Original research article

Influence of preparation conditions on the properties of silver doped copper-zinc sulfide thin films prepared via sol-gel spin coating technique

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ARTICLE INFO

Keywords:
CuZnS thin films
Sol-gel spin coating method
Doping of CuZnS with Ag
Annealing temperature
Structural and optical properties

ABSTRACT

This work reports the preparation of Ag/Cu-Zn-S nanocomposite thin films using a sol-gel spin coating technique without sulfurization. For comparison, a pure Cu-Zn-S (CZS) sample, as well as CZS embedded with silver nanoparticles of various thicknesses, grown on heated substrates at 280 °C and 320 °C, were well fabricated. Several films like pristine CZS and Ag/CZS with different Ag % (0.5, 1, and 2 %) were deposited on various kinds of substrates like glass, n-type and p-type silicon with 5 and 8 layer thicknesses. The impact of annealing temperature 320 °C of the prepared film on the surface morphology, optical, structural, and electrical properties of the deposited films on various kinds of substrates were investigated. The field emission scanning electron microscopy images displayed homogeneous spreading with a smooth uniform surface of the substrates. Formation of Nano-rods (≈ 600 nm) dimension of the deposited pristine film with 5 layers on n-Si and annealed at 320 °C was observed. The energy dispersive spectroscopy results confirmed that a trace amount of metals was presented in the film. The X-ray diffraction for pristine and Ag/CZS films depicted peaks confirming to the polycrystalline of hexagonal and cubic crystal structure. It was observed that the optical bandgap energy (Eg) reduces with increasing the thickness of the film. The values of the index of refraction (n), high frequency and optical static dielectric constants (ε, εr) of deposit films on Si and glass substrates through the calculation of Eg as a function of the Ag concentrations were also calculated.

1. Introduction

A great deal of interest has been motivated on the growth of the nano-composite films which can be applied as an absorber in solar cells and optoelectronics applications [1,2]. The characterization of copper-zinc sulfide plays an important role because of its brilliant p-type inorganic materials with a direct wide-bandgap for solar cell applications [3]. These films have good efficiency, cheap, abundant, stability, and simple ternary compound. Furthermore, it is a mixed structure of Cu₅S and ZnS films with high %Cu to be employed as a worthy absorber to visible light in optoelectronics and photovoltaic applications. While the film with a low %Cu may be employed as a window/buffer layer of solar cells. Silver-based nanomaterials have unique properties, specific surface plasmon resonance (SPR) effect, high surface area, and induced in a wide diversity of applications [4,5].

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https://doi.org/10.1016/j.ijleo.2020.165561
Received 19 June 2020; Received in revised form 1 September 2020; Accepted 3 September 2020
Available online 9 September 2020
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Peng et. al. were manufactured the copper NPs with various concentrations (0–2 mol.%) doped zinc sulfide (ZnS: Cu) nanoparticles by wet chemical methods. [6]. The XRD patterns showed the cubic phase of the ZnS structure for all the samples and no other crystalline phase was discovered. The photoluminescence intensity is decreased at 2% Cu2+/ZnS NPs. The concentration quenching of the luminescence may result from the creation of the CuS compound. Yildirim et. al. [7] described the effect of heat treatment on structural, electrical, and optical properties of CuS, CuZnS and ZnS thin films deposited by the SILAR method. The current values of the annealed CuS and Cu0.5Zn0.5S films at 400 °C were obviously increased. However, the annealed ZnS thin film has fewer current values than the as-grown film. This is the first study that led to the growth of the CuZnS thin films by using the SILAR method. While Kumar et. al. [8] synthesized the CuZnSnSx thin films that deposited by spray pyrolysis technique onto soda-lime glass substrates held at a substrate temperature of 643 K and studied the effect of copper salt and thiourea concentrations on the prepared films.

Yeh et. al. [9] deposited the Cu2ZnSnS4 thin films on glass and n-type Si substrates using spin-coater technique and thus annealed at high temperatures that enhanced the crystallinity and morphology of the thin films. They showed that the atomic content ratios of Cu/ (Zn + Sn) and Zn/Sn and the annealing temperature have a greater effect on the electrical properties of CZTS. While Tong [10] synthesized the CuZnS thin films by the photochemical deposition method and annealed the prepared samples to study changes in their properties as a result of annealing. They found that the sample composition before annealing was Cu: Zn: Sn: O = 0.04: 0.51: 0.31: 0.14 and show amorphous structure. Oxygen (O) appeared in the compositions as it diffused from the zinc oxide substrate. By annealing at 400 °C for 1 h, the ZnS phase was noted by X-ray diffraction measurement and the bandgap did not change significantly, the samples became close to intrinsic.

Kumar et. al. [11] studied the structural, optical and magnetic properties of ZnS, Mn/ZnS (MZS) & Co/ZnS (CZS) thin films grown on cleaning glass substrates by a spin-coating method. It was reported that MZS film has a good absorbance intensity than CZS and ZnS films. B. Tong et. al. [12] studied the annealing of p-type wide-gap CuZnS thin films deposited by the photochemical deposition method. After annealing at 400 °C for 1 h, the formation of the ZnS phase was noticed by XRD measurement and the conduction type became close to intrinsic. The annealing of Cu2ZnSn(S, Se)4 thin films and their effects on solar cells were studied by Yi REN [13]. The Cu–Zn–S thin films via a simple preparation method of spray pyrolysis were synthesized and the effect of substrate temperature on structural, optical, compositional, morphological, and photovoltaic properties of the deposited CZS film was studied by X. Xu et. al. in 2017 [14]. It was noted that the prepared films have good crystallinity with energy bandgap of 2.21 eV.

J. Li et. al. [15] synthesized ternary CuZnS nanocrystals (NCs) through a simplistic, scalable, non-injection method at low temperatures and found that the crystal structure of NCs is totally changed from a covellite CuS structure into a digenetic CuS0S structure when the NCs are annealed above 350 °C. While Gad Allah et. al. [16] carried out the effect of Al doping on the structural, morphological, optical, and electrical properties of Cu2ZnSnS4 thin films prepared by sol-gel spin coating. By annealing at 350 °C, the resistivity of 3% Al-doped film has the smallest value of about 9 × 10−2Ω·cm, compared to the other samples. Alkhayatt et. al. [17] reported on optical band gap modification and photodetector properties of Au NPs doped Cu-Zn-S thin films that deposited by spray pyrolysis method onto the glass and silicon substrates at temperatures of 330 °C and annealed at 450°C. The intensity of diffraction peaks and the crystallite size increased with the increase of Au NPs dopant ratio.

The optical, electrical, and structural properties of Cu–Zn–S films deposited via CSP (chemical spray pyrolysis) were attained by Sreejith et. al. [18]. It was observed that varying the Cu to Zn ratio leads to change in the film from p- to n-type. In addition, increasing the copper content reveals to decline in the Eg from 3.4 eV to 1.8 eV. To improve and modify the CZS properties in our work, the various transition metal silver additives were inserted into the clean host CZS sample to be applied as a good absorber in solar cells with low embedded films as window/buffer layers.

Our main goal is to prepare the thin films of Ag/Cu–Zn–S nano-crystalline via cost-effective Sol-Gel spin coating technique and study the influence of annealing temperature on surface morphology, optical, structural, and electrical properties of the prepared films. We observed that by increasing the Ag doping at certain concentrations leads to change the surface morphology and increase the film crystallite size. In order to enhance the prepared film properties and obtain an optimum condition for great performance, we explored the impression of film thickness and type of substrate on the film properties. Thus, we deposited the Ag/Cu–Zn–S thin films with 5 and 8 layers on the glass substrates using ultrasonic, spin coating deposition (SPD) system with a various Ag% (x = 0.5, 1, 2% by weight). Consequently, we deposited the Ag/Cu–Zn–S thin films with 5 and 8 layers on Si (n- and p-types) substrates. We estimated the Eg for all thin films. It was found that the Eg is reduced with increasing Ag-doped concentration, which is in a worthy matching with the stated literature [17,18]. The structure of the prepared films was attained via XRD and optical investigation like transmittance (T), reflectance (R), and optical Eg of the as-grown films via UV–vis–NIR spectrophotometer. From the author’s knowledge, this is the first time to grow Ag/Cu–Zn–S thin films with multi-layers through the most cost-effective sol-gel spin coating method for the applications of solar cells.

2. Experimental setup

2.1. Materials and methods

2.1.1. Preparation of Ag/Cu–Zn–S solution

We employed the following chemicals: copper chloride dehydrate CuCl2·2H2O (Cu precursor), zinc acetate dehydrate salt – (CH3COO)2 Zn·2H2O (zinc precursor), Thiourea CH4N2S (sulfide precursor), silver nitrate (silver precursor), acetone (solvent), distilled water, acetone, isopropanol, distilled water, HF (2%) to synthesize the films on clean substrates.

A sol-gel method was installed to prepare the Ag/Cu–Zn–S solution by employing 0.022 M, 0.045 M and 0.088 M molar concentrations of AgNO3 (Ag precursor) and dissolved in a mixture of acetone in distilled water with 3.5: 1.5 mL ratio, respectively, as listed in
A magnetic stirrer was utilized in the dissolution process with a stirring speed of 500 rpm at 60 °C for 25 min. In order to obtain a uniform solution, the mixture was agitated 120 s in the ultrasonic system.

2.1.2. Coating of Ag/CZS films on glass substrates

The glass substrates of 2 cm × 2 cm dimensions were submerged in acetone for 24 h, rinsed in distilled water after washing with detergent, and dried in air. The polished surface supplies nucleation center for the film progress onto the surface of the substrate which reveals to obtaining uniformly deposited films and highly adhesive on the substrate surfaces. The thin Ag/Cu-Zn-S films were spun on the cleaned glasses using a sol-gel spin coating (model Spin-1200D, MIDAS system) in a vacuum with 3000 RPM spin velocity for 1 min. The films were preheated at 280 °C temperature for 30 min. The steps of spin coating using a syringe nozzle and heat treatment were repeated another 4 times to have a sample with 5 layer film thickness (S0, 5 L) and repeated another seven times to have a sample with 8 layer film thickness (S0, 8 L). The solution drops were put in the substrate until it completely covered its surface as shown in Fig. 1. The spin speed for both S0, 5 L, and S0, 8 L was 3000 RPM for 60-seconds. The samples were carried out from the spin coater and directly inserted into the Ney Vulcan furnace, Model 3–1750, and heated at a temperature of 280 °C for 30-min in order to evaporate any remaining solvents from the deposited layer. The samples were cooled down in 300 K to be ready for second layer deposition. This process is repeated with the described sequence until gaining 5 layers and 8 layers of several samples.

Two groups of the 5, 8 -layers samples, one group was inserted into the Ney Vulcan furnace, Model 3–1750, and heated at a temperature of 280 °C, 320 °C, and 360 °C for 30-min to obtain film crystallization. The samples were then left to cool down to room temperature. The other group of S0, 5 L and S0, 8 L samples were heated at 360 °C for 45-minutes, thus we have different samples of S0,5 L and S0,8 L annealed at different temperatures of 280 °C, 320 °C, and 360 °C. We tested the conductivity of all the samples using Avometer and ruled out the samples with poor conductivity. It was found that the S0, 5 L annealed at 360 °C became an insulator due to evaporation in the main film and the sample has been damaged. We have now five samples of S0, 5 L and S0, 8 L with different heat treatments. The doped sample with an amount of 0.5 %, 1%, 2% by weight Ag/Cu-Zn-S concentration, was named S1, S2, and S3, respectively. While the deposited films at 280 °C with 5 layers and 8 layer thickness, were called S1, 5 L, S2, 5 L, S3, 5 L, S1, 8 L, S2, 8 L, and S3, 8 L, respectively as tabulated in Table 2 and then annealed at 320 °C and 360 °C. It was noted that all Ag-doped Cu-Zn-S samples couldn’t bear a high temperature of 360 °C and films became insulators. Table 2 shows all deposited samples on glass substrates with their different annealing conditions.

We selected the best-prepared samples S0, 5 L, S2, 5 L to be deposited on the n-type and p-type silicon substrates as shown in Figs. 2a, 2b. The deposited films on n-type Si were called S0, 5 L, n-Si, S2, 5 L, n-Si, and on p-type Si were called S0, 5 L, p-Si, S2, 5 L, p-Si. The films were deposited on 1 cm × 1 cm cleaned Si substrates using a sol-gel spin coating technique by the same method of deposition on a glass substrate. Subsequently, S0, 5 L, n-Si, S2, 5 L, n-Si, S0, 5 L, p-Si, and S2, 5 L, p-Si were deposited on different Si substrates with 5 layer thickness by the spin coating and then inserted into the Ney Vulcan furnace (model 3–1750) at 280 °C for 30 min to evaporate any remaining solvent or liquids from the deposited layer (Table 3). We recurrent these stages till reach to the desired layer thicknesses.

Table 1

<table>
<thead>
<tr>
<th>Precursor’s</th>
<th>Molar ratio (M)</th>
<th>Weigh ratio (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCl2·2H2O</td>
<td>1</td>
<td>0.639</td>
</tr>
<tr>
<td>(CH3CO)2Zn·2H2O (ZAD)</td>
<td>0.75</td>
<td>0.617</td>
</tr>
<tr>
<td>CH3NO3</td>
<td>6</td>
<td>2.50</td>
</tr>
<tr>
<td>AgNO3 (0.5%)</td>
<td>0.022</td>
<td>0.019</td>
</tr>
<tr>
<td>AgNO3 (1%)</td>
<td>0.045</td>
<td>0.038</td>
</tr>
<tr>
<td>AgNO3 (2%)</td>
<td>0.088</td>
<td>0.075</td>
</tr>
</tbody>
</table>

Fig. 1. A sol-gel spin coating technique with connected vacuum and spin speed of 3000 rpm for 1 min.
Hereafter the samples were annealed at 320 °C for 45 min in order to improve film crystallization, hence, their resistivity was established using Avometer ruled out samples of poor conductivity as depicted in Table 3. In order to verify that the Ag/Cu-Zn-S thin films on silicon substrates act as photovoltaic devices, we painted a silver paste as electrodes in front and backside of Si and glass substrates to determine the electrical behavior of the prepared samples. A hot plate at 100 °C for 5 min was used to dry the prepared samples and cool down to room temperature. The schematic diagram for the structure layer of the samples after painting with Ag electrodes was depicted in Figs. 2 c, 2d.

In order to explore the structural property and morphological surface of the samples, we employed the x-ray diffractometer (XRD, model Philips PW1710, operating with 1.54 Å x-ray wavelengths at 25 mA and 40 KV) and the FESEM (field emission scanning electron microscope) model Quanta 250 FEG operated at 20 KV. The XRD results were attained in the range of 10–80 degrees with 0.0500 deg step and 2theta/theta scans. The EDX (energy-dispersive X-ray spectroscopy) was also induced for the constituent’s analysis and characterization of the samples.

### Table 2

<table>
<thead>
<tr>
<th>Type</th>
<th>Sample name</th>
<th>Ag concentration (%)</th>
<th>Number of layers</th>
<th>Heat treatment (˚C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pure Cu-Zn-S</strong></td>
<td>S₀,5L</td>
<td>0</td>
<td>5 layers</td>
<td>280, 320</td>
</tr>
<tr>
<td></td>
<td>S₀,8L</td>
<td>0</td>
<td>8 layers</td>
<td>280, 320, 360</td>
</tr>
<tr>
<td><strong>Ag doped Cu-Zn-S</strong></td>
<td>S₁,5L</td>
<td>0.5</td>
<td>5 layers</td>
<td>280, 320</td>
</tr>
<tr>
<td></td>
<td>S₁,8L</td>
<td>0.5</td>
<td>8 layers</td>
<td>280, 320</td>
</tr>
<tr>
<td></td>
<td>S₂,5L</td>
<td>1</td>
<td>5 layers</td>
<td>280, 320</td>
</tr>
<tr>
<td></td>
<td>S₂,8L</td>
<td>1</td>
<td>8 layers</td>
<td>280, 320</td>
</tr>
<tr>
<td></td>
<td>S₃,5L</td>
<td>2</td>
<td>5 layers</td>
<td>280, 320</td>
</tr>
<tr>
<td></td>
<td>S₃,8L</td>
<td>2</td>
<td>8 layers</td>
<td>280, 320</td>
</tr>
</tbody>
</table>

Fig. 2. (a-d). Schematic diagram for the layer structure of the samples after painting electrodes Cu-Zn-S (Ag) on (a) n-type Si substrate; (b) p-type Si substrate; (c) silicon substrate and (d) glass substrate.

The optical (transmittance and reflection) spectra of the arranged films were recorded in the domain (500–2500 nm) consuming an optical programmable double-beam UV–vis–NIR spectrophotometer (JASCO Corp., V-670, Rev. 1.00.) with photometric of ±0.002 to ±0.004 accuracy absorbance and transmittance of (± 0.3 %) attached with a self-tuned wavelength personal computer. The \( E_g \) was deliberated through an extrapolation of the linear part of \((\alpha h \nu)^{2}\) versus the photon energy \((h \nu)\). We measured the electrical resistivity of all samples consuming the Keithley device, model 2400 at room temperature, and thus carried out the refractive index, the static dielectric, and the high-frequency dielectric constants of the synthesized films.

#### 2.1.3. Optical instruments

The optical (transmittance and reflection) spectra of the arranged films were recorded in the domain (500–2500 nm) consuming an optical programmable double-beam UV–vis–NIR spectrophotometer (JASCO Corp., V-670, Rev. 1.00.) with photometric of ±0.002 to ±0.004 accuracy absorbance and transmittance of (± 0.3 %) attached with a self-tuned wavelength personal computer. The \( E_g \) was deliberated through an extrapolation of the linear part of \((\alpha h \nu)^{2}\) versus the photon energy \((h \nu)\). We measured the electrical resistivity of all samples consuming the Keithley device, model 2400 at room temperature, and thus carried out the refractive index, the static dielectric, and the high-frequency dielectric constants of the synthesized films.

#### 2.1.4. current-voltage measurement on pristine and Ag/Cu-Zn-S thin films

First, the current-voltage (I–V) trend for all samples in dark was measured using inject carriers into the circuit with electrical means rather than with light generated carriers. In this case, the resistivity is related to the film thickness \( w \), the voltage \( V \), and the current I...
through the following equation;

$$\rho = \frac{V}{I} \omega \pi \ln 2$$  \hspace{1cm} (1)

$\frac{V}{I}$ is the slope of the $I$–$V$ curves that were obtained. A photovoltaic cell in the dark is a large flat diode. Secondly, the electrical trend of pristine and 1% Ag/CZS thin films under illumination via lamp or diode laser was also studied. If there is no contact of the cell under illumination, thus, it is in "open-circuit" condition \[19\]. In this case, it does not deliver a current but the open-circuit voltage ($V_{OC}$). Hence, the output power is zero. If the cell under illumination is short-circuited, it cannot deliver a voltage, but the short-circuit current ($I_{SC}$) only. In this case, the output power is again zero. However, the cell delivers an output power at any other point on the $I$–$V$ curve. Measuring both $V_{OC}$ and $I_{SC}$ is very useful for characterizing solar cells. In this work, we illuminated the samples under a white lamp (2800 lm) and a diode laser of 405 nm wavelength. The $V_{OC}$ in an open circuit condition was measured via the Avometer while $I_{SC}$ in a short-circuit condition was measured via Keithly device as depicted in Fig. 3.

3. Results and discussions

3.1. The influence of heat annealing on pristine and Ag/Cu-Zn-S thin films

It is interesting to study the influence of heat annealing on the structural, morphological, optical, and electrical properties of pristine and Ag/Cu-Zn-S thin films. We suggested doing heat annealing at 320 °C, 360 °C, 400 °C. Firstly, we put the first group such as the pristine and Ag/Cu-Zn-S samples in the Furnace (1000 °C) (Ney Vulcan, Model 3–1750) at first temperature of 320 °C for 45 min. Thus all films were stable and ready for investigation. Secondly other group of samples were put in the Furnace at 360 °C for 45 min. It was found that only the prepared pristine film of 8 layer thickness was still stable and has good conductivity while the other prepared pristine film of 5 layer thickness and Ag/Cu-Zn-S samples become an insulator. Finally, we heat another group of the prepared pristine film of 8 layers at 400 °C for 45 min, in this stage we also found that the sample becomes an insulator. The observed results are in agreement with the reported literature \[7\]. Whereas in the literature, the researchers heating the Cu-Zn-S sample at high temperature and found that the vaporization of copper elements reveals to reduce the sample conductivity and the phase of ZnS still unaffected and the sample become an insulator material but it can be used as absorber material in solar cell applications.
Fig. 4. XRD patterns of the deposited films with 5 layers $S_0$, $S_1$, $S_2$, $S_3$, and $S_5$ on glass substrate with different Ag concentrations of 0%, 0.5%, 1%, and 2% by weight, respectively at (a) 280 °C [36] and (b) 320 °C.

3.2. X-ray and EDX investigations

Fig. 4a, 4b depicts the XRD patterns of the deposited films with 5 layers $S_0$, $S_1$, $S_2$, $S_3$, and $S_5$ on the glass substrate with different Ag concentrations of 0%, 0.5%, 1%, and 2% by weight, respectively at 280 °C and annealing at 320 °C, respectively. In Fig. 4b, the main reflection peaks for all samples appear sharper and higher intensity than that obtained for the same unheated samples and appear in the same position (20 angle) in the vicinity of 28 reflected from the same (111) plane. The obtained results in Fig. 4b are in agreement with the JCPDS 26–0575 card. By calculating the crystallite size (D) for $S_0$, $S_1$, $S_2$, $S_3$, and $S_5$ films at 320 °C through the Debye-Scherer formula, $D = \frac{0.94 \lambda}{\beta \cos \theta}$, and comparing with the results obtained of the same prepared samples at 280 °C. Table 4 shows the main peak reflection angle 2θ, the crystallite size D, and the crystal defect of prepared samples δ in 5 layer thickness. It was found that the crystal size of the samples heated at 320 °C was higher than those obtained at 280 °C as tabulated in Table 4. This result indicates that the samples heated at 320 °C have more crystalline and the $S_2$ 5 L sample heated at 320 °C has the biggest crystal size of about 86.4 nm. The crystallinity of Ag-doped films, indicated by the magnitude, intensity of the diffraction peaks, is superior compared to the pristine film.

Fig. 5a, 5b depicts the patterns of X-ray diffraction of the coated films with 8 layers $S_0$, $S_1$, $S_2$, $S_3$, and $S_5$ on a glass substrate heated at 280 °C and 320 °C. In Fig. 5b, it was observed that for the coated films with 8 layers, all main reflection peaks of samples become narrower and sharper with high intensity which means more crystallinity of the films was achieved. The crystallite size for $S_0$, $S_1$, $S_2$, $S_3$, and $S_5$ layers heated at 320 °C are 32.18, 51.30, 36.03, 43.70 nm, respectively as shown in Table 5. In addition, the crystallite size with 5 layer thickness for $S_0$, $S_1$, $S_2$, $S_3$, and $S_5$ layers heated at 320 °C is 48.20, 36.02, 86.40, and 39.70 nm, respectively. Hence, it can be concluded that the crystallinity increases for the heat annealing samples with higher thickness. In addition, the value of the reflection intensity peak in the vicinity of 28.49 °C has more crystalline and the $S_2$ 5 L sample heated at 320 °C to be deposited on silicon substrates because they have the highest peak intensity of X-ray measurement and were uniform, and homogeneous through the handling process. Fig. 6a shows the XRD patterns of the deposited $S_0$, $S_1$, $S_2$, $S_3$, and $S_5$ films on n-type Si substrates, and heated at 320 °C. It was noted that the main peak position shifted compared to the same unheated samples which may be due to the vaporization of some elements of the films. In addition, the main reflection peak of $S_0$, 5 L, n-Si appears in the vicinity of 55.6 °C and shows more crystallinity. From Fig. 6a and Fig. 6b we found that by calculating the crystallite size D of heated $S_0$, 5 L, n-Si sample at 320 °C, it was about 33.6 nm which is larger than the value of D = 18.8 nm of the heated $S_0$, 5 L, n-Si sample at 280 °C (see Fig. 6a). While the value of D of heated $S_2$, 5 L, n-Si sample at 320 °C was about 37.8 nm which is larger than the value of D = 15 nm of the heated $S_0$, 5 L, n-Si Sample at 280 °C (see Fig. 6a). Hence, it is worth to mention that the crystallite size increases with heat annealing at 320 °C. Furthermore, the crystallite size value (D = 18.01 nm) of the coated film with 5 layers of $S_2$, 5 L, p-Si on p-type Si substrate with 1% by weight Ag/CZS sample did
Table 4
The main peak reflection angle $\theta$, the crystallite size $D$ and the crystal defect of samples $\delta$ prepared with 5 layers thickness and heated at 280 °C and 320 °C.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Ag concentration (%)</th>
<th>Main peak reflection angle $\theta$</th>
<th>$D$ (nm) crystallite size</th>
<th>$\delta$ crystal defect (nm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>At 280 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_0$,5L</td>
<td>0</td>
<td>28.36˚</td>
<td>33.30</td>
<td>0.00059</td>
</tr>
<tr>
<td>$S_1$,5L</td>
<td>0.5</td>
<td>28.49˚</td>
<td>32.40</td>
<td>0.00097</td>
</tr>
<tr>
<td>$S_2$,5L</td>
<td>1</td>
<td>28.45˚</td>
<td>29</td>
<td>0.0012</td>
</tr>
<tr>
<td>$S_3$,5L</td>
<td>2</td>
<td>28.52˚</td>
<td></td>
<td></td>
</tr>
<tr>
<td>At 320 °C</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$S_0$,5L</td>
<td>0</td>
<td>28.40˚</td>
<td>48.20</td>
<td>0.00059</td>
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<tr>
<td>$S_1$,5L</td>
<td>0.5</td>
<td>28.49˚</td>
<td>36.02</td>
<td>0.00077</td>
</tr>
<tr>
<td>$S_2$,5L</td>
<td>1</td>
<td>25.37˚, 28.45˚</td>
<td>86.40</td>
<td>0.00013</td>
</tr>
<tr>
<td>$S_3$,5L</td>
<td>2</td>
<td>28.50˚</td>
<td>39.70</td>
<td>0.00063</td>
</tr>
</tbody>
</table>

Fig. 5. XRD patterns of the deposited films with 8 layers $S_0$, 8L, $S_1$, 8L, $S_2$, 8L and $S_3$, 8L on glass substrate with different Ag concentrations of 0%, 0.5%, 1%, and 2% by weight, respectively at (a) 280 °C [36] and (b) 320 °C.

Table 5
The main peak reflection angle $\theta$, the crystallite size $D$ and the crystal defect of samples $\delta$ prepared with 8 layers thickness and heated at 280 °C and 320 °C.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Ag concentration (%)</th>
<th>Main peak reflection angle $\theta$</th>
<th>$D$ (nm) crystallite size</th>
<th>$\delta$ crystal defect (nm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>At 280 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_0$,8L</td>
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not affect by heating the sample and the main diffracted peak still appear in the same position compared to the unheated one as depicted in Fig. 6c.

3.3. Surface morphology

In order to study the effect of high temperature on the pristine and Ag/Cu-Zn-S thin films and confirm that the increase of the crystallite size matched with the X-ray results. Hence, the surface morphological images were carried out by FESEM to investigate the morphological structure of pristine and deposited Ag/Cu-Zn-S thin films with 8 layer thickness on glass substrates and annealed at 320 °C with magnification x13000 as shown in Figs. 7a-e. The images display a good homogeneity of particles that covered well with very small pores in the substrate, especially in Fig. 7b with magnification x13000. Fig. 7a illustrates the image of the annealed S₀ 8 L sample at 320 °C with an average size of particles of ~ 11.4 nm. Fig. 7b illustrates the image of the annealed S₁ 8 L sample at 320 °C with good homogeneity, and an average size of particles of ~ 12.3 nm. While Fig. 7c illustrates the image of the annealed S₂ 8 L sample at 320 °C and shows the overlapping of particles over the sample area with an average size of particles of ~ 12.5 nm. Fig. 7d illustrates the image of the heated S₃ 8 L sample at 320 °C and shows a lot of voids in the film due to vaporization of some constituent elements like Cu, Zn, S with an average size of particles ~ 11.8 nm. While Fig. 7e shows the image of the annealed S₄ 5 L sample. Fig. 7d illustrates the image of the heated S₃ 8 L sample at 320 °C and shows a lot of voids in the film due to vaporization of some constituent elements like Cu, Zn, S with an average size of particles ~ 11.8 nm. While Fig. 7e shows the image of the annealed S₄ 5 L sample at 320 °C with 5 layer thickness and shows a homogeneity of the film with creating Nano rods beside the spherical particles with an average particle size of ~ 10.6 nm at 320 °C with 5 layer thickness and shows a homogeneity of the film with creating Nano rods beside the sphere particles with an average particle size of ~ 10.6 nm. Figs. 7f, 7h, 7i illustrate the surface morphological images with magnification x13000 of the deposited pristine and 1% Ag/CZS thin films with 5 layers (S₀ 5 L, n-Si, S₂ 5 L, n-Si, and S₂ 5 L, p-Si) on n-type and p-type silicon substrates, respectively and annealed at 320 °C. It was found that the films were smooth, good homogeneity, and the particles cover all the substrate areas with no voids appeared. The average sizes of particles of S₀ 5 L, n-Si, S₂ 5 L, n-Si, and S₂ 5 L, p-Si were measured as 7.7 nm, 6.9 nm, 8.2 nm, respectively. Fig. 7g depicts the surface image with large magnification x26000 of the deposited pristine CZS thin film with 5 layers (S₀ 5 L, n-Si) on n-type Si substrate and annealed at 320 °C. It can be seen that the formation of Nano-rods, shapes of ~ 600 nm dimension with magnification x50000 as depicted in the inset of Fig. 7g. All the measurements of average size matched well and good agreement with the XRD measurements of crystal size. The thickness layers were measured using the FESEM cross-section side view images for 5 layers and 8 layers as depicted in Figs. 8a, 8b, respectively. The thickness of 5 layers was about 720 nm while the thickness of 8 layers was about 1.79 micrometers.
We recorded the transmittance (T) and reflectance (R) optical spectra of the pristine CZS and implanted films with 5 layers of S0, 5L, S1, 5L, S2, 5L, and S3, 5L on glass substrates with 0%, 0.5 %, 1%, and 2% by weight of Ag/CZS, respectively and annealed at 320 °C as shown in Fig. 9. It can be seen that there are two regions A and B, whereas a transition of the transmittance behavior between the films was acquired. Region A denotes the transmittance and region B denotes the reflectance of the deposited films. It was observed that the transmittance of all samples increases between the regions of 500 nm–900 nm. In region A, the sample S1, 5L shows the highest transmittance of about 0.175 % in the spectral region (500–900 nm) compared to the samples S0, 5L, of about 0.128 % and S2, 5L, of about 0.14 %. While the sample S3, 5L shows the lowest value of transmittance ~ 0.082 %. Regarding the reflectance in region B, it was also observed that fringes of interference in the reflectance of S0, 5L, S1, 5L, S2, 5L, and S3, 5L samples were noted, which means that all film surfaces have high-quality deposition with low reflectivity. All samples show low reflectivity in particular sample S2, 5L shows the lowest reflectivity of about 0.018 in the region of 500 nm–900 nm. In addition, we recorded the transmittance (T) and reflectance (R) optical spectra of the pristine CZS and implanted films with 8 layers of S0, 8L, S1, 8L, S2, 8L, and S3, 8L on glass substrates with 0%, 0.5 %, 1%, and 2% by weight of Ag/CZS, respectively and annealed at 320 °C as shown in Fig. 11. It can be seen that all samples have small reflectivity less than 0.04 and increases between the regions of 500 nm–900 nm. In region A, the sample S1, 8L shows the highest peak of transmittance of about 0.152 % in the spectral region (490–1000 nm) compared to the samples S0, 8L, of about 0.079 % and S2, 8L, of about 0.05 %. While the sample S3, 8L shows the lowest value of peak transmittance ~ 0.046 % in the region 500 nm–800 nm. Regarding the reflectance in region B, it was observed that the fringes of interference in the reflectance of S0, 8L, S1, 8L, S2, 8L, and S3, 8L samples were noted, which means that those film surfaces have high-quality deposition with low
Fig. 8. FESEM cross-section side view images for measuring the 5 and 8 layer thicknesses.

Fig. 9. Optical transmittance and reflectance spectra of the deposited films with 5 layers thickness of $S_0$, $5L$, $S_1$, $5L$, $S_2$, $5L$, and $S_3$, $5L$ on glass substrates with 0%, 0.5%, 1%, and 2% by weight of Ag/CZS, respectively.

Table 6
The values of the $E_g$, $n$, $\varepsilon_\infty$, of samples $S_0$, $5L$, $S_1$, $5L$, $S_2$, $5L$, and $S_3$, $5L$ at 280 $^\circ$C and annealed at 320 $^\circ$C.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Ag concentration (%)</th>
<th>$E_g$ (eV)</th>
<th>refractive index ($n$)</th>
<th>$\varepsilon_\infty$ (eV)</th>
<th>$\varepsilon_\infty$ (eV)</th>
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</thead>
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<td></td>
</tr>
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scattering loss.

The measurement of transmittance was beneficial for evaluating the optical energy band gap ($E_g$) of the films by plotting the $(ahv)^2$ against $(hν)$, whereas the absorption coefficient, $α = \frac{2}{hν} ln \frac{1}{T}$, $d$ is the thickness of thin-film and $t$ is the transmission. The method of estimating the energy gap has been reported in literatures [20,21]. The values of $E_{opt}$ were evaluated for samples $S_0$, 5 L, $S_1$, 5 L, $S_2$, 5 L, and $S_3$, 5 L by extrapolation of the linear part of the curves until they intercept the $hν$ axis (i.e. $α = 0$) at 280 °C and annealed at 320 °C as stated in Table 6 and Fig. 10 (a, b). Thus the index of refraction ($n$), the dielectric at high frequency ($ε$) and the static dielectric ($ε$) constants of the samples can be evaluated for all deposited films with 5 layer thickness. The observed values of the $E_g$ of $S_0$, 5 L, $S_1$, 5 L, $S_2$, 5 L, and $S_3$, 5 L samples at 280 °C were 2.29, 2.32, 2.30, and 2.09 eV, respectively as depicted in Fig. 12a. While the values of the $E_g$ of the same samples but annealed at 320 °C were 2.26, 2.38, 2.23, and 2.16 eV, respectively, as tabulated in Table 6 and Fig. 12b. The values of $E_g$ were slowly increased, particularly in samples $S_1$, 5 L and $S_3$, 5 L compared to the values obtained for the un-annealed samples at 280 °C. The prepared 3% Ag/CZS films at 280 °C have the smallest edge of absorption ~ 2.09 eV, and ~ 1.91 eV with 5 and 8 layer thicknesses, respectively, demonstrating that those films are the most appropriate conduction as shown in Table 6, Table 7 and Fig. 12. This implies that the rise of %Ag drives the CZS film to a high semiconductor behavior. The dropping in $E_g$ values may result from the initiation of Ag$_2$O particles, i.e. the construction of localized states, among the conduction and the valence bands in the electronic arrangement of the film [22]. By growing the density of %Ag/CZS (salt content) leads to a drop in the $E_g$ values of $E_g$ as reported in [24, 28]. By $E_g$ raising the deposition layers of the film thickness, which may be due to growing in lattice defect consistency of nano-arranged coatings [24,25]. The results are well matching with our obtained results that demonstrate the decreasing of transmittance (T) and reflectance (R) peak intensities with increasing the film layer thickness (see Fig. 9 and Fig. 11), due to thickness effect. The reduction in T and R revealed to the absorbance of light by the presence of more oxygen vacancies and grains [26]. By decreasing the thickness of the film, the structural homogeneity and crystallinity will be improved and that reveals to higher transmittance [27].

In this work, the suppressing of the $E_g$ leads to upgrade the CZS phase. In addition, the values of the optical energy bandgap, the refractive index ($n$), the static and high-frequency dielectric constants ($ε_s$ & $ε$) for the coated films with 5 and 8 layers on glass substrates were calculated in our work as tabulated in Tables 6,7. The “n” values are correlated to the $E_g$ values by using the Moss equation as reported in [24,28]. By $E_g n^4 = k$, where the constant $k = 108$ eV. The $ε_s$ is conveyed to $E_g$ using $ε_s = 18.52 \times 3.08 E_g$ and the dielectric constant at high-frequency $ε$ is conveyed to $n$ using $ε = n^4$ [24,28]. It was noted that the values of $n$, $ε_s$ and $ε$ in 8 deposition layers, were higher than those attained in 5 deposition layers.

3.5. **UV-vis-NIR diffuse reflectance spectroscopic analysis of pristine and deposited 1%Ag/Cu-Zn-S thin films on substrates of n- & p-types Si and annealed at 320°C**

We measured the UV–vis-NIR diffuse reflectance spectra of the films and annealed at 320 °C using a programmable optical double-beam spectrophotometer (UV–vis–NIR, JASCO Corp., V-670, Rev. 1.00.). The UV–vis-NIR diffuse reflectance spectra were directed at

![Fig. 10](image)

**Fig. 10.** The $(ahv)^2$ versus $hν$ for samples $S_0$, 5L, $S_1$, 5L, $S_2$, 5L and $S_3$, 5L of 5 layers thickness at (a) 280 °C [36], and (b) 320 °C.
Fig. 11. Optical transmittance and reflectance spectra of the deposited films with 8 layers thickness of $S_0$, 8L, $S_1$, 8L, $S_2$, 8L, and $S_3$, 8L on glass substrates with 0%, 0.5%, 1%, and 2% by weight of Ag/CZS, respectively.

Fig. 12. The $(\alpha h \nu)^2$ versus $h \nu$ for samples $S_0$, 8L, $S_1$, 8L, $S_2$, 8L and $S_3$, 8L of 8 layers thickness (a) 280 °C [36], and (b) 320 °C.

Table 7
The values of the $E_g$, $n$, $\xi$, $\epsilon_{\infty}$ of samples $S_0$, 8L, $S_1$, 8L, $S_2$, 8L and $S_3$, 8L at 280 °C and annealed at 320 °C.

<table>
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<th>Sample name</th>
<th>Ag concentration (%)</th>
<th>$E_g$ (eV)</th>
<th>refractive index ($n$)</th>
<th>$\xi$ (eV)</th>
<th>$\epsilon_{\infty}$ (eV)</th>
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</table>
the edge of absorption and converted into absorbance through the Kubelka–Munk (KM) relation [29,30]:

$$F(R_{\infty}) = \frac{\alpha}{s} = \frac{(1-R)^2}{2R}$$

where $F(R_{\infty})$, $s$, $\alpha$, and $R$ are the Kubelka–Munk function, the scattering coefficient, the absorption coefficient, and the diffuse reflectance, respectively. The $E_g$ of the samples was estimated from the absorbance edge at the base of the Tauc plot, via the subsequent equation [29,30]:

$$[F(R_{\infty})]^2 = A (\hbar \nu - E_g)$$

where $A$ and $\hbar \nu$ are a proportional constant, and the incident photon energy, respectively. The value of $n$ proceeds a value of 0.5 or 2 indirect or direct transition, respectively. Hence, the value of $E_g$ was evaluated from the relation between $[F(R)\hbar \nu]^2$ against photon energy ($h \nu$, eV). The UV–vis-NIR diffuse reflectance spectra of the deposited pristine and 1%Ag NPs doped CZS films with 5 layers on substrates of n- & p-types Si ($S_0$, 5 L, n-Si, $S_2$, 5 L, n-Si, and $S_2$, 5 L, p-Si) at 280 °C and annealed at 320 °C as shown in Fig. 13. It was noted that the reflectance of $S_0$, 5 L, n-Si at 280 °C was the highest peak intensity of about 0.085 % compared to the reflectance of sample $S_2$, 5 L, n-Si, and $S_2$, 5 L, p-Si at 280 °C and 320 °C in the region from 200 to 1700 nm. In addition, the reflection was decreased for the CZS film doped with 1% Ag NPs in the visible region. While the reflectance of sample $S_2$, 5 L, n-Si becomes the lowest reflectance less than 0.04 then using F(R) the Kubelka–Munk function and drawing relation between $[F(R) h \nu/t]^2$ versus $(h \nu)$ for the samples, thus we can evaluate the energy band gaps of these samples from Fig. 14a and Fig. 14b. The sample $S_0$, 5 L, n-Si annealed at 320 °C has the lowest energy band gap of about 1.45 eV as tabulated in Table 8 (3.17), whereas the energy band gap $E_g$, refractive index $n$, the high-frequency dielectric constant $\varepsilon_\infty$ and the static dielectric constant $\varepsilon_0$; the high-frequency dielectric constant $\varepsilon_\infty$ as 8.58, 6.30, and 6.00; and the static dielectric constant $\varepsilon_0$ is 2.93, 2.51, and 2.45; the high-frequency dielectric constant $\varepsilon_\infty$ of samples ($S_0$, 5 L, n-Si, $S_2$, 5 L, n-Si, and $S_2$, 5 L, p-Si) annealed at 320 °C were carefully calculated. The determined values of $E_g$ were 1.45, 2.70, and 2.97 for $S_0$, 5 L, n-Si, $S_2$, 5 L, n-Si, and $S_2$, 5 L, p-Si compounds, respectively, as listed in Table 8. The value of $E_g$ was higher for sample $S_2$, 5 L, p-Si than that obtained for samples $S_0$, 5 L, n-Si, and $S_2$, 5 L, n-Si samples. In addition, the refractive index, ($n$) was evaluated as 2.93, 2.51, and 2.45; the high-frequency dielectric constant ($\varepsilon_\infty$) as 8.58, 6.30, and 6.00; and the static dielectric constant ($\varepsilon_0$) as 14.00, 10.20, and 9.37 for $S_0$, 5 L, n-Si, $S_2$, 5 L, n-Si, and $S_2$, 5 L, p-Si compounds, respectively.

3.6. Electrical Properties of the pristine and coated %Ag/Cu-Zn-S films on glass substrates which annealed at 320 °C in the dark

We measured the current-voltage (I–V) behavior of the coated pristine Cu-Zn-S ($S_0$, 5 L) and 0.5, 1, 2% by weight of Ag/Cu-Zn-S thin films ($S_1$, 5 L, $S_2$, 5 L and $S_3$, 5 L) with 5 layer thickness on glass substrates and annealed at 320 °C as shown in Fig. 15. A silver paste was painted on the top of the films as electrodes and the I–V curves of the samples were measured. Whereas the variation of current and voltage was measured by installing the 2401 Keithley device model in the dark. The trend of Ohmic performance was obtained on the I–V curve of $S_0$, 5 L, $S_1$, 5 L, $S_2$, 5 L, and $S_3$, 5 L thin films.

Thus the electrical resistivity ($\rho$) of these samples can be calculated as 5.5, 2.25, 1.95, and 9.2 Ω cm for $S_0$, 5 L, $S_1$, 5 L, $S_2$, 5 L, and $S_3$, 5 L films which annealed at 320 °C, respectively. It can be noted that the annealed sample $S_2$, 5 L at 320 °C has the lowest resistivity of 1.95 Ω cm. While the annealed sample $S_2$, 5 L at 320 °C has the highest resistivity of 9.2 Ω cm.

Fig. 16 elucidates the I–V trends of the coated pristine CZS ($S_0$, 8 L) and 0.5, 1, 2% by weight of Ag/CZS thin films ($S_1$, 8 L, $S_2$, 8 L and $S_3$, 8 L) with 8 layer thickness on glass substrates and annealed at 320 °C. The electrical resistivity for all samples was calculated as 1.72, 0.68, 0.95, and 3.29 Ω cm for $S_0$, 8 L, $S_1$, 8 L, $S_2$, 8 L, and $S_3$, 8 L thin films, respectively. It was perceived that the annealed samples $S_1$, 8 L, and $S_2$, 8 L at 320 °C have the lowest resistivity of 0.68 Ω cm, and 0.95 Ω cm, respectively. It is worth to mention that the coated samples with 8 layer thickness and annealed at 320 °C have lower resistivity than those coated with 5 layer thickness and
Fig. 14. \((F(R)hv)^2\) versus \((hv)\) depicting the energy band gap \((E_g)\) of samples (a) S0, 5L, n-Si, (b) S2, 5L, n-Si, and S2, 5L, p-Si.

Table 8
Depicts the energy band gap \(E_g\), refractive index \(n\), the high frequency dielectric constant \(\varepsilon\) and \(\varepsilon_{\infty}\) the static dielectric constant for samples (S0,5L,n-Si, S2,5L,n-Si, and S2,5L,p-Si) samples annealed at 320 °C.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Type of Si</th>
<th>Ag concentration (%)</th>
<th>(E_g) (eV)</th>
<th>refractive index (n)</th>
<th>(\varepsilon) (eV)</th>
<th>(\varepsilon_{\infty}) (eV)</th>
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<tbody>
<tr>
<td>S0,5L,n-Si</td>
<td>n</td>
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<td>1.45</td>
<td>2.93</td>
<td>8.58</td>
<td>14.00</td>
</tr>
<tr>
<td>S2,5L,n-Si</td>
<td>n</td>
<td>1</td>
<td>2.70</td>
<td>2.51</td>
<td>6.30</td>
<td>10.20</td>
</tr>
<tr>
<td>S2,5L,p-Si</td>
<td>p</td>
<td>1</td>
<td>2.97</td>
<td>2.45</td>
<td>6.00</td>
<td>9.37</td>
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</tbody>
</table>

Name (%) index (n) (eV) (eV).

Fig. 15. Current-voltage (I-V) characteristic curves of S0, 5L, S1, 5L, S2, 5L and S3, 5L films with thickness of 5 layers grown by varying the Ag concentrations 0, 0.5, 1, and 2 % by weight Ag/CZS.
annealed at 320 °C. In other words, the electrical resistivity of the films decreased, which means increasing conductivity ($\sigma = 1/\rho$), with increasing the film thickness of large free carrier concentration. The lowest resistivity of $S_{1.8}$ sample, according to the XRD patterns can be assigned to diminish structural disorder and to enlarge the crystallite size, which can lead to maximize carrier mobility and to suppress the electron scattering at the grain boundaries. The obtained results are fit well with the reported results by Kitagawa et. al. [3,31]. The decline in porosity and interface influences could cause a drop in resistivity of the films [31–38]. This work could be employed for new technological applications like optoelectronics and solar cells.

3.7. Photovoltaic results

In this section, the electrical behavior of the coated pristine CZS ($S_{0.5}$ L) and 1\% Ag/CZS thin films ($S_{2}$ 5 L) with 5 layer thickness on n-type and p-type silicon substrates and annealed at 320 °C under a lamp and laser diode was presented. We classified the samples into two groups, one group is the samples $S_{0.5}$ L, n-Si, $S_{0.5}$ L, p-Si, $S_{2}$ 5 L, n-Si and $S_{2}$ 5 L, p-Si prepared at 280 °C and the second group is the samples $S_{2}$ 5 L, n-Si, $S_{2}$ 5 L, p-Si, $S_{2}$ 5 L, n-Si annealed at 320 °C. The $V_{oc}$ and $I_{sc}$ of the synthesized samples for both two groups were well measured. Under optimum conditions, it was easy to select the samples having large values of $V_{oc}$ and $I_{sc}$ and give great photovoltaic cell behavior. It can be summarized the photovoltaic results (i.e., $V_{oc}$ and $I_{sc}$ values under illumination) of the two groups as depicted in Table 9. Fig. 17 shows the $I$–$V$ trend of the prepared sample $S_{0.5}$ L, p-Si, in dark and (a) under diode laser illumination at 280 °C, and (e) under white lamp illumination at 280 °C; for sample $S_{0.5}$ L, p-Si, in dark and under diode laser illumination at (b) annealing 320 °C, and (d) 280 °C; and (e) for sample $S_{2}$ 5 L, n-Si, in dark and under diode laser illumination at 280 °C. It is known that if the current under illumination larger than the dark current of the samples, hence, those samples have good photovoltaic. It is worth to

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>$V_{oc}$ (mV)</th>
<th>$I_{sc}$ (μA/cm²)</th>
<th>$V_{oc}$ (mV)</th>
<th>$I_{sc}$ (μA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>White lamp illumination</td>
<td>White lamp illumination</td>
<td>Laser illumination</td>
<td>Laser illumination</td>
</tr>
<tr>
<td>$S_{0.5}$ L, n-Si</td>
<td>280 °C</td>
<td>0.05</td>
<td>1.60</td>
<td>0.31</td>
<td>47.70</td>
</tr>
<tr>
<td>$S_{0.5}$ L, p-Si</td>
<td>280 °C</td>
<td>0.65</td>
<td>0.02</td>
<td>4.50</td>
<td>79.60</td>
</tr>
<tr>
<td>$S_{2}$ 5 L, p-Si</td>
<td>280 °C</td>
<td>0.01</td>
<td>0.02</td>
<td>0.22</td>
<td>13.6</td>
</tr>
<tr>
<td>$S_{2}$ 5 L, n-Si</td>
<td>280 °C</td>
<td>0.01</td>
<td>0.03</td>
<td>0.13</td>
<td>10.40</td>
</tr>
<tr>
<td>$S_{0.5}$ L, n-Si</td>
<td>320 °C</td>
<td>0.04</td>
<td>0.03</td>
<td>1.20</td>
<td>58.90</td>
</tr>
<tr>
<td>$S_{2}$ 5 L, p-Si</td>
<td>320 °C</td>
<td>0.04</td>
<td>0.60</td>
<td>0.40</td>
<td>366</td>
</tr>
<tr>
<td>$S_{0.5}$ L, p-Si</td>
<td>320 °C</td>
<td>0.02</td>
<td>0.04</td>
<td>0.11</td>
<td>41.70</td>
</tr>
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</table>
mention that the sample $S_0 \cdot 5 \cdot L_{p-Si}$ shows a highest value of $V_{oc} = 0.65$ mV, and 4.5 mV during the illumination under the white lamp and diode laser, respectively. While the sample $S_0 \cdot 5 \cdot L_{n-Si}$ gives a highest value of $I_{sc} = 1.6 \mu A/cm^2$ under the illumination of white lamp and the annealed sample $S_2 \cdot 5 \cdot L_{p-Si}$ at $320 ^\circ C$ gives a highest value of $I_{sc} = 366 \mu A/cm^2$ under diode laser illumination. These tests may be applicable for improving solar cells, arrays, photovoltaic, and detectors during service life. The objective of this study is preparation and characterization of a p-doped semiconductor thin film that can be acting as a multifunctional material in optoelectronic applications. For example it can be an electrode for solar cell applications or a light emitting diode. In additions, we presented this film as an absorbing material in photo voltaic, however still more optimizations for applications are needed but we try to open the door for this work to be used in optoelectronic applications.

4. Conclusion

The impact of annealing temperature on the pristine and Ag NPs-doping with various concentrations ($x = 0.5, 1$ and $2\%$ by weight) films with 5 and 8 layer thicknesses and the type of substrates (glass, n-type and p-type silicon) on surface morphology, structural,

![Fig. 17. Current-voltage (I-V) trend of the prepared sample $S_0 \cdot 5 \cdot L_{p-Si}$ in dark and (a) under diode laser illumination at $280 ^\circ C$, and (e) under white lamp illumination at $280 ^\circ C$; for sample $S_2 \cdot 5 \cdot L_{p-Si}$ in dark and under diode laser illumination at (b) annealing $320 ^\circ C$, and (d) $280 ^\circ C$; and (e) for sample $S_2 \cdot 5 \cdot L_{n-Si}$ in dark and under diode laser illumination at $280 ^\circ C$.](image)
electrical and optical properties of the prepared films were explored. The cost-effective sol-gel spin-coating technique was utilized to prepare pristine and silver nanoparticles (NPs) doped Cu-Zn-S (CZS) thin films at 280 °C. We started to do heat annealing for three groups of samples with 5 and 8 layers at 300 °C, 360 °C, 400 °C, consequently for 45 min. It was found that the annealed samples at 320 °C were stable and homogeneous, while the annealed samples with 5 layers at 360 °C, and with 8 layers at 400 °C become insulators. The results reveal that the annealed samples at 320 °C have more crystallinity and the sample S2, 5 L has the biggest crystal size of about 86.4 nm. In addition, the crystallinity of Ag-doped films is superior compared to the pristine film and it increases for the heat annealing samples with higher thickness. The value of the reflection intensity peak in the vicinity of 28.49 becomes higher for heated S2, 5 L sample at 320 °C. It was found that the formation of Nano-rods, shapes of ~ 600 nm dimension of the deposited pristine CZS thin film with 5 layers (S0, 5 L, n-Si) on n-type Si substrate and annealed at 320 °C. In addition, the reflectance of S0, 5 L, n-Si at 280 °C was the highest peak intensity of about 0.085 % compared to the reflectance of sample S2, 5 L, n-Si, and S2, 5 L, p-Si at 280 °C and 320 °C in the region from 200 to 1700 nm. The rise of %Ag drives the CZS film to highly semiconductor behavior and decreasing of the Eg leads to upgrade the CZS phase. The electrical resistivity (ρ) was calculated for the annealed samples S0, 5 L, S1, 5 L, S2, 5 L, S3, 5 L, S4, 5 L, S5, 8 L, S1, 8 L, S2, 8 L, and S3, 8 L at 320 °C, respectively. We noted that the annealed samples S2, 5 L, and S3, 8 L at 320 °C have the lowest resistivity of 1.95, and 0.68 Ω cm, respectively. While the annealed sample S1, 5 L at 320 °C has the highest resistivity of 9.2 Ω cm. Furthermore, the coated samples with 8 layer thickness and annealed at 320 °C have lower resistivity than those coated with 5 layer thickness and annealed at 320 °C. In other words, the electrical resistivity of the films decreased with increasing the film thickness of large free carrier concentration. The sample S0, 5 L, p-Si, gives the highest values of Voc = 0.65, and 4.5 mV during the illumination under a white lamp and diode laser, respectively. Whereas the deposition of pristine Cu-Zn-S on p-type silicon substrate improves all the characteristic parameters of the sample due to the matching between the p-type Cu-Zn-S material and the p-type silicon substrate. While the sample S0, 5 L, n-Si gives the highest value of Voc = 1.6 μA/cm² under the illumination of the white lamp and the annealed sample S2, 5 L, p-Si at 320 °C gives the highest value of Voc = 366 μA/cm² under diode laser illumination. Hence, the doping with Ag nanoparticles into the Cu-Zn-S sample leads to enhance the photovoltaic properties of this material by increasing the values of the short current circuit Isc. This work could be employed for new technological applications like optoelectronics and solar cells using a cost-effective sol-gel spin-coating system as a promising technique for the preparation of Ag/CZS thin films. Whereas the deposited 1% Ag/CZS films in 5 and 8 layers have a good electrical conductivity that favors its practice as absorber films for solar cell and photovoltaic devices.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References


