Optimization of Electrodeposition Time on the Properties of Cu2ZnSnS4 Thin Films for Thin Film Solar Cell Applications

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Research Article

Keywords: CZTS, Electrodeposition, Deposition Time, SCAPS-1D, Performance, Simulation

Posted Date: October 12th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-963102/v1

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Abstract

Electrochemical deposition was used to create a quaternary CZTS (Cu$_2$ZnSnS$_4$) kesterite thin layer. An aqueous solution of CZTS was used to deposit a thin layer over Indium Tin Oxide. The effects of deposition time (variation) on CZTS thin films under ambient conditions were investigated in this study. Several available characterization systems were used to study the samples as they were produced. The polycrystalline description of the layer is inveterate by X-ray diffraction (XRD). The SEM as well as AFM study show that deposition time improved surface morphology and topography of CZTS thin films which increase several nm in grain size. Furthermore, depending upon the deposition duration, the optical study reveals an acceptable bandgap in a range of 1.44 to 1.71 eV. Characteristics of high-quality CZTS absorber layers for solar cell applications are discovered to be affected by deposition time variation. To check the effect of this bandgap variation (1.44 to 1.71 eV) on the performance of a CZTS based thin film solar cell, a simulation software SCAPS-1D is being used.

Introduction

Researchers are looking at the Copper-Zinc-Tin-Sulfur (CZTS) absorber material as a promising alternate for CdTe and CIGS thin-film technology. To date, CdTe and CIGS-based devices have achieved photoconversion efficiency of 22.5 percent and 23.4 percent, respectively (PCE). The lack of In and Ga, as well as a toxicity of Cd, may limit the usage of such materials in solar systems. CZTS is regarded for its low cost, ease of manufacturing, environmental friendliness, earth-richness, non-toxicity, and good absorption coefficient (104 cm$^{-1}$) when used with direct bandgap material. The CZTS semiconductor material's above-mentioned characteristics make it an ideal absorber thin film for solar applications. The best CZTS efficiency to yet is 12.6 percent, which is still below the theoretical Shockley-Queisser limit efficiency of about 32 percent. Secondary phases, high intrinsic defect density, compositional variation, Cu-rich and Cu-deficient structure, and rapid carrier recombination might all explain the difference between theoretical and reported efficiency. For kesterite CZTS thin films, several techniques have been utilized like dip-coating, SILAR, spray pyrolysis, thermal evaporation, and pulsed laser deposition.

We preferred deposition for CZTS through electrodeposition technique over the other methods because of its non-expansive, easy-to-control deposition parameter, homogeneity, and large-scale deposition. To enhance the performance of CZTS thin films, the deposition duration impact was examined in this study, which resulted in considerably better film crystallography and morphology. The films were further examined by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Atomic Force Microscopy and optical transmission and absorption. At the end simulation is performed to examine the effect of deposition time variation (bandgap variation) on the characteristics parameters of CZTS based thin film solar cells.

Experimental Details
CuSO₄, ZnSO₄, SnSO₄, Na₂S₂SO₃, Na₃C₆H₅O₇, and HCL for pH correction were bought from Sigma Aldrich to manufacture CZTS thin film. Without any additional purification, all of the ingredients were combined in a chemical bath aqueous solution as supplied. As previously reported, commercial ITO-coated soda lime glass (10-17 sq-ft) was ultrasonically cleaned. As described in the research article, the electrodeposition was done in three-electrode configurations. Trisodium citrate and diluted hydrochloric acid were used to adjust the pH of the solution up to 5.16 pH. Cyclic voltammetry in the range of 0.5 to -1.3 mV, containing all the precursors in the chemical bath, was used to ensure proper and precise deposition. The reduction potential was determined to be -1.05 mV, and the deposition procedure was carried out with the same reduction potential. After 300, 480, 720 and 900 seconds, the as-deposited samples were removed from the mixture with sample IDs CZTS-1, CZTS-2, CZTS-3, CZTS-4 respectively. The as-deposited samples were washed with distilled water to remove loosely bounded particles before being dried with nitrogen gas. Subsequently, all prepared four as-deposited samples were annealed in a vacuum with the presence of sulfur powder at 450 to 500°C for 45 min.

X-ray diffraction (XRD) Rigaku Ultima IV diffractometer with CuKα radiation (λ = 1.54060 Å) was used to analyze the thin films for crystallographic and structural information. Surface morphology was analyzed by SEM. The geography of the films was investigated by AFM Bruker Multimode 8 AFM Nanoscope V controller. UV-Visible spectroscopy was used to examine optical transmission and absorption.

Figure 1 shows the schematic flow of the procedures/techniques that have been carried out in this experimental study.

**Results And Discussions**

The figure 2 is showing the cyclic voltammograms (CV) of CZTS solution at 300K temperature obtained at the range of 0.5 mV to -1.3 mV vs. Ag (reference electrode). CZTS bulk reduction is ascribed to the cathodic processes at -1.05 mV, indicating that CZTS may be effectively deposited on ITO substrate even without electrolyte interference. The CZTS combination decomposed at -1.05 mV, which is acceptable for CZTS thin film deposition on ITO substrate, according to the reduction potential.

Figure 3 depicts the CZTS thin films XRD diffraction patterns that are deposited at various deposition times. The polycrystalline character of the CZTS film can be observed in all of the XRD samples. The more strong peaks at (112), (200) and (220) at 2 theta degrees 28.16, 34.45 and 47.16 degrees, respectively, match to standard JCPDS card -00-026-0575.

CZTS thin film sample CZTS-4 is showing good peaks as compare to CZTS-1, CZTS-2 and CZTS-3 because of maximum deposition due to 900 seconds of deposition time.

The deposition time of CZTS-4 sample was maximum (900 seconds) from all of the other ones, that’s why the peak of this sample is more intense. So, we see that as we increase the deposition time, the more deposition is happen on ITO substrate and gives more intense peaks hence the grain size also as shown in the table 1 where the structure parameters are also calculated.
Scherer’s equation was used to compute the crystallite size (D) of CZTS thin film [18]:

$$MC_t = \frac{(m_t - m_e)}{m_e}$$  \hspace{1cm} (1)

Where D is the crystallite size, λ is the X-ray radiation wavelength (λ=0.1540 nm), k is a Scherer’s constant (0.9), β is full-width at half maximum (FWHM) of peaks (in radians), and θ is the Bragg’s diffraction angle at the peak position. The dislocation density (δ) and lattice strain (ε) have also been computed using the formulae below [19,20].

$$\delta = \frac{1}{D^2}$$  \hspace{1cm} (2)

$$\varepsilon = \frac{\beta}{4 \tan \theta}$$ \hspace{1cm} (3)

The obtained results of crystallite size (D), dislocation density (δ) and lattice strain (ε) are summarized in Table 1. As noticed the deposition times strongly affect the film structure parameters. The typical crystallite dimension improves from 10 to 24 nm with deposition time of 15 min. The dislocation density (δ) and lattice strain (ε) have been founded to decrease with increase in deposition time. In conclusion that crystallite size (D), dislocation density (δ) and lattice strain (ε) strongly depend on deposition time. The dislocation density (δ) and lattice strain (ε) are reduced because the stress is released in the formation of high-quality film during deposition.

Table 1: The average crystallite size (D), dislocation density (δ), and lattice strain function (ε) of the high intense peak of CZTS thin film.

| Samples ID | Deposition Time (Seconds) | B(FWHM) | Average D (nm) | δ x 10^{-3} (nm^{-2}) | ε x 10^{-3} |
|------------|--------------------------|---------|----------------|------------------------|-------------|
| CZTS -1    | 300                      | 0.52    | 10             | 2.6                    | 4           |
| CZTS -2    | 480                      | 0.52    | 15             | 4.0                    | 5           |
| CZTS -3    | 720                      | 0.28    | 24             | 1.2                    | 3           |
| CZTS -4    | 900                      | 0.35    | 28             | 1.7                    | 6           |

Furthermore, surface morphology of CZTS thin film deposited by different deposition times is shown in fig 4. All the thin film morphology are uniformly covering the substrate except the film deposited for 5 min is not homogeneous, poor adhesion to substrate fig 4 (a). Moreover, the film deposited at 15 min was found quite dense, homogenous, adhesion to the substrate, compact and improved in grain size fig 4 (d), which is in good agreement with XRD results.

Morphology analysis of CZTS thin films was taken via SEM microscopy illustrated in figure.4. All the films of the different deposition time displayed homogenous and polycrystalline structures. Furthermore, a
remarkable variation was seen in the surface microstructure of a sample prepared with 15 min deposition fig 4 (d), which also showed a bigger grain size and rough surface concerning the other samples.

Fig 5 represents the topography studies of CZTS thin film performed by AFM measurement with different time grown on ITO substrate. As we can observe that the homogeneity of the film and the normal particle size is systematically increased from 133 to 324 nm with 12 min deposition time. CZTS thin film is an absorber layer for a photovoltaic device where the surface should be homogenous and densely packed. The uniform surface has the effect of lowering the dark current and the number of states between the absorber and the window layer for the solar device \(^2\).

An increase in a grain size is evident in XRD analysis where crystallinity of a film increased with more deposition time from 5min to 15min. As the crystallinity increases the grain size and grain boundary decrease which increases the charge carrier and short-circuit current of the device.

**Optical analysis**

Figure.6 shows energy bandgap of CZTS thin film. The absorption, transmission spectrum was recorded in a range of 300 to 1000 nm with UV-Vis spectroscopy. It is observed from the results that the absorption decreased as we increase deposition time this change may be due to the excess CZTS film layer deposition. The optical bandgap is calculated using the Tauc formula (4).

\[
\alpha \nu = A(\nu - E_g)^n \quad (4)
\]

Where the formula parameters are, \(\alpha\) is absorption coefficient, \(h\) is energy of a photon with frequency \(\nu\), \(A\) is an optical conversion for direct bandgap its value is 2 and for indirect bandgap is \(1/2\). We measured a direct bandgap by extrapolating a straight line to \(\alpha = 0\) axes. The estimated bandgap for CZTS thin films is around 1.42 eV to 1.71 eV depending upon the deposition time.

Deposition time for CZTS-1 was 300 seconds, for CZTS-2, CZTS-3, and CZTS-4 was 480 seconds, 720 seconds, and 900 seconds respectively. As the time of deposition was increased, the band gap also was gone on increasing in view of that as described in the table.2 below.

Table 2: Effect of Deposition Time on bandgap of CZTS Thin Films

| Sample ID | Deposition Time (s) | Bandgap (eV) |
|-----------|---------------------|--------------|
| CZTS-1    | 300                 | 1.42         |
| CZTS-2    | 480                 | 1.44         |
| CZTS-3    | 720                 | 1.54         |
| CZTS-4    | 900                 | 1.71         |

**Numerical Simulation:**
To observe an effect of deposition time variation on a performance of solar cell through the change in bandgap, SCAPS-1D software is being used. The simulation parameters of CZTS as absorber layer, CdS as buffer layer and ZnO as buffer layer are taken from literature as shown in table 3. But the the bandgap of CZTS absorber layer is taken from our experimental calculated data where bandgap is varying from 1.42 to 1.71 eV.

Table 3: CZTS, CdS and ZnO layers' physical parameters utilized in simulation [22, 23].

| Parameters | CZTS | CdS | ZnO |
|------------|------|-----|-----|
| W (µm)     | 2.0  | 0.1 | 0.05|
| E₀ (eV)    | Variable | 2.45 | 3.40 |
| χ (eV)     | 4.500 | 4.450 | 4.550 |
| εₚ         | 10.000 | 10.000 | 10.000 |
| N_c (cm⁻³) | 2.000E+18 | 2.000E+18 | 4.000E+18 |
| N_p (cm⁻³) | 2.000E+18 | 1.500E+19 | 9.000E+18 |
| Vₚ (cm/s)  | 1.000E+7 | 1.000E+7 | 1.000E+7 |
| V_p (cm/s) | 1.000E+7 | 1.000E+7 | 1.000E+7 |
| μₑ(cm²/(Vs)) | 5.000E+1 | 5.000E+1 | 5.000E+1 |
| μ_p(cm²/(Vs)) | 2.000E+1 | 2.000E+1 | 2.000E+1 |
| N_d (cm⁻³) | 0.000E+0 | 1.000E+15 | 5.000E+17 |
| N_A (cm⁻³) | 5.500E+15 | 0.000E+0 | 0.000E+0 |
| α          | Variable | Scaps Value | Scaps Value |

To check the performance of CZTS based solar cell with respect to the band gap variation of CZTStin film as an absorber layer, a simulation tool SCAPS-1D is used, where CdS is used as a buffer layer and ZnO as a window layer, having solar cell model “Back.Contact/CZTS/CdS/ZnO/Front.Contact/Glass”.

Table 4 shows the front and back contact parameters that are taken from the SCAPS simulation tool as well

Table 4: Simulation Parameters used for back and front contact in SCAPS simulator

| Parameters | Front Contact | Back Contact |
|------------|---------------|--------------|
|             | 1.00E+7       | 1.00E+5      |
|             | 1.00E+5       | 1.00E+7      |
|             | 4.6039        | 5.8973       |
|             | 0.0539        | 0.1527       |
|             | 0.0000        | 0.0000       |

As the CZTS-1 thin film is initially deposited for 300 seconds, so its band gap is 1.42 eV. By applying this bandgap Voc achieved 0.764 V, Jsc of 26.665 mA/cm². Similarly fill factor was 66.17% and efficiency of 13.89% was achieved. Table 5 shows the characteristics parameters of CZTS based solar cell depending upon deposition time.
Table 5: Effect of deposition time on the characteristics parameters of solar cell

| Sample ID | Deposition Time | Voc   | Jsc   | FF   | Eta  |
|-----------|----------------|-------|-------|------|------|
|           | Seconds | V     | mA/cm² | %    | %    |
| CZTS-1    | 300     | 0.764087 | 26.66582 | 68.1744 | 13.8905 |
| CZTS-2    | 480     | 0.782824 | 26.02267 | 68.3407 | 13.9218 |
| CZTS-3    | 720     | 0.876459 | 23.09173 | 69.0555 | 13.9761 |
| CZTS-4    | 900     | 1.034967 | 18.52739 | 69.8465 | 13.3932 |

Similarly for 480, 720 and 900 seconds the Voc calculated as 0.783, 0.876 and 1.03 V, Jsc of 26.02, 23.09 and 18.52 mA/cm², fill factor in percent was 68.34, 69.05 and 69.84, where the efficiency of 13.92, 13.97 and 13.39% achieved respectively. Here it can be observed that at 720 seconds time deposition, the purposed solar cell is giving maximum efficiency, because at 300, 480 and 900 seconds the efficiency is less as compared to at 720 seconds.

The effect of deposition time is observed in the figure 8. The figure 8 (a) is showing the J-V characteristic curve and Figure. 8 (b) showing P-V characteristics curve of CZTS based solar cell with respect to deposition time. The P-V curve shows that the maximum power is at 720 seconds deposited CZTS thin film.

Figure 9 is showing the Quantum Efficiency curve. Here in this graph we can also observe the effect of deposition time in corresponding of bandgap variation on the quantum efficiency of CZTS based solar cell. From the above calculated results we concluded that the CZTS sample with 720 seconds deposition time with 1.54 eV bandgap is the most promising sample as compared to other ones.

Conclusion

It was concluded that CZTS kesterite thin films were successfully prepared using the electrochemical deposition technique, so this technique is a cost-effective way to control the crystallography and structure-property of CZTS using ITO back contact. It is observed that the variation of deposition time has a great impact on the CZTS thin film preparation. The XRD analysis of the CZTS-3 thin film indicated pure kesterite phases with high crystallinity among the other samples deposited for 720 seconds. The SEM and AFM analysis also confirmed the formation of homogenous and increase in grain size up to 324 nm. The optical bandgap values were determined between 1.42 eV and 1.71 eV. Using SCAPS-1D simulation software, it is observed the effect of deposition time on the performance of a solar cell upon its characteristics parameters. From the simulation and experimental data, it can be concluded that deposition for 720 seconds is a suitable time for high-quality of the CZTS absorber layer.

Declarations
Acknowledgements

The work was supported by Higher Education Commission of Pakistan, International Research Support Initiative Program (IRSIP) under grant No: 1-8/HEC/HRD/2020/10744 PIN: IRSIP 45 Engg 17.

Conflict of Interest

The authors declare that they have no conflict of interest

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Figures

Figure 1

Schematic Diagram of CZTS preparation to characterization
Figure 2

CZTS combined cyclic voltammetry in aqueous solution.
Figure 3

Patterns of X-ray diffraction of CZTS thin films produced at various deposition periods.
Figure 4

Surface morphology of CZTS with different deposition times a) 300 seconds b) 480 seconds c) 720 seconds and d) 900 seconds
Figure 5

Two-dimensional AFM images of CZTS thin film prepared by different deposition time a) 300, b) 480, c) 720 and d) 900 seconds.

Figure 6
Energy bandgap variation of CZTS thin film according to deposition time.

Figure 7

Schematic of Solar Cell used in Simulation
Figure 8

(a) J-V Characteristics Curve  
(b) P-V Characteristics Curve

J-V and P-V Characteristics curves for 2 and 10 cycles as deposited and annealed respectively
Figure 9

Effect of Deposition cycles and deposition on characteristics parameters of solar cell