Effect of ZnS nanowire ARC on CZTS/CdS thin film solar cell by Nebulizer Spray Pyrolysis Technique

M Ismail Fathima, A M S Arulanantham and K S Joseph Wilson

PG & Research Department of physics Arul Anandar College, Karumathur—625514, India
E-mail: wilsonpra@yahoo.co.in

Keywords: antireflection coating, nebulizer spray pyrolysis technique, reflection, short circuit current

Abstract

The main intention of this experimental work is to eliminate the reflection of the CZTS/CdS thin film solar cell by depositing the ZnS Antireflection coating (ARC) by Nebulizer Spray Pyrolysis Technique. The CZTS/CdS thin films with and without ZnS Antireflection coating (ARC) deposited using nebulizer spray pyrolysis method is reported in this work. The prepared films were characterized by X-ray diffraction, scanning electron microscopy and UV–Vis spectroscopy analysis. Structural parameters such as lattice constants, texture orientation factor, micro strain, dislocation density and crystallite size were estimated using XRD data. The efficiency of CZTS/CdS solar cell is calculated using I–V characteristics. The experimental results exhibit the short circuit current increased from 9.269 × 10⁻³ A to 1.250 × 10⁻⁴ A and efficiency raised from 0.21% to 0.45%. with ZnS as a ARC. The theoretical quantum efficiency of CZTS solar cell with ZnS ARC is increased from 0.020% to 0.030%. The results indicates that the ZnS ARC is one of the perfect ARC in the CZTS solar cell.

Introduction

Solar energy is very essential source of energy move to clean and green energy in the future. Sun provides unlimited energy to meet the whole world’s energy demands. Every day, the sun radiates numerous amount of energy. Sunlight obtained by earth in one hour is sufficient to meet the annual energy demand of all people worldwide and also environmental secured are the major drivers in promoting solar energy [1]. The semiconductor materials play an essential role to improve the photovoltaic cells. Different kinds of photovoltaic cell’s research are going on to improve the efficiency within the least cost. Commonly Si is supreme material in the solar industries. In behalf of indirect band gap the Si is incapable to absorb the large number of photon energy as a result a low absorbability with efficiency [2]. So, the research has been turned on the thin film solar cells. In recent time most of the research works explores the thin film materials for highly efficient solar energy conversion by cause of low cost and sufficient materials with large scale production [3]. Conventionally, CuInGaSe₂ (CIGS) and CuInSe₂ (CIS) have been used as absorber layer in solar cells by the reason of their great conversion efficiency (20%) [4]. However, the application of these materials in high scale solar cell production could cause an environmental dispute due to the toxic nature of selenium and expensive raw materials. To overcome these complication substitute materials search for absorber layers is still on the processing.

Freshly the copper zinc tin sulphide (CZTS) thin film have engaged researchers with their good properties, and they play crucial performance in the utilization of absorber layer in the solar cell. The elements of CZTS are earth abundant, economical, environmental beneficial, harmless, and pollution-free [2]. CZTS has the optimal band gap of 1.5 eV which facilitate a generation of 33% conversion efficiency confer to Shockley-Queisser theory [3].

CZTS has active optical absorption (absorption coefficient is above 1 × 10⁴ cm⁻¹), therefore a very thin layer of film (1–2 μm) will absorb over 90% of the photons over the spectrum with photon energy greater than the band gap. So far Exhibits the CZTS absorber material solar cell having Successful theoretical and experimental conversion efficiency such as 32.2% and 10% [5, 6].

© 2020 The Author(s). Published by IOP Publishing Ltd
Different type of deposition technique has been obtained by thin film coating in solar cell such as atom beam sputtering, RF magnetron sputtering, hybrid sputtering, thermal evaporation, sulphurization of electron beam evaporated precursors, pulsed laser deposition electro deposition, spin coating, and nebulizer spray pyrolysis [7–10].

Among the various techniques of preparing CZTS thin films as nebulizer spray pyrolysis [NSP] technique is an attractive non-vacuum technique by the reason of its obvious to deposit the film in a broad area, low expensive than other method and also proportion of the films could be disciplined excellently. In present paper depicts the spray pyrolysis process for the fabrication of Cadmium sulfide [CdS] as a n layer CZTS thin film. The films are characterized by optical, structural and morphological and I-V characteristics are investigated experimentally with compared theoretical result [11]. There are number of deposition techniques are used but difficult to attain the theoretical efficiency of CZTS thin film solar cell by the reason of some considerable losses such as optical losses, resistivity loss, recombination loss, etc [9]. In this work effort to achieve the low reflection loss by help of zinc sulfide [ZnS] Antireflection Coating (ARC) on the top of CdS/CZTS thin film solar cell and also the conversion efficiency of CdS/CZTS without ARC and CdS/CZTS with ZnS nanowire ARC are investigated [12, 13]

**Experimental details**

**ZnS, CdS and CZTS layers preparation**

Spray pyrolysis established to be a convenient approach for the deposition of large area metal oxide, spinel oxide, chalcogenide and completely different sulphide films [14, 15]. The approach is even now broadly practiced and fascinating for the deposition of economical thin film photovoltaic solar cells [16]. In this experimental study the FTO/Ag/CdS/CZTS/Ag and FTO/ ZnS/Ag/CdS/CZTS/Ag solar cell structure were prepared by using NSP deposition technique The SnO: F fluorine doped tin oxide [FTO] film on soda lime glass [SLG] was prepared by the NSP technique [17]. The NSP technique endue the usability of depositing stratified films and films with content gradients around the thickness of the film by altering the distribution of the spray solution and deposition specification.

Commercial FTO substrate is used as electrode. The formation of CZTS thin films by deposition of precursor solutions using spray pyrolysis technique in close environment the SLG substrates used for the thin film structure were scrubbed and soaked with deionized water, and acetone in that order. The thin film layers of CZTS were formed from 20 ml distilled water be contained the solvent compositions such as CuCl2 (0.1 M), ZnCl2 (0.1M), SnCl4 (0.1M) and thiourea (0.8M). To prevent precipitation of Cu-thiourea complex in the precursor solution, pH of the precursor solution was regulated to adding the few drops of Conc. HCl. Compressed air with pressure 0.15 Mega pascal was recovered as carrier gas to form the vapour in the nebulizer spray. [14, 17].

The nozzle substrate distance was fixed at 50 mm and the effective substrate area as approximately 2.5 cm² and with hold the substrate at 450 °C. The chamber was provided with an exhaust fan to periodically eject the solvent steam and other aeriform output. A microprocessor-controlled stepper motor system was used to move the nebulizer spray gun in x–y direction and get smooth coatings. After deposition and cooling down to room temperature the films were purified from the heater for further characterization and thickness measurement. Similarly, the CdS films were also sprayed using cadmium chloride and thiourea of each 0.1 M in 5 ml of distilled water keeping the substrate at 320 °C. In the same NSP method the CdS and ZnS films were also sprayed using such as cadmium chloride and thiourea of each 0.1 M in 5 ml of distilled water and zinc chloride and thiourea of each 0.1 M in 5 ml of distilled water reserve the substrate at 450 °C [18–20].

**Characterization**

The figure 1 shows that the schematic diagram of CdS/CZTS thin film solar cell without and with ZnS ARC structure were prepared by using NSP deposition technique. Before present of the solar cell design the assembled ZnS, CdS and CZTS thin film on substrates X-ray diffraction patterns were attained by x-ray diffractometer at a grazing angle of 10°. The average crystallite size was approximated adopting the classical Scherrer’s formula [21]. The optical properties of assembled films were analysed from transmittance and reflectance spectra of the films deposited on SLG and were measured using UV-Visible spectrophotometer in the range 400–1100 nm [22, 23]. Surface morphological properties of fabricated films were investigated by scanning electron microscopy (SEM). Subsequently the FTO/CdS/CZTS and ZnS/FTO/CdS/CZTS solar cell are designed and measured their I-V characteristics to calculated the efficiency change and analysed the role of ARC in the efficiency of the CZTS solar cell [24].
**Result and discussion**

**Structural studies**

XRD patterns of the ZnS, CdS, and CZTS thin films prepared by NSP are shown in figure 2. To identify the structural parameters such as crystalline size and presence of material phase of fabricated thin film. It can be noticed from the figure 2 that the XRD pattern show two peaks at $(2\theta \sim 27.27^\circ, 28.81^\circ)$ corresponding to [103], [108] crystal orientations of ZnS hexagonal phase and the particular result are attributed with standard XRD data of JCPDS card number 89–2206. The dominant peak is (108) indicating that the crystallites have preferential orientation in (108) direction. The morphology view that the CdS thin film was in hexagonal phase and the particular results were similar with standard XRD data of JCPDS card number 80–0006. A specific peak was revealed at $2\theta \sim 26.64^\circ$ with the $(002)$ orientation plane direction. [25, 26]. The XRD patterns, for CZTS thin films exhibits diffraction peaks around $(2\theta \sim 28.50^\circ, 47.47^\circ, 56.33^\circ)$ corresponding to (112), (220) and (312) crystal orientations of CZTS kesterite tetragonal phase which is in suitableness with JCPDS data card number 26–0575. The dominant peak obtains at $2\theta \sim 28.50^\circ$ which is remarked to (112) plane, the diffraction peaks and therefore the position of the peaks lead to the conclusion that the film are crystalline in nature with a tetragonal crystalline

---

**Figure 1.** Schematic Structure of CZTS/CdS solar cell with and without ZnS ARC.

**Figure 2.** XRD pattern of CZTS, CdS and ZnS thin films prepared by the Spray pyrolysis method.
structure, which is in the agreements with other reports [6]. The different peaks in the diffractogram were indexed and the ideal values of interplanar spacing \( d \) were calculated and compared with the standard values [4].

The electrical and photovoltaic properties of the solar cell are influenced by the average crystallite size, dislocation density \( \delta \) and strain \( \varepsilon \). Average crystallite size of ZnS, CdS, CZTS films was determined from predominant XRD peak such as \((108), (002)\) and \((112)\) using Scherrer equation (1) [27]

\[
D = \frac{k \lambda}{\beta \cos \theta}
\]

where \( k = 0.9 \) the numerical shape factor which is a constant, \( D \) is crystallite size, \( \lambda \) is wavelength of incident radiation, \( \beta \) is the FWHM in radians, and \( \theta \) is Bragg angle taken in radians Dislocation density \( \delta \) was calculated from crystallite size using equation (2) [28].

\[
\delta = \frac{1}{D^2}
\]

Also strain \( \varepsilon \) of ZnS, CdS, and CZTS film was calculated using the equation (3) [29]

\[
\varepsilon = \frac{\beta \cos \theta}{4}
\]

The lattice constants \( a \) and \( c \) are calculated for hexagonal Structures

\[
a = \frac{\lambda}{\sqrt{3} \sin \theta}
\]

\[
c = \frac{\lambda}{\sin \theta}
\]

For tetragonal structures

\[
a = \sqrt{3}d_{\text{spacing}}
\]

\[
\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}
\]

Where \( d \) is interplanar spacing, \( h, k, l \) = miller indices

The calculated values of crystallite size, dislocation density \( \delta \) and strain \( \varepsilon \) are shown in table 1. generous grains are appropriated to fabricate high efficiency solar cells. The increment of grain size decreases the grain boundaries that reduce the recombination centres and through the active diffusion length of the minority carriers is expanded lead to greater short circuit photocurrent in the solar cells. The micro strains are convinced throughout the growth of thin films, and can be built the stretching or compression in the lattice. The strain advancing is caused by the shift of the atoms with respect to their reference lattice positions and it is persistent with inter planar spacing of \((112)\) plane. The three film’s XRD results provide minimum micro strain value and dislocation density it could be produced several defect centres.

### Surface morphological analysis

Figure 3 shows the SEM images of ZnS, CdS, and CZTS thin films prepared by spray pyrolysis method. The spray pyrolysis method prepared ZnS SEM image shown the pattern resembling a nano wire pattering. A nano wire arrays show anti-reflection and light trapping properties. This reduction in reflectance seems to be a common characteristic of nano wire arrays [16, 30]. Tapered nanowire arrays (nanocones) with tips much smaller than the wavelength of light act as an effective medium, with a gradual change in refractive index given by the weighted average of the material and air.

SEM studies were carried out to assess the quality of the CdS films spray deposited at temperature 310 °C for a deposition time of 10 min is shown in figure (b). The surface of thin film preparation without cracking is very important. As seen in figure (C) the CdS thin film have densely packed with homogenous surface structure without any cracks. From the micrographs one can see the uniform distribution of grain size over total coverage of the substrate with a compact and fine-grained morphology. It had uniform and roughness surface with less smooth coating. There were no visible cracks between struts or signs of peptide aggregation [31]. SEM images of the CZTS thin film sample by are shown in figure 2(c). The morphology is similar to micrometric-sized hexagonal platelets, which form small aggregates known as ‘gypsum flowers’. The same morphology was

| Sample | 2θ (degree) | hkl | \( d(Å) \) | Crystallite size (nm) | Dislocation density \( (δ \times 10^3 \) lines m\(^{-2}) \) | Strain \( (ε \times 10^{-3}) \) | Lattice constant \( a \) | Lattice constant \( b \) |
|--------|------------|-----|---------|---------------------|---------------------------------|-----------------|-----------------|-----------------|
| ZnS    | 28.8187    | (108)| 3.09803 | 41.39              | 0.583                           | 3.37            | 3.57            | 6.190           |
| CZTS   | 28.5079    | (112)| 3.13109 | 30.66              | 1.06                            | 4.6             | 5.425           | 10.851          |
| CdS    | 26.6432    | (002)| 3.34584 | 44.42              | 0.506                           | 3.39            | 3.859           | 6.684           |

Table 1. Structural properties prepared of ZnS, CdS and CZTS thin films.
reported for vaccum free processed CZTS thin film absorber preparation. It clearly showed that no well-defined grains and irregular pattern were observed in the film. It exhibits flower like structure have granular and denser as a result have a small grain boundary so recombination rate of electron and hole at grain boundary decreases and there by short-circuit photo current.

Optical analysis

UV–Vis–NIR spectroscopy

The optical properties such as transmittance, absorption coefficient and band gap of the CZTS, CdS and ZnS thin film was investigated in the UV-Visible region in the range 400–1000 nm of the spectrum. The thin film quality is determined by the optical parameters such as transmittance, absorption, reflectance, refractive index, extinction coefficient etc. The variations of transmittance and absorbance and reflectance with wavelength are shown in figure 4. The figure 4(a) displays the variation of absorption profile of the microsphere of CZTS thin film. From the figure it is clear that the sample absorbs radiation spanning the whole range of the visible spectrum. An excellent optical absorption profile suggests that CZTS is wonderful absorber layer material in next generation thin film solar cells. Figure 4(b) shows the transmittance spectra of CdS film. The prepared film shows average transmittance is $>70\%$, which is the pre requisite for good buffer layer in solar cell applications [32]. The ZnS thin film exhibits the average transmittance is 90% and above as a result confirmed the ZnS coating act as perfect ARC coating to reduce the reflection on the top of the CZTS/CdS solar cell [33]. In the figure 4(c) exhibits the reflectivity of the three layers such as CZTS, CdS and ZnS. The reflectivity range of three layers is better sequence to the photovoltaic operation. The maximum transmission is the crucial role to improve the efficiency of the solar cell. Here the top layer of the ZnS employed as absolute ARC in the CZTS/CdS solar cell. In the figures 7(a) and (b) reveal the absorption and reflectance spectrum of CZTS/CdS thin film solar cell with and without ZnS ARC. The reflectance drops to 7.5% from 10% and absorption increase from 4 arbitrary unit to 6 arbitrary unit. Because of the present of ZnS ARC layer. The value of refractive index frequently changes. It results the maximum absorption which leads to improve the effective efficiency of CZTS/CdS thin film solar cell

Band gap analysis

The transmission outcome assists to estimate the optical band gap ($E_g$) of the thin films. The bandgap of the ZnS, CdS and CZTS films has been imported from Tauc formula [32].

Figure 3. SEM image of deposited ZnS, CdS and CZTS films.
\[ (\alpha h\nu) = A (h\nu - E_g)^{1/2} \]  

(6)

Where \( \alpha \) is the absorption coefficient, \( A \) is the constant, \( E_g \) is the energy gap and \( h\nu \) is the incident photon energy. The optical bandgap deduced by extrapolating the light portion of the \((\alpha h\nu)^2 \) versus \( (h\nu) \) plot to meet the \( h\nu \) axis shown in the figure 5. The optical bandgap values of the films was found to be 1.57 eV, 2.43 eV and 3.4 eV of CZTS, CdS and ZnS respectively which is good approving with previously revealed value in literature thin films by nebulizer spray\[34, 35\]. The optical band gap of CZTS found to be \( \sim 1.77 \) eV value for a direct band gap material is quite close to the optimum value band gap for ideal for solar cell applications absorber layer of photovoltaic energy devices. The figure 5 represents Tauc plot for the estimation of the optical band gap of CdS film was found \( \sim 2.4 \) eV, which is in good agreement with the earlier reports \[27, 32\] and also the ZnS film, was found to be \( \sim 3.45 \) eV \[3\].

**Refractive index and absorption coefficient analysis**

The refractive index \( (n) \) and extinction coefficient \( (k) \) of semiconducting materials are very important in determining the optical and electrical properties of the film. This is essential for designing in solar cell applications \[36\]. The refractive index and \( n \) and extinction coefficient of the sprayed CZTS, CdS and ZnS films have been calculated from the transmission and reflection spectra of the film using the equations (7) and (8) \[25, 26\].

\[ n^2 = N + (N^2 + n_0^2 n_i^2)^{1/2} \]

Where

\[ N = \frac{(n_e^2 + n_i^2)}{2} + 2n_e n_i T \]  

(7)
and \( n_s \) are the refractive indices of substrate, air, and the ZnS films, respectively. \( T \) is the transmittance value at a particular wavelength.

\[
k = \frac{\alpha \lambda}{4\pi}
\]  

(8)

Where \( \alpha \), \( \lambda \) and \( k \) are the absorption coefficient, wavelength and the extinction coefficient respectively [1]. Figure 6(a) admits that the index of refraction decreases with decrease in wavelength and becomes constant at higher wavelengths. The CZTS refractive index rapidly decreases with wavelength and becomes constant at higher wavelengths [37]. One common strategy to reduce reflection is to add one or more coatings that have a
refractive index intermediate between that of the semiconductor and that of air. Using an appropriate coating thickness and refractive index leads to destructive interference between reflected light and incident light, eliminating reflection at both interfaces. The figure 6(a) that the ZnS thin film coating refractive index value 2.3 is the appropriate anti-reflective coating for CZTS/CdS design [38].

**Skin depth and optical conductivity analysis**

The thickness at which current density becomes 1/e of the value at the surface is called skin depth which is accountable of optical energy. It describes the exponential decay of the electric, magnetic field and also induced current density of the thin film layers. The value of skin depth (\( \chi \)) of CZTS, CdS and ZnS thin films can be calculated using the formula

\[
\chi = \frac{\lambda}{2\pi k}
\]  

(9)

Figure 6(d) shows the variation of optical conductivity (\( \sigma \)) with the incident photon energy in the absence of applied electric field. The value of optical conductivity depends concentration of carriers in different region of semiconductor layers. The optical conductivity of CdS thin films is constant up to 2.4 eV afterward it gradually increases above 2.5 eV. When the photon possess low energy, it is observed by the thin films, hence optical conductivity is very less. In the case of ZnS, it retains low and constant optical conductivity. It is due to the minimum absorbance of photon in that visible region [33]. This suggests that the high optical conductivity is due to electrons excited by photon energy [39]. The value of optical conductivity (\( \sigma \)) of CZTS, CdS and ZnS thin films can be calculated using the formula

\[
\sigma = \frac{\alpha nc}{4\pi}
\]  

(10)

Figure 6(d) shows the variation of optical conductivity (\( \sigma \)) with the incident photon energy. It means optical excitation in the absence of applied electric field. The value of optical conductivity depends concentration of carriers in different region of semiconductor layers. The optical conductivity was determined using the equation (10) [38]. The optical conductivity of CdS thin films is constant up to 2.4 eV afterward it becomes gradually increased above 2.5 eV for all the films. The CZTS thin film optical conductivity reduced rapidly in higher photon energy region to low photon energy region. This reduction is due to the low absorbance of the films in low photon energy region. The ZnS have low and constant optical conductivity is due to the minimum absorbance of ZnS thin films in that visible region [33]. This suggests that the high optical conductivity is due to electrons excited by photon energy [39].

**Electrical studies**

Different deposition techniques of CZTS solar cell are reported earlier. They have obtained an efficiency up to 12%. Various reasons can be identified to rectify the efficiency such as metal contact layer materials effect, defect formation Cu and Zn with negative energy formation, sulfurization temperature, crystal disorder, diffusion length of p type material, recombination mechanism in the interface and optical losses etc. Different experimental works revealed the sulfurization temperature optimization can be increased the efficiency of solar cell in 450°C–550°C temperature. It can change the roughness, crystal Structure of absorber material as a result decrease the band gap value up to 1.38 eV and hence to improve the efficiency of solar cell.

The CZTS absorber material obtain band gap 1.51 eV deposited by in this spray Pyrolysis technique in 450°C. The solar cell with FTO/Ag/CdS/CZTS/Ag with ZnS ARC and without ARC structure were prepared by spray pyrolysis technique in order to investigate the photovoltaic properties of these structures. The efficiency is found to be increased from 0.21% to 0.45% with ARC. The short circuit current density and the open circuit voltage for the cell 1 and cell 2 are calculated using I-V data. They are found to be 9.269×10⁻⁵A and 1.525×10⁻⁴A and 0.38 V and 0.57 V respectively. Using the above said parameters the fill factor of the cell 1 and cell 2 are calculated using equation (11).

The fill factor (FF) and efficiency (\( \eta \)) are evaluated from the relation [40]

\[
FF = \frac{V_m \times I_m}{V_oc \times I_oc}
\]  

(11)

Where the \( V_m \) and \( I_m \) are the values of maximum voltage and maximum current. The fill factors are found to be 1.019 and 1.023 respectively. The efficiency \( \eta(\%) \) is calculated from the relation.

\[
\eta = \frac{V_oc \times I_oc \times FF \times 100}{P_{input}}
\]  

(12)

Where \( P_{input} \) is the input light energy.
Hence the conversion efficiencies are found to be 0.218% and 0.45% when illuminated by Xenon source of light with 185nm–2000 nm range of wavelength at 100 mW cm$^{-2}$. The figure 8 shows the I-V characteristics of FTO/Ag/CdS/CZTS/Ag with ZnS ARC and without ARC structure.

The CZTS absorber diffusion length is very low by the reason of less than 2.5 ns low life time of minority carriers. So, the recombination process occurs before generation carrier. The ZnS ARC deposited on the CZTS solar cell can increase the path length of light to increase the light absorption and improve the number of carrier generation. The effect of prepared ZnS ARC on the FTO/Ag/CdS/CZTS/Al solar cell can reduce the reflection loss mechanism and enhance to trap the maximum light energy in the upper surface of CZTS/CdS solar cell [21]. The figure 7 (a) and (b) shows that the variation of absorbtion and refection properties without and with ZnS ARC in CdS/CZTS solar cell.

**Theoretical work**

*External quantum efficiency CdS/CZTS with and without ZnS ARC*

Spectral response, particularly the external quantum efficiency, to determine the response of the cell as a function of wavelength and allows the study of the constraint factors in performance of the solar cell. The reflection loss is the crucial parameter to determine the External quantum efficiency (EQE) of solar cell. The effect of photons conversion of the FTO/Ag/CdS/CZTS/Ag thin film solar cell with ZnS ARC and without ARC structure were theoretically analysed to a reference wavelength from 400 to 1000 nm

$$EQE = (1 - R) \times EQE$$

$$EQE = \frac{h \nu}{q \lambda} \frac{J_c}{P_{input}}$$  \hspace{1cm} (13)

Where $R$ is the reflectance value of material, $J_c$ is the short circuit current
Equation (13) allow tracing their specific spectra in figures 9(a) and (b). The same figures show the spectral responses difference in cases where the cell is bare and with an ZnS ARC. These curves show the variation of the external quantum efficiency of bare FTO/Ag/CdS/CZTS/Ag thin film solar cell and the FTO/Ag/CdS/CZTS/Ag thin film solar cell with ZnS ARC as a function of the material wavelengths.

For a wavelength range between 400 and 1000 nm, it is noted that the external quantum efficiency increases for bare FTO/Ag/CdS/CZTS/Ag thin film solar cell to 10% and the one with ZnS antirefection layer. The outcome is explained by the fact that in this wavelength ranges of the solar spectrum the CZTS material is more absorbent. The observation is more important for the cell with ZnS ARC, as it there’s a minimum of reflection caused by the deposition of a CZTS layer. For a wavelength range between 850 and 1100 nm that is to say, to the rapid visible and progressive decline in spectral response can be explained by a very low absorption of incident light with photon energies close to the gap of CZTS. It is also noted for large lengths corresponding waves at lower photon energies in the gap of silicon, the spectral response is cancelled [41–44]. However, we note that the performance of ZnS ARC is much more important FTO/Ag/CdS/CZTS/Ag thin film solar cell to obtain better improvement from 0.21 to 0.45% efficiency [45].

Conclusion

To summarized this study represents the, experimental optimization of the CZTS/CdS thin film solar cell by Spray pyrolysis method with and without ZnS ARC were fabricated and studied. The CZTS, CdS and ZnS thin films XRD diffraction shows polycrystalline kesterite structure with (112) oriented, hexagonal structure and high intense peak (002) as preferred orientation and hexagonal structure and high intense peak (108) as preferred orientation. The surface morphological studies shows gypsum flower, densely packed homogenous and tapered nanowire arrays structures. The optical studies revealed that the CZTS, CdS and ZnS thin films band gap values are shown such as 1.57eV, 2.43eV and 3.41eV. The I-V characterization clearly explains the effect of ZnS ARC coating on CZTS/CdS thin film solar cell and the conversion efficiency increases from 0.21% to 0.45%. Additionally the theoretical work exhibits the role of ZnS ARC on the external quantum efficiency (EQE) improves that the 0.20% to 0.30%. This is because the ZnS ARC extract the wasted reflected energy from the solar energy as a result the input light intensity of the solar cell rapidly increased which shows the importance for the use of the ZnS ARC on CZTS/CdS thin film solar cell.

Acknowledgments

The authors wish to express their sincere thanks to the PG and Research Department of Physics and FIST lab in Arul Anandar College Karumathur.

ORCID iDs

K S Joseph Wilson https://orcid.org/0000-0003-1791-2092
References

[1] King R R, Law D C, Edmondson C M, Fetzer, Kinsey S H, Yoon, Sherif R A and Karam N H 2007 40% efficient metamorphic GaInP/GaInAs/Ge multijunction solarcells Applied Phy letter 90 183516

[2] Parameswaran M, Gaithersburg Hong-Ng, Raghu and Bhattacharya N 2016 Semiconductor materials for solar photovoltaic cells Springer Series in Mat. Sci 218 1–25

[3] Nadeem M Y and Waqas A 2000 Optical properties of ZnS Thin Films Turk J Phy 24 651–9

[4] Lynda R and Seedhara Reddy P 2013 Effect of pH on the characteristics of Cu2ZnSnS4 nanoparticles J Mater. Sci. 48 6551–25

[5] Wang W, Winkler M T, Gunawan O, Gokmen T, Todorov T K, Zhu Y and Mitzi D B 2014 Adv. Energy Mater. 4 0470–2

[6] Nabel A B, Sabah A S, Sabreen and Hameed A 2018 Influence of substrate temperature and thickness on structural and optical properties of CZTS nanostructures thin films Int. J. Appl. Eng. 13 3379–3379

[7] Kelllanae A, Tarzalt H, Sebboua B, Zerrouki H and Kesria N 2015 AIP Conf. Proc 1697 090003

[8] Akyaz N, Zaretskaya E P and Ozeckl S 2019 Development of a CZTS solarcell with CdS buffer layer deposited by RF magnetron sputtering J. Alloys Compd. 772 782–810

[9] Acirrat M et al 2011 Hybrid sputtering/evaporation deposition of Cu(In2Zn2Sn4) thin film solar cells Energy Procedia 10 138–55

[10] Wang K, Gunawan O and Todorov T 2010 Thermally evaporated Cu2ZnSnS4 solar cells Appl. Phys. Letters 97 143508

[11] Kondrotas R et al 2015 Characterization of Cu 2 ZnSnSe 4 solar cells prepared from electrochemically co-deposited Cu–Zn–Sn alloy Solar Energy Materials & Solar cells. 133 21–8

[12] Bahrami A, Mohammadnejad S, Abkenar N J and Soleimanihezhad S 2013 Optimized single and double layer antireflection coatings for GaAs solar cells Int. J. Renewable Energy Research 3 79–83

[13] Jung K T, Kim S and Yoo S 2011 Optimization of antireflection multilayer for industrial crystalline silicon solar cells Curr. Appl. Phys. 11 1338–41

[14] Kumar S, Kasubouala B, Loorits M, Raudoja J, Mäki V, Altsosmar and Grossberg M 2016 Synthesis of Cu2ZnSnS4 solar cell absorber material by Sol-gel method Energy Procedia 102 102–9

[15] Chaudhuri T and Tiwari D 2012 Earth-abundant non-toxic Cu2ZnSnS4 thin films by direct liquid coating from metal–thiourea precursor solution Sol. Energy Mater. Sol. Cells 101 46–50

[16] Qinwei, Meng X, Xiong K, Qiu Y and Lin W 2017 One-step fabrication of single-crystalline ZnS nanotubes with a novel hollow structure and large surface area for photodetector devices Nanotechnology 28 105302–12

[17] Sahooeune N, Nceaihba A, Ziane A, Dabou1 R, Bouraiou A, mostefaoui M and Rouabhia A 2018 Realization and modeling of multilayer antireflection coatings for solar cells application Mater. Res. Express 5 066515–25

[18] Kim J H, Rho H, Kim J, Choi Y J and Park J G 2012 Raman spectroscopy of ZnSn nanostructures Wiley Online Library 43 906–10

[19] Rohit S 2012 High efficiency and cost effective Cu2S/CdS thin-film solar cell JOSA-IEEE 2 47–51

[20] Dahi N and Arafah D N 2012 Characterization and processing of CdS/ZnSn thin layer films deposited onto Quartz for solar cell applications Energy Procedia 18 85–90

[21] Arulanantham A M S, Valanarasu S, Jayadeepan K, Ganesh V and Shikir M 2018 Development of SnS (FTO/CdS/SnS) thin films by nebulizer spray pyrolysis (NSP) for solar cell applications J. Molecular Structure 1152 137–44

[22] Selim M, Gouda M, El-Shaarawy M, Salem A and El-Ghany A W 2013 Effect of thickness on optical properties of thermally evaporated SnS films Thin Solid Films 527 164–9

[23] Patel M, Mukhopadhyay I and Ray A 2013 Effect of annealing on the optical properties and photocconductivity of SnS thin film Opt. Mater. 35 1693–9

[24] Koteswara Reddy N and Ramakrishna Reddy K T J 1998 Growth of polycrystalline SnS films by spray pyrolysis Thin Solid Films 325 4–6

[25] Challal K K, Magnone E and Kim E T 2012 Highly photosensitive properties of CdS thin films doped with boron in high doping levels Mater. Lett. 85 135–7

[26] Rondiya S, Rokade A, Funde A, Kartha M and Jadkar S 2017 Synthesis of CdS thin films at room temperature by RF-magnetron sputtering and study of its structural, electrical, optical and morphology properties Thin Solid Films 613 41–9

[27] Feng K, Wu W, Shan B and Nan H 2016 Structure and property of ZnS thin films with different residual chlorine content Mater. Res. Express 3 016404–14

[28] Khercachi B I, Saidi H, Attaf A, Attan N, Bouchar A, Bendjilidi H, Benkhetta Y, Azizi R and Jlassi M 2016 Influence of solution flow rate on the properties of SnS2 films prepared by ultrasonic spray Optik 127 4043–6

[29] Arulanantham A M S, Valanarasu S, Jayadeepan K and Katagiri H 2017 Effect of sulfur concentration on the properties of tin disulfide thin films by nebulizer spray pyrolysis technique J. Mater. Sci., Mater. Electron. 28 18675–85

[30] Yan R X, Gargas D and Yang P D 2009 Semiconductor nanowire lasers Nanowire photonics Nat. Photon. 3 569–76

[31] Demir R and Gode F 2015 Structural, optical and electrical properties of nanocrystalline cds thin films grown by chemical bath deposition method Chalcogenide letters 12 43–50

[32] Kassim A, Saravanan Nagalagam H O, Son Min and Noraini K 2010 XRD and AFM studies of ZnS thin films deposited by spray deposition method Arabian J of Chemistry 3 243–9

[33] Cheng S, He Y, Cheng G, Cho E C and Comoibe G 2008 XRD and AFM studies of ZnS thin films produced by electrodeposition method Surf. Coat. Technol. 202 6070–4

[34] Saikia D, Gogoi P K and Saikia P K 2010 Structural and optical properties of nanostructured CdS thin films deposited at different preparative conditions Chalcogenide Letters, 7 317–24

[35] Sarker S, Chattarjee K, Dash G C and Chattopadhyay K K 2014 Self-sacrificial template directed hydrothermal route to kesterite-Cu2ZnSnS4 microspheres and study of their photo response properties CrystEngComm 16 2634–44

[36] Mohammad and Ali 2015 Effect of annealing temperature on the structural and optical properties of ZnSn thin films deposited by CBD Baush Journal of Science 33 156–81

[37] Katagiri H, Saitoh K, Washio T, Shinbara H, Kurmadani T and Miyajima S 2001 Development of thin film solar cell based on Cu2ZnSnS4 thin films Sol Energy Mater Solar Cells 65 141–8

[38] Ogwu A A, Bouquerel E, Ademosu O, Mok S, Crossan E and Placido F 2005 The influence of rf power and oxygen flow rate during deposition on the optical transmittance of copper oxide thin films prepared by reactive magnetron sputtering Phys. D: Appl. Phys 38 266–271

[39] Yang T, Wang X, Liu W, Shi Y and Yang F 2013 Double-layer anti-reflection coating containing a nanoporous anodic aluminium oxide layer for GaAs solar cells Opt. Express 211 8

[40] Scragg W J 2010 Studies of Cu2ZnSnS4 films prepared by sulphurisation of electrodeposited precursors PhD Thesis University of Bath
[41] Martínez-Escobar D, Ramachandran M, Sánchez-Juárez A, Sergio J and Rios N 2013 Optical and electrical properties of SnSe₂ and SnSe thin films prepared by spray pyrolysis Thin Solid Films 535 390–3

[42] Boutebakh F Z, Batibay D, Aida M S, Ocak Y S and Attaf N 2018 Thermal sulfurization effect on sprayed CZTS thin films properties and CZTS/CdS solar cells performances 2018 Mater. Res. Express 5 015511–23

[43] Gershon T, Shin B, Bojarczuk N, Gokmen T, Lu S and Guha S 2013 Relationship between Cu₂ZnSnS₄ quasi donor-acceptor pair density and solar cell efficiency J. Appl. Phys. 103 193903–193903

[44] Kamoun N, Bouzouita H and Rezig B 2007 Structural and optical properties of spray-deposited Cu₂ZnSnS₄ thin films Thin Solid Films 515 5949–52

[45] Chantaa E, Wongratanaphisana D, Gardchareona A, Phadungdhithidhadaa S, Ruankhama P and Choopuna S 2015 UV sensing properties of ZnO nanowires/nanorods Energy Procedia 79 879–84