sublimation of liquids or solids with a crystalline surface is produced under ultra-high-vacuum conditions to form the epitaxial layer [51, 52]. These vacuum conditions together with the highest standards of cleanness used in the construction of the techniques and apparatus allows for a high purity of the grown samples.

The reactants were evaporated from separated graphite effusion ovens (Knudsen cells), heated radiatively to a suitable temperature to adjust the evaporation rate (in particular an overpressure of As_4 is a maintained to compensate its low sticking coefficient). To ensure the uniformity of the layers the substrate rotates once per monolayer grown. The growth rate of this techniques is lower than for MOCVD (Molecular Organic Chemical Vapor Deposition) $<1\mu m$/hr. The ability to stop and start the beams in a shorter time than required for growing a layer allows for monolayer precision and a unique doping profile in the growing process [53, 54]. When molecular organic compounds are used the method called Molecular Organic MBE (MOMBE, also known as Chemical Beam Epitaxy, CBE) [55] was explained. This allows for a uniform source flux over a large area. In the Gas Source MBE (GSMBE) gases are changed form outside the ultra-high-vacuum chamber, which makes the process more flexible [56].

Yoo et al studied the influence of Cu content on the structure and morphology of CZTS films. Their results indicated that Cu-rich or a stoichiometric Cu content would lead to the formation of $Cu_{2-x}S$ in the films whereas a Cu-poor composition favoured the formation of a smooth film surface [26]. The films made from the precursor with a stacking order of Mo/Cu/Zn/Sn showed larger grain size than that with Mo/Cu/Sn/Zn. The direct contact of Cu and Zn layer should be responsible for the formation of large grains. The best efficiencies can be obtained with the precursor where Zn is the bottom layer and Sn is the top layer (stacking order: Mo/Zn/Cu/Sn). This phenomenon was explained by avoiding of the formation of voids between Mo and CZTS if the Cu layer was in direct contact with the Mo conductive layer [27]. The low formation energy of many of the acceptor defects will lead to the intrinsic p-type character, i.e., n-type doping is very difficult in this system. The p-type conductivity is attributed to the CuZn antisite which has a lower formation energy and relativity deeper acceptor level compared to the Cu vacancy. The role of electrically neutral defect complexes is predicted to be important, because they have remarkably low formation energies and electronically passivate deep levels in the band gap. The low formation energy of acceptor defects makes n-type doping difficult in Cu_2ZnSnS_4. The low formation energy of many of the acceptor defects will lead to an intrinsic p-type character, i.e., n-type doping is very difficult in this system [28]. It was suggested that the intrinsic p-type conductivity in CZTS was attributable to the CuZn antisite, which had lower formation energy [29].

The order Zn/Cu/Sn was used because Araki et al. [45] showed it produced the most efficient solar cell. The conduction band edge of the absorber layer is higher than that of the buffer layer [46]. In order to remove the CuS secondary phase the film was etched with a KCN solution, as is routinely performed on copper-rich grown $Cu(In,Ga)S_2$ thin films [47]. The melting point of tin sulphides and copper sulphides are lower than that of zinc sulphide, and Cu atoms aggregate easily in the films [48]. The carrier concentration of the films was estimated to be less than 5 x 10^{16} cm^{-3}, which is suitable for a thin-film absorber [49, 50].

5. Complete Device Formation

CZTS light absorber layer which is in contact with a n-type CdS layer to create a p-n junction, with a thin i-ZnO/Al:ZnO layer on top of the CdS layer playing the role of a window layer and electrical contact. As a direct band gap semiconductor, CZTS has strong optical absorption (absorption coefficient is above $1x10^4$ /cm), thus a very thin layer of film (1-2 um) can absorb over 90% of the photons over the spectrum with photon energy higher than the band gap. In the stable crystal, the Cu_{Zn} antisite contributes mostly to the p-type conductivity, different from $CuInSe_2$ where the Cu vacancy dominates, and the transition energy level of this antisite is relatively deeper than V_{cu}. The n-type doping of this quaternary kesterite material should be

difficult due to the facile formation of compensating acceptor defects, which can be understood through the same Fermi-level pinning mechanism established for $CuInSe_2$ and $CuGaSe_2$.

6. Current challenges of CZTS

The fact that CZTS solar cells are being touted as one of the most promising photovoltaic material only applies for solar cells with low band gap in the range of 1.4 eV ~ 1.5 eV. The effort to replicate the high efficiency cells with higher band gap is so far futile. The increase in the performance of CZTS thin film solar cells partially depends on the development of solar cells with higher band gaps as the optimum band gap value for terrestrial single junction solar cells is 1.5 eV. During the fabrication of the CZTS layer impurities such as ternary and quaternary compounds can be formed. It was reported that the open-circuit voltage was 165 mV [57]. In 1989, by annealing the same device in air, they achieved the open-circuit voltage of 250 mV and the short-circuit current of 0.1 mA/cm^2 [58].

7. Conclusions

CZTS film with p-type conductivity is required to fabricate a heterojunction solar cell with a transparent conductive oxide layer which is generally n-type. According to the result of hot-probe measurements, all thin films fabricated at a substrate temperature below 400°C exhibited p-type conductivity. The low formation energy of acceptor defects makes n-type doping difficult in Cu_2ZnSnS_4. In order to improve the efficiencies of CZTS-based thin film solar cells, a deeper understanding of the fundamental properties of CZTS, particularly the nature of the defects as well as their impact on the properties of CZTS material is important. CZTS material for thin film solar cells which have produced good efficiency normally always show Cu-poor/Zn-rich in their composition. Therefore, secondary phase(s) should exist in the light absorbers. It is necessary to identify those secondary phases and their effects in order to optimize the fabrication process to make CZTS thin films with desired properties.

Acknowledgement

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