Effects of Zn doping concentration on the optical and photovoltaic properties of $\text{Zn}_x\text{Pb}_{1-x}\text{S}$ thin film-based solar cell prepared by chemical spray pyrolysis

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Abstract

The metal dopants in PbS thin films make a significant impact on its optical and electronic transport properties that make it useful for photovoltaic and other optoelectronic applications. The photovoltaic properties of Zn-doped nanostructured PbS thin films synthesized from zinc acetate, lead acetate, and thiourea as an absorber layer prepared using chemical spray pyrolysis were investigated. Rutherford backscattering spectroscopy (RBS), X-ray diffraction (XRD), and UV–visible spectrophotometry techniques were used to obtain stoichiometry, thickness, structural, and optical properties of the thin films before fabrication of $\text{Zn}_x\text{PbS}/\text{CdS}$ solar cell. The RBS revealed the stoichiometry ratio as $\text{Zn}_x\text{Pb}_{1-x}\text{S}$ and thickness range of 189.05–251.64 (10^{15} atoms/ cm^2). The inclusion of the Zn dopant drastically reduced the concentration of lead from the initial 40.93–14.95%. Optical analysis of the films gave high optical absorption and relatively low reflectance from visible toward the NIR region. An increase in energy bandgap was observed with Zn dopants inclusion from 0.53 to 1.65 eV, which fits the path of the solar radiation for maximum absorption. Photovoltaic properties revealed from the J – V measurement confirmed that Zn-doped sample 6% ZnAcet thin film solar cell gave a maximum short-circuit current density (J_{sc}) of 17.30 mA/cm^2 , open-circuit (V_{oc}) 390 mV, fill factor (FF) 0.48, and conversion efficiency (η) of 2.7%.

Keywords Thin film · Spray pyrolysis · Optoelectronic · Solar cell · Conversion efficiency

1 Introduction

Recently, efforts on the development of thin film solar cell have been more concentrated on the use of nanostructured PbS due to its exceptional properties such as large excitation Bohr radius (18 nm) [1, 2] which results in strong quantum confinement effect in nano-sized structures. It is an excellent based material for near-infrared light absorber in solar cells [3, 4], perovskite solar cell [5, 6], and it can tailor-make lattice parameters and energy bandgap that

matches idea energy bandgap for maximum solar radiation absorption [7, 8].

Also, when doped, it exhibits perfect electronic transport properties, high absorption coefficient [9], and refractive index which enables light absorption and lower reflection in the UV–visible region of the solar radiation spectrum. Doping impurities introduced interstitial defect at the Pb vacant site or substitutional in the PbS lattice site which causes improvement in the optoelectronic properties of PbS. Studies on some metal-doped PbS like Al-doped PbS [10], PbS: Co^{2+} [11], Ni:PbS [8] Cd:PbS [12]

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Fe²⁺ doped [13] Ag: PbS [14, 15] and Zn:PbS [16–18] indicated that doping enhanced the properties of PbS in the production of electronic devices. 0.4% solar cell conversion efficiency was reported by Rosario et al. for Al: PbS thin film photovoltaic cell [19]. Touati et al. reported Cd: PbS cells with 2.5% conversion efficiency with 12.36 mA/cm², 635 mV and 0.32 short-circuit density, open-circuit voltage and fill factor, respectively [20].

Among all the metal-doped PbS, Zn-doped PbS thin film prepared by various methods such as chemical bath deposition CBD [16] Chemical vapor deposition [21], spray pyrolysis [7, 15], and thermal evaporation [22] has been reported to have some unique optical and electrical which makes it useful for optoelectronic applications. Besides, Zn has a smaller ionic radius (0.741 Å) than Pb (1.15 Å), which makes it easier to diffused into PbS lattice to improve PbS properties. According to the literature, increase in Zn dopant in PbS host causes a decrease in grain size which enhanced its morphological, electrical, and optical properties [7, 15, 18, 23]. More so, Zn-doped PbS prepared by CBD, having bandgap tailored from 1.14 to 1.74 eV with high electrical carrier electrical concentration of $2.82 \times 10^{17} \text{ cm}^{-3}$, mobility of $11.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and decreased electrical resistivity of $10.8 \Omega^{-1}$ was reported as a good potential material for ideal solar cells absorber layer [9]. Despite the promising properties of Zn–PbS thin films for solar cell and other optoelectronics, little or no report is available on solar cell fabricated using Zn–PbS thin films. Also, the development of affordable Zn–PbS thin film material for solar cell application using less expensive chemical spray pyrolysis, with promising conversion efficiency which can easily be improved upon is the focus of this work. Notably, among various thin film preparation methods, chemical spray pyrolysis offers a high advantage over others as it encourages doping, multiple layer deposition, low cost, and ability to scale up, and it has the tendency of reducing structure with mixed phase. Hence, the aim of the present study is to investigate the enhancement effect of the zinc doping concentration on the properties of Zn-doped lead sulfide thin film solar cell. This paper hereby presents the results of the effect of Zn dopant on stoichiometry, optical, and photovoltaic of the nanostructured Zn–PbS thin film heterojunction solar cell with CdS window layer prepared by low-cost spray pyrolysis.

2 Materials and Methods

2.1 Experimental Details

Indium tin oxide (ITO)-coated glass with resistivity ranging from 8 to $10 \Omega^{-2}$ from Stigma Irish, UK, and soda–lime glass

cut into $(15 \times 15) \text{ mm}^2$ were used as the substrate. The substrates were cleaned following the procedure reported by Adeoye et al. [18]. Zn–PbS thin films were prepared on the substrate with different Zn doping concentrations. Equal molarity of commercially available zinc acetate, lead acetate, and thiourea was prepared with distilled water as the source of dopant (Zn), host (Pb and S), respectively. The mixing ratio of the precursors was such that lead acetate and thiourea were taken in 1:2 by volume and doping with Zn by adding the appropriate volume from 0%, 2%, 4%, 6%, and 8% by volume of the lead acetate. The solution was stirred thoroughly at room temperature for 30 min before stepwise spraying onto the substrate, placed on the hot plate of $(250 \pm 5) ^\circ\text{C}$. Deposition parameters such as nozzle substrate distance, carrier gas flow rate and pressure of the carrier gas were maintained at (27 cm, $(3\text{--}3.5) \text{ dm}^3/\text{min}$) and 2.3 bar, respectively, to obtain good quality nanostructured thin film of Zn:PbS. The chemical equation of the reaction is depicted in Eq. (1).

For the CdS/Zn–PbS heterojunction solar cell fabrication, the CdS window layer was prepared on cleaned ITO coated substrate using spray pyrolysis before Zn:PbS absorber layer deposition. The CdS window layer was prepared from a precursor solution of equal molarity of cadmium chloride (CdCl_2) and thiourea (NH_2CSNH_2) dissolved in distilled water (mixing ratio 2:1 by volume) and stirred thoroughly before stepwise spraying on heat substrate placed on the hot plate $(300 \pm 5) ^\circ\text{C}$. The corresponding chemical reaction equation is as follow:

2.2 Characterization details

The elemental composition and thickness of the deposited Zn–PbS films were obtained by Rutherford backscattering spectroscopy using the 1.7 MeV tandem accelerator available at the Center for Energy Development (CERD), Obafemi Awolowo University, Ile-Ife. The crystallographic property of the prepared Zn:PbS thin film was studied with the GBC EMMA X-ray diffractometer having CuK α radiation with $\lambda = 1.5514 \text{ \AA}$. AvaSpec-2048 Fiber Optic spectrometer interfaced to a computer system was used to measure the optical transmittance and diffused reflectance at room temperature within 350–110 nm wavelength range. To determine the photovoltaic properties of the samples, the

Aluminum (Al) contact electrode was made on the samples by DC sputtering through a suitable mask to form Al/Zn–PbS/ITO structure (inset Fig. 7b). The work function of Al (4.0 eV) is less than those of PbS and ITO (4.4 eV), which is greater than CdS (4.3 eV) [24–26]. Therefore, ITO makes ohmic contact with the CdS film and the Al electrode serves as ohmic contact with the Zn–PbS film. In this way, five sets of heterojunctions solar cell devices at different doping concentrations of 0%, 2%, 4%, 6%, and 8% of the absorber Zn–PbS layer were fabricated.

The photovoltaic properties of the fabricated Zn–PbS/CdS heterojunction cells were obtained from the current density–voltage (J – V) characteristics of the cells in dark and under illumination using a two-point probe coupled with a Keithley source meter 2400 that was interfaced to a computer system with a software (LabVIEW). The Newport solar simulator with 1.5 air mass (A.M) was used as a source of illumination. Under illumination, photo-generated charge carriers within the depletion region are separated by inbuilt electric potential with holes drifting to the end of the Zn–PbS layer and electrons drifting to the end of the CdS layer. Excess electrons in the CdS flow through the external circuit to recombine with the excess holes in the PbS side when the device terminals are short-circuited and these constitute the photocurrent.

3 Results and discussion

3.1 Stoichiometry analysis

The spectrometric analysis of the films was carried out to ascertain the composition of the deposited films, and this was achieved by the RBS technique via the use of the Tandem accelerator described in Sect. 2.2. The RBS spectra for Zn–PbS thin films are shown in Fig. 1. From the nature of the peaks, as shown in the spectra corresponding to the absorbing edges of each element present in the films, it can be inferred that the thin films are relatively uniform and adhere to the substrate well and without diffusion between layers. The distinctive arrangements of the peaks further suggested that the starting precursor completely pyrolyzed to have a stable solid film formed by constituent elements. There are no traces of impurity elements like carbon or hydrogen earlier present in the starting materials, detected in the final product. The experimental data were fitted over the simulation to achieve a perfect match to determine the areal densities, stoichiometry, and depth profile data. The chemical compositions and the thickness are given in Table 1, while depth profile plots (showing the elements in different layers) are shown in Fig. 2. It is observed from the compositions that while Zn in the thin film increases relatively with the Zn dopant

Fig. 1 RBS spectra of the prepared Zn: PbS **a** 0%, **b** 2%, **c** 4%, **d** 6% and **e** 8%

Table 1 Elemental composition and RBS thickness values of Zn-doped PbS thin films

Sample	Compositions (%)			Thickness (10^{15} atoms/ cm^2)
	Pb	S	Zn	
0% ZnAcet	40.93	59.07	0.00	189.05
2% ZnAcet	36.08	57.45	6.47	170.83
4% ZnAcet	35.14	56.46	8.40	228.29
6% ZnAcet	24.41	56.03	19.56	231.17
8% ZnAcet	14.95	55.81	29.24	251.64

concentration, the Pb composition decreases linearly from 40.93 to 14.95%. The effect of zinc dopant on the Pb concentration can also be verified from the spectra (Fig. 1) which indicated a linear reduction in the peak intensity of Pb. The depth profile plots of the samples are shown in Fig. 2, it shows the concentration of the elements in each layer corresponding to the thickness of the films and the Soda–lime glass substrate.

3.2 Structural characterization

The XRD patterns of the prepared Zn:PbS thin films are shown in Fig. 3, the presence of well-defined peaks confirms the polycrystalline nature of the film, prominent peaks were observed for every same sample at $2\theta = 26.02^\circ$, 30.14° , 43.13° , 51° , and 62.6° which matches the plane (111), (200), (220), (311), and (222) of PbS indexed to the rock salt structure of PbS, based on reference standard JCPDS (card number 5-592 [27, 28]. It is also worth to note

Fig. 2 SIMNRA depth profile data plots of Zn: PbS samples **a** 0%, **b** 2%, **c** 4% and **d** 6%

that the presence of the Zn dopant in PbS does not cause a mixed phase of the PbS. Moreover, there is a slight shift in the diffraction angle and a decrease in the intensity of the peaks as Zn increases in PbS. This is an indication that Zn^{2+} is placed in the Pb vacant or substitutional sites rather than interstitial sites to form substitution solid solution of Zn: PbS. Similar effect was reported for Cd^{2+} -doped thin films [20], Sr-doped PbS [29], Cu-doped PbS thin film [30]. Also, the average grain size of the prepared thin film was calculated using the Debye–Scherrer equation [28, 31]

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (3)$$

where D is the average crystallite size, λ is the wavelength (1.5406 Å for CuK α), β is the full width at half maximum (FWHM) and $K = 0.94$. The diffraction constants obtained indicated that the crystallite size decreases from 14.28 to 10.77 nm as the concentration of Zn increases in the deposited films. This result confirmed the nanostructure nature of the prepared Zn: PbS thin films. More so, the grain size also decreased with increasing Zn dopant (Fig. 6). The decrease in crystallite size with the addition of Zn^{2+} impurity is in agreement with a recently published study [9], and this could be attributed to the slight peak broadening and the marked decrease in diffraction peak intensity with dopant concentration. The introduction of Zn^{2+} in the PbS matrix is suggested to increase the number

Fig. 3 Diffraction spectra of the prepared Zn: PbS **a** 0%, **b** 2%, **c** 4%, **d** 6% and **e** 8%

of crystal nuclei, crystallization rate, and grain refinement, which induced grain size reduction (Table 2).

3.3 Optical characterization

In this study, to determine the bandgap energy properties from the optical analysis data using Eq. 6, the RBS thickness (10^{15} atoms/cm²) of Zn–PbS thin films was converted to linear SI unit thickness using Eq. 4. Since the density of the deposited cannot be determined directly, hence, a density value similar to stoichiometric PbS (7.60 g/cm³) was assumed, and a factor of 0.523 was obtained for the conversion of the atoms area density (10^{15} atoms/cm²) into the linear unit. The evaluated linear values in nm for the Zn–PbS films are presented in Table 2.

$$\text{Linear thickness (nm)} = \frac{\text{Atoms per unit area}}{\text{Atoms per unit volume}} \quad (4)$$

Table 2 Stoichiometry, thickness, grain size, and energy bandgap of prepared Zn: PbS thin films

Sample	Stoichiometry	Linear thickness (nm)	Crystal-size (nm)	Bandgap (eV)
0% ZnAcet	Pb _{0.83} S	98.87	14.28	0.53
2% ZnAcet	Zn _{0.113} Pb _{0.628} S	91.81	12.94	1.39
4% ZnAcet	Zn _{0.149} Pb _{0.622} S	119.39	12.15	1.45
6% ZnAcet	Zn _{0.350} Pb _{0.436} S	120.90	11.68	1.58
8% ZnAcet	Zn _{0.523} Pb _{0.267} S	131.60	10.77	1.65

The optical transmittance and diffused reflectance spectra for the Zn–PbS films are shown in Fig. 4, it can be seen that the undoped PbS thin film has the lowest transmission in the UV–Vis–NIR regions. The transmission of the films generally increased in the near IR region of the spectrum from between 40 and 60% with increasing Zn dopant. There is also a conspicuous shift of the absorption edge toward a shorter wavelength (blue shift) as Zn dopant increases in the PbS. A similar effect was reported for Zn-doped PbS quantum dot [32] and PbS/ZnS nanocrystals [33]. The diffused reflectance spectra of the films shown in Fig. 4b confirm that an increase in Zn dopant lowered the reflectance in the UV–Vis–near IR region of the spectrum. The UV–visible spectra as given in Fig. 4 indicate that doping with Zn does not have much effect on the transmission of the films in the visible region compared to the NIR region where the changes are more pronounced, meanwhile, prominent changes are also observed in the reflectance characteristics of the films. High absorption and low reflection in the visible to the near-infrared region of the spectrum makes the samples a good absorber of solar radiation. The energy bandgap of the films was obtained using the Tauc formula (Eq. 5) [34, 35].

$$\alpha(h\nu) = C(h\nu - E_g)^m \quad (5)$$

where E_g is the energy bandgap, C is a photon independent parameter, $h\nu$ is the incident photon energy, m is a factor that determines the transition type, PbS is a direct bandgap material, therefore, the effect of Zn dopant on the band structure is determined by considering m to be

Fig. 4 Optical properties of Zn: PbS thin films **a** transmittance and **b** diffused reflectance

2 and $\frac{1}{2}$ for direct allowed and indirect allowed transition, respectively. α is the absorption coefficient, given by Eq. 6 [36].

$$\alpha = \frac{1}{t} \ln \left(\frac{1}{T} \right) \quad (6)$$

where t is the linear conversion of film thickness obtained from the RBS analysis and T is the optical transmittance. Variation of $(\alpha h\nu)^2$ against $(h\nu)$, gave the energy bandgap of the films by extrapolation of the straight part to the $(h\nu)$ axis as shown in Fig. 5. The direct energy bandgap value of 0.53 eV obtained for 0% Zn-doped PbS agrees well with the PbS bandgap reported in the literature [5]. Meanwhile, a progressive increase in direct energy bandgap values was observed for Zn: PbS thin films, ranging from 0.53 to 1.65 eV shown in Table 2. An increase in E_g with an increase in zinc concentration indicates the widening of the forbidden gap due to zinc ions inclusion. The increase in optical bandgap could also be related to the structural deformation in the PbS film caused due to substitutional defect as a result of the replacement of Pb^{2+} in the PbS lattice by Zn^{2+} leading to a reduction in grain size that causes an increase in energy bandgap. The decrease in semiconductor grain size accompanied by the shift of the absorption edge and increase in bandgap may also be due to quantum confinement effect [30, 37, 38]. The bandgap values (0.53–1.65 eV) obtained matches the energy bandgap for maximum absorption of solar radiation. Meanwhile, the representative SEM images of some of the thin film samples are presented in Fig. 6, and the evolution in the surface morphology of the thin films with the Zn dopant concentration is observed.

3.4 I–V characterization

The J – V characteristics of the Zn: PbS-based solar cells are studied under forward bias condition. Figure 7a shows the J – V characteristics plots of the fabricated cells (M1–M5) measured in dark at room temperature. The rectifying nature of the plots indicates the existence of a barrier between the interface of p -type Zn:PbS and n -type CdS thin films and can generally be described by any of the emission, diffusion, or recombination model from which the relation is represented by the standard diode. Meanwhile, Fig. 7b illustrates the J – V characteristics of Zn: PbS/CdS heterojunction solar cells (M1–M5) under illumination (100 mW/cm^2). The parameters derived from the J – V plots are presented in Table 3. The fabricated solar cells exhibited short-circuit current density (J_{sc}) ranging from 14.5 to 17.3 mA/cm^2 , open-circuit voltage (V_{oc}) from 340 to 390, fill factor (FF) from and conversion efficiency (η) from 1.6 to 2.7% as Zn dopant increases from 0 to 6%. However, V_{oc} , J_{sc} , FF and η decreased slightly to 16.8 mA, 380 mV, 0.39, and 2.4%, respectively, when doing increased by 8%. The lowering of the solar parameters for 8% Zn-doped PbS solar cell may be as a result of the comparative higher reflectance compare to sample 6% ZnAcet in the wavelength range 350–700 nm. Besides, from the plots of Zn doping concentration against the photovoltaic parameters shown in Fig. 8, it can be seen that the Zn dopant plays a major role in tuning the energy bandgap of PbS toward higher energies from 0.53 to 1.65 eV. Also, an increase in conversion efficiency was observed until it reached an optimum of 2.7% when the thin film solar cell stoichiometry was $\text{Zn}_{0.350}\text{Pb}_{0.436}\text{S}$ (6% ZnAcet) based on RBS analysis. This is an improvement on the conversion efficiency of the cell

Fig. 5 Bandgap energy plots of the prepared Zn: PbS thin films

Fig. 6 Representative SEM micrographs of the Zn–PbS thin films **a** 0% ZnAcet, **b** 4% ZnAcet, **c** 6% ZnAcet, and **d** 8% ZnAcet

when compared with the result of 0.82% for PbS/CdS thin film solar cell [26], 1.63% for PbS/CdS [4], 0.44% for Al: PbS/CdS [19], and 2.5% for Cd-doped PbS solar cell [20]. The efficiency of 2.7% can be associated with the Zn^{2+} dopant which provides an electronic state within the bandgap that can trap the thermal relaxation and reversed photo-generated carrier recombination, thus, prolong the life of electronically excited states.

4 Conclusion

Zn: PbS thin films solar cells were successfully prepared from the stated materials using chemical spray pyrolysis technique. The introduction of the Zn^{2+} as a dopant element in the PbS-based thin film was done to enhance the photovoltaic performance of the solar cell. The actual concentration of the dopant based on the initial mixing conditions was determined using Rutherford backscattering spectroscopy, and its influence on the structural properties was studied using XRD and SEM. The increase

in the Zn dopant concentration has effects on the morphology of the Zn–PbS thin films, and it also strongly influenced the optical and photovoltaic properties of the solar cell. An average increase in the bandgap energy from 0.53 to 1.65 eV and conversion efficiency from 1.6 to 2.7% were observed. The optimum conversion efficiency (2.7%) of the Zn–PbS thin film solar cell was achieved at the dopant concentration of 6% ($\text{Zn}_{0.350}\text{Pb}_{0.436}\text{S}$). However, the highest bandgap energy of 1.65 eV was obtained for sample 8%ZnAcet with stoichiometry $\text{Zn}_{0.523}\text{Pb}_{0.267}\text{S}$. The observed improvement in optical and photovoltaic performance is evidence that zinc dopants positively influence the properties of PbS thin films for solar cell applications. Besides, in terms of material and environmental safety concerns, the zinc component could reduce the lead concentrations in PbS-based solar cells, thereby leading to a more environmental-friendly solar cell product. Meanwhile, to further understand the losses in conversion efficiency, more studies on carrier recombination could be done in the future.

Fig. 7 J - V Characteristics of Zn: PbS thin film-based solar cell **a** dark, **b** under illumination, with the schematic representation of photovoltaic device configuration (inset)

Table 3 J - V characteristics data for Zn: PbS thin film samples

Sample code	I_{sc} (mA)	V_{oc} (mV)	FF	η (%)
0% ZnAcet	14.50	380.00	0.34	1.6
2% ZnAcet	15.60	347.72	0.35	1.9
4% ZnAcet	17.00	389.00	0.41	2.6
6% ZnAcet	17.30	390.00	0.48	2.7
8% ZnAcet	16.8	380.00	0.39	2.4

Fig. 8 Relationship between Zn concentration, bandgap, and conversion efficiency

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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