



Variation of ZnS deposition time on chemically prepared $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ternary compound from CdS/ZnS bilayers

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ABSTRACT

Chemical bath deposition (CBD) was successfully used for the preparation of cadmium zinc sulphide ($\text{Cd}_{1-x}\text{Zn}_x\text{S}$) ternary alloy thin film with x composition, in the range of 0 and 1, from post annealing treatment of bilayer cadmium sulphide (CdS)/zinc sulphide (ZnS) thin film. Increasing the ZnS layer deposition time leads to an increase in the overall thickness of the bilayer with an attendant increase in zinc ion concentration. From the XRD measurement, thin film samples presented hexagonal structure, with a shift in the peaks position to higher angles coupled with a decreasing crystalline size and lattice constants as zinc ion is continuously incorporated into the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films. The continuous addition of the wider band gap energy ZnS into the ternary compound as the ZnS deposition time increases constantly brought about the widening of the band gap energy. Energy dispersive spectroscopy (EDS) measurement established the presence of the major elements Cd, Zn and S. The room temperature electrical resistivity determined from the point probe measurement ranges between 2.1×10^{-3} and $1.2 \times 10^1 \Omega\text{m}$, and showed a decrease with increasing zinc ion contents. In this study, it was established that $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ternary compounds can be prepared starting with CdS/ZnS bilayer, and its post thermal annealing, with the band gap energy able to be accurately controlled by modifying the CdS/ZnS thickness ratio through variation of ZnS deposition time. The results from CdZnS thin film compounds prepared under this present condition established its superior effectiveness as a buffer layer in thin film solar cells.

1. Introduction

Thin film solar cell is a foremost branch in solar cell research because of its relatively cost reduction benefits (Akhand et al, 2017), with the chemical bath deposition (CBD) method been the most frequently employed technique in thin film solar cell fabrication technology (Green et al, 2018). Group II-VI binary semiconductor thin films have gained substantial attention among researchers as a result of their exceptional electrical and optical properties (Zhang et al, 2007; Chakrabarti et al, 2016).

Considering the second generation solar cells, that is established on thin films' technology, cadmium sulfide (CdS) has been the most sorted after as a buffer layer as it has given excellent results in terms of device efficiency (Green et al, 2018), because of its high electron affinity and n-type conductivity (Kariper et al, 2011; Munikrishna and Negendra Vara Prasad, 2013). It has been widely employed as a buffer material in CuInSe_2 , $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ and CdTe-based solar cells (Zakria et al, 2015).

Nonetheless, as a result of its relatively small band gap energy (2.42 eV), its applicability as buffer layer in solar cells have resulted into a significant drop in conversion efficiency because of the optical absorption in the blue region of the solar spectrum (Shin et al, 2011). Aside this, harmful nature of CdS due to the presence of cadmium content has posed a great challenge to the research community. In view of these, research efforts has recently geared at producing materials that are environmentally benign, and with buffer properties that agrees well with that of the absorber layers.

Zinc sulphide (ZnS) thin films was well-thought-out as a better substitute for CdS because of its non-toxic constituents and a wide band gap energy of 3.5–3.8 eV at room temperature (Yu et al, 2014; Balachander et al, 2015), but its large conduction band, difficulty in n-type doping and high lattice mismatch with certain absorber layers has remain a huge problem (Liu et al., 2015). These short comings have informed the use of bilayers that combines a cadmium-free layer, such as ZnS with CdS. Different solar cells such as, CdTe and CuInGaSe_2 (CIGS)

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have in the meantime been fabricated involving bilayers of CdS/ZnS as buffer layers (Ho et al., 2017). For instance, Ho et al. (2017) achieved an enhancement in CIGS based solar cell efficiency by using CdS/ZnS thin film stacked layer with 25% absolute gain over the standard CdS thin film. In this case, CdS/ZnS films stack was prepared by chemical bath method with 5 mins/10 mins deposition time configuration while the standard CdS single layer was deposited for 15 mins. The result of their work revealed that the CdS film is partly substituted by a ZnS film, resulting in a successful enhancement of the device short-circuit current density (JSC) and also justified the Cd-reduction environmental benefit.

This procedure took place in the absence of post thermal annealing of the arrangement which would have probably resulted into the formation of $Cd_{1-x}Zn_xS$ ternary compound within the structure.

An alternative approach to the foregoing has been the use of $Cd_{1-x}Zn_xS$ alloy thin films prepared by direct mixture of Cd, Zn and S precursors via chemical bath technique or by post thermal treatment of Zn/CdS or CdS/ZnS bilayers. The ionic radius of cadmium (Cd) is 0.97 Å and that of zinc (Zn) is 0.74 Å. Aside this, CdS and ZnS possess nearly similar electron affinity, equal valences and electronegativities (1.69 and 1.65 Pauling for Cd and Zn respectively) (Liu et al., 2010). Hence, zinc ions have the tendency to penetrate into CdS crystal lattice or even substitute cadmium ions. Thus, the bilayers post thermal treatment approach mentioned above will support Zn diffusion into CdS resulting in the formation of $Cd_{1-x}Zn_xS$ ternary compound (Islam et al., 2009). From literature, it was revealed that $Cd_{1-x}Zn_xS$ have a superior property of higher n-doping ability when compared to the ZnS layer (Haight et al., 2011). Additionally, it has a favourable property of its band gap energy been able to be tuned between 2.42 and 3.86 eV (Muradov, et al., 2020), by controlled addition of Zn, subject to device requirements (Ahamed Ikbail et al., 2020). The lattice constant of this compound can also be altered according to its dependence on the concentration ratio of Cd and Zn, which is associated with the composition variation of Cd and Zn in $Cd_{1-x}Zn_xS$ (Patidar et al., 2008). As a result of these, when used as a substitute for CdS in solar cells, the challenge of optical absorption losses will be tackled and this will eventually lead to an increase in the short circuit current and open circuit voltage in solar cell (Chavhan et al., 2008; Parameshwari and Naik, 2014).

Thin films deposition time has been reported to have a direct relationship with films' thickness, leading to increasing composition of the precursor's ions (Hernandez-Calderon et al., 2020). By varying the Zn concentration in $Cd_{1-x}Zn_xS$ via increased deposition times, a superior lattice parameter match and most favourable band offset can be produced (Kumar et al., 2009). The material has been successfully utilized as a buffer layer for p-n junction devices without lattice mismatch based on absorber materials such as CdTe (Oladeji et al., 2000) and Cu(In,Ga)Se₂ (Bhattacharya et al., 2006), and has produced a better performance when compared with CdS.

Experimentally, the use of buffer layer prepared using chemical bath method has produced the best conversion efficiency when compared to other methods such as physical vapour deposition in the fabrication of thin films solar cells based on CuInGaSe₂ (CIGS). This has been reported to be as a result of the enhancement in the interface chemistry between CIGS and buffer during the course of the chemical processes (Shin et al., 2011). This exceptional property has informed the growing attention in $Cd_{1-x}Zn_xS$ compound prepared by chemical bath technique. The aims of this study therefore is to ascertain the formation of $Cd_{1-x}Zn_xS$ ternary compound thin films via post thermal treatment of chemical bath deposited CdS/ZnS biayer, and investigate the effects of ZnS thin film layer deposition time on its structural, optical and electrical properties.

2. Experimental detail

2.1. Substrate cleaning

In this study, commercially available glass slide of dimension 25.4 mm × 76.2 mm × 1.2 mm was used as substrate, and since substrate

cleaning plays a significant role in thin films deposition, the substrates were subjected to detailed cleaning before thin films deposition. The cleaning was done successively in an ultrasonic bath using methanol, acetone and distilled water, each taking a period of 45 min. The pre-cleaned substrates were subsequently dried in air.

2.2. Thin films preparation

CdS and ZnS thin films were prepared using chemical bath deposition technique. The CdS bath contains an aqueous solution of 50 ml Cd(CH₃COO)₂·2H₂O (0.2 M) and 50 ml CS(NH₂)₂ (0.5 M). ZnS bath, on its part was prepared using the mixture of 50 ml ZnSO₄ (0.2 M) and 50 ml CS(NH₂)₂ (0.5 M). In both cases, ammonia (NH₃) was used as the complexing agent, and the solution baths were prepared at pH of 10.5 and a temperature of 343 K. The pre-cleaned glass substrates were vertically inserted into the baths and subsequently removed after 45 mins in order to prepare the single layer CdS and ZnS thin films. The films were thereafter rinsed with distilled water in order to remove loosed particles. In the preparation of the bilayer CdS/ZnS thin film samples, previously prepared glass/CdS thin films were used as the substrate, and were introduced into the ZnS bath for different times of 10, 15 and 20 min, in such a way as to vary the ZnS layer thickness while keeping the thickness of CdS layer constant. The prepared thin film samples were thermally annealed in air at 673 K for 1 h using Muffle furnace (model SXL), and thereafter labeled as CdS/ZnS-10, CdS/ZnS-15 and CdS/ZnS-20, for films with ZnS layer deposition times of 10, 15 and 20 min respectively.

The structural characteristics of the thin films were investigated through x-ray diffraction pattern. PANalytical multipurpose (X' Pert-Pro) was used for the measurements and it utilizes Cu Kα radiation (λ = 0.15406 nm) operating at 40 kV and 30 mA. The surface morphology and elemental composition were studied using scanning electron microscope coupled with energy dispersive X-ray (EDS) spectrometer (JEOL JSM 7600F Field emission SEM). The optical transmittance and current-voltage (I-V) measurement were carried out using Avantes-SAI-07086751 model UV-Vis spectrophotometer in the range 300 nm to 1000 nm and four probe respectively. The thickness of the films was calculated using the gravimetric technique with the masses of the films measured in two steps using a digital measuring scale.

2.2.1. CdS deposition mechanisms

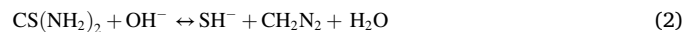
The chemical reaction processes for the deposition of glass/CdS thin film can be described by the following previously reported steps (Ouafi et al., 2018):

(i) Action of ammonia in controlling Cd²⁺ concentration:



The formation of $(CdNH_3)_4^{2+}$ averts the precipitation of $Cd(OH)_2$

(ii) Hydrolysis of thiourea in alkaline medium to produce S²⁻:



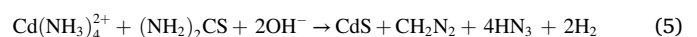
where SH⁻ ions and water are in equilibrium given rise to S²⁻ ions in accordance with this equation:



(iii) Formation of cadmium sulphide:



The general reaction of CdS formation can be written as:



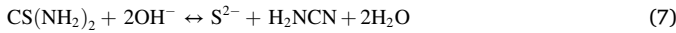
2.2.2. ZnS deposition mechanisms

The chemical reaction processes for the formation of ZnS films are listed as follows: (Martín-Varguez et al., 2013):

(i) Controlling the concentration of Zn^{2+} using ammonia:



(ii) Hydrolysis of thiourea in alkaline medium to produce S^{2-} :



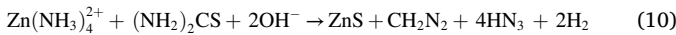
(iii) Formation of ZnS films:



As the unbound Zn^{2+} and S^{2-} surpassed the solubility product of ZnS, the precipitation of ZnS can take place either in solution or on the substrates surface:

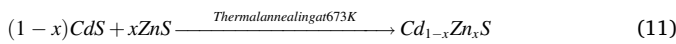


The formation of ZnS can be generally summarized as thus:



2.2.3. $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ formation mechanism

The following reaction signifies the formation of ternary $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ alloy thin films from chemically prepared glass/CdS/ZnS stacked binary layers through subsequent thermal annealing (Li et al., 2013).



3. Results and discussion

3.1. Single layer CdS and ZnS thin films

The single layer glass/CdS and glass/ZnS thin films deposited for 45 mins and annealed at 673 K are used as references, with their thicknesses being 103 and 91 nm respectively, as determined using gravimetric technique (Erken et al., 2017). The higher thickness value recorded for CdS thin film reveals a greater growth rate when compared with that of ZnS thin film, an outcome that is consistent with what was previously reported by Sadhu and Patra (2008). Fig. 1 shows the XRD spectra for the glass/CdS and glass/ZnS thin films together with the CdS reference pattern. From Fig. (1) it can be inferred that CdS film have a noticeable peak at 2θ value of 26.54° and another weak peak at 44.05° which relates to the zinc blende cubic structure of CdS. The reflections can be indexed as (111) and (220) of CdS planes respectively and corresponds well with the standard CdS JCPDS 01-075-0581 card number. The ZnS

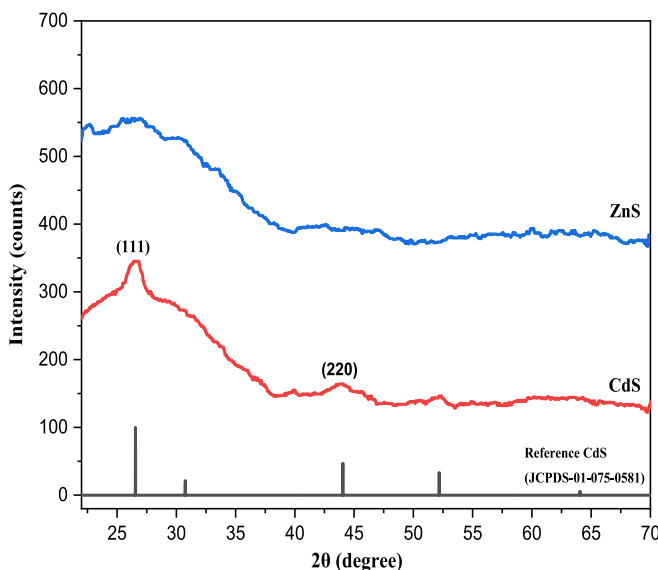


Fig. 1. XRD spectra for CdS and ZnS thin films deposited for 45 mins.

thin film spectra did not show any reflection, suggesting an amorphous structure. The lattice parameter ($a = 5.8126 \text{ \AA}$) of the CdS thin film has been determined from the relation:

$$1/d^2 = \frac{h^2 + k^2 + l^2}{a^2} \quad (12)$$

The structural parameters such as, crystallite size (D), dislocation density (δ) and microstrain (ϵ) for the single layer CdS film has been determined from the following equations (Yadav et al., 2010; Tariq et al., 2014; Taunk et al. 2015; Bashar et al. 2019):

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (13)$$

$$\delta = \frac{1}{D^2} \quad (14)$$

and

$$\epsilon = \frac{\beta \cos \theta}{4} \quad (15)$$

where h, k, l are miller indices, d is the interplanar spacing, K is a dimensionless parameter known as Scherrer constant whose value is approximately 0.94, λ is the wavelength of the X-ray used (0.15406 nm), β is the full width half maximum (FWHM) of the most intense peak (in radians) and θ is the Bragg's angle. The values of the crystallite size, dislocation density and microstrain are 11.44 nm, $7.64 \times 10^{15} \text{ lines/m}^2$ and 3.17×10^{-3} respectively. The crystallite size is almost the same as the value reported by Abza et al., 2017.

The optical transmission spectra for the single layer films are shown in Fig. 2a and b. The films exhibit maximum transmittance values of 87% and 81% in the visible region, for the CdS and ZnS films respectively. The absorption coefficient (α) for the films was determined from the transmission data using the following relation (Singh and Kumar, 2012);

$$\alpha = -\frac{1}{t} \ln \left(\frac{1}{T} \right) \quad (16)$$

where t is the thickness of the film and T is the percentage transmittance.

The optical band gap energy was determined by bearing in mind its reliance on absorption coefficient (α) and photon energy ($h\nu$), as revealed by the famous optical transition equation: (Nien and Chen, 2009).

$$\alpha h\nu = A(h\nu - E_g)^n \quad (17)$$

where A is a constant value, E_g the band gap energy and $n = 1/2$ for direct band gap energy materials.

By plotting $(\alpha h\nu)^2$ against $h\nu$ as shown in the inset of Fig. 2, the band gap energy for CdS and ZnS can be deduced as 3.45 and 3.75 eV respectively. The determined band gap energy for CdS thin film is seen to be larger than that of the bulk (2.42 eV), and this may be related to the grains dimension otherwise referred to as quantum confinement effect (Osanyinlusi and Aregbesola, 2021). This obtained value of band gap energy is very close to the one reported by Thambidurai et al. (2009) (3.56 eV), for CdS thin film prepared using spin coating technique and annealed at 450°C . In case of ZnS thin film, the band gap energy is within the value of the bulk (3.6–3.8 eV) (Yu et al, 2014).

3.2. Bilayer CdS/ZnS thin films

The bilayer CdS/ZnS thin films structure with glass/CdS layer constant deposition time of 45 mins and ZnS layers with varying deposition times of 10, 15 and 20 min were subsequently annealed in air at 673 K and labeled respectively as CdS/ZnS-10, CdS/ZnS-15 and CdS/ZnS-20. Thicknesses of the ZnS layers were determined as 17, 42 and 57 nm, resulting in overall thickness of 120, 145 and 160 nm respectively for the

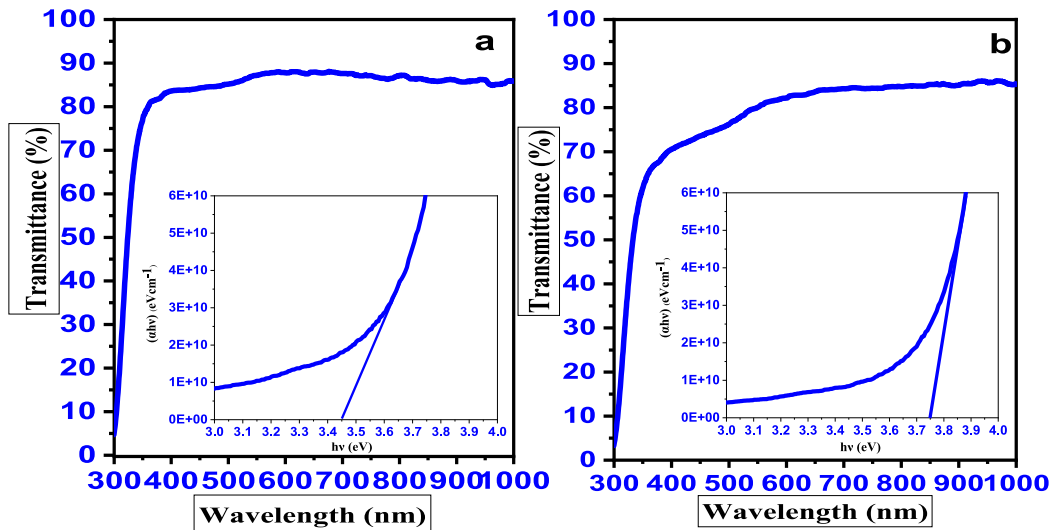


Fig. 2. Transmission spectra for (a) CdS and (b) ZnS prepared for 45 mins. Inset: corresponding plot of $(\alpha h\nu)^2$ against $h\nu$ for the annealed thin films.

bilayers.

3.2.1. Structural properties

Fig. 3 shows the X-ray diffraction pattern for CdS/ZnS-10, CdS/ZnS-15 and CdS/ZnS-20 thin film samples. The X-ray diffraction patterns of all the samples show peaks related to the (100), (002), (101), (110) and (200) reflections of the hexagonal CdZnS structure, with no evidence of phase change as the ZnS layer deposition time increases. It is observed that the interdiffusion of amorphous ZnS and cubic CdS binary thin films leads to the formation of hexagonal CdZnS ternary films through thermal annealing process. This occurrence may be attributed to the thermal-induced intermixing of the two layers and the subsequent movement of their atoms within the lattice sites. These atoms eventually assume a stable and regular hexagonal crystal structure arrangement in the process of the formation of CdZnS alloy thin film (Tripathi et al., 2006; Shah et al., 2021). It can also be ascribed to the introduction of Zn atoms into the CdS crystal thereby influencing the positions of Cd atoms

and subsequently changing the lattice structure of CdS during the formation of the $Cd_{1-x}Zn_xS$ under thermal annealing treatment (Li et al., 2013). The observed peak positions (2θ) are in good correspondence with the JCPDS-card No.49-1302 data of CdZnS as shown in Fig. 3 (Kumar and Shankarnaryanan, 2009), and closely resembles earlier reported result (Sadhu and Patra, 2008), with the preferred orientation along (002) crystal plane.

The peaks position is seen to shift to higher 2θ values as the ZnS layer deposition time increases, as it can be clearly observed in the enlarged (002) plane shown in Fig. 3. The structural parameters were respectively calculated using equations (13), 14, 15 and the lattice constants (a, c) were calculated using equations (18) (Bashar et al. 2019), and the values are presented in Table 1.

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (18)$$

The lattice constants, a and c were obtained from (110) and (002)

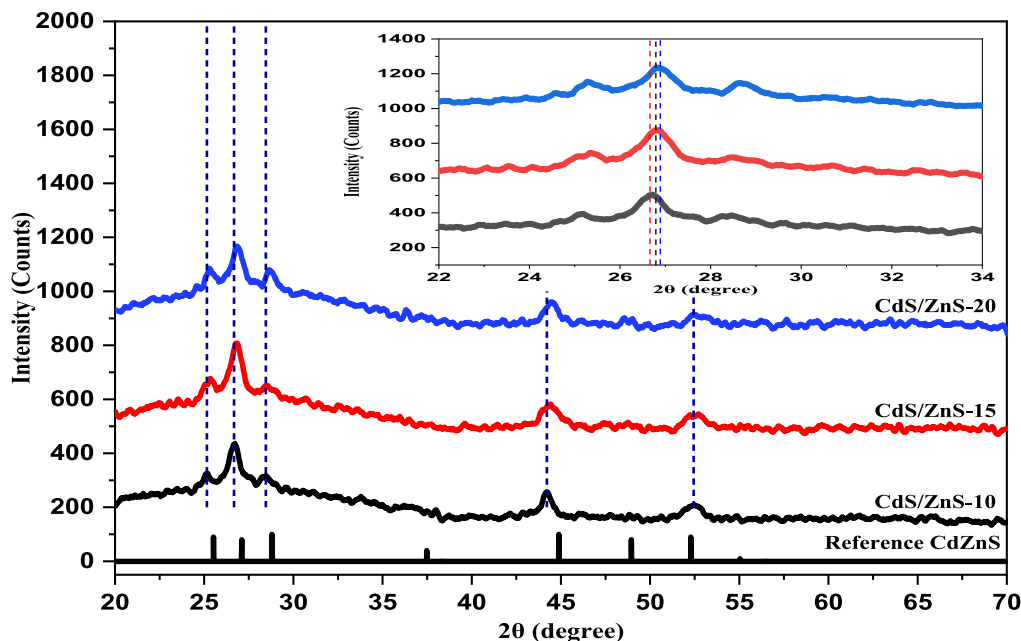


Fig. 3. XRD patterns for CdS/ZnS-10, CdS/ZnS-15 and CdS/ZnS-20 thin film samples.

Table 1

Structural parameters of CdS/ZnS-10, CdS/ZnS-15 and CdS/ZnS-20 samples, for the (002) plane.

Samples	2 θ (deg.)	FWMH (deg.)	D (nm)	$\delta \times 10^{15}$ (lines/m ²)	$\epsilon \times 10^{-3}$	d (nm)	Lattice constants a(nm)	c(nm)
CdS/ZnS-10	26.66	0.4093	19.89	2.52	1.74	0.335137	0.4098	0.6703
CdS/ZnS-15	26.79	0.4093	19.02	2.76	1.82	0.332802	0.4081	0.6656
CdS/ZnS-20	26.86	0.5117	15.92	3.95	2.18	0.331905	0.4071	0.6638

planes, respectively.

It is clear from Table 1 that increasing ZnS layer deposition time has evident effect on the crystallite size, dislocation density (δ) and micro strain (ϵ) of the prepared $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films. Increasing the ZnS deposition times was observed to bring about a decreasing trend in the crystallite size, lattice constant and interplanar spacing, as well as a progressive increase in the dislocation density and microstrain. The same reduction in the crystallite size, lattice constant and interplanar spacing has been observed for $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ compound thin films deposited by Close Space Sublimation process (CSS), using CdS and ZnS as the starting materials (Zakria et al. 2012). The noticeable reduction in the lattice constant and interplanar spacing can be attributed to the repeated introduction of more zinc ions into the CdS crystal lattice as a result of the increasing ZnS layer deposition times. In this situation, introduction of zinc ions into the CdS crystal lattice, or even the replacement of cadmium ion occurred owing to the smaller zinc ionic radius dimension (0.74 Å) as compared to that of cadmium (0.94 Å) (Liu et al. 2010). This observed result affirms the successful substitution of Cd^{2+} by Zn^{2+} and

therefore further confirm the formation of the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ films. The interplanar spacing values, $d_{(110)}$, as gotten from XRD measurement was seen to decrease from 2.049 to 2.036 Å and that of $d_{(002)}$ decreases from 3.351 to 3.319 Å, as the Zn composition increases from 0.31 to 0.70. The plot of d-spacing against Zn composition is shown in Fig. 4c, where the decrease is vastly gradual and the variation approximately linear.

Also from the result, the c/a ratio for the prepared films was evaluated, given a range of values between 1.6306 and 1.6359, which falls between that of CdS's (1.6240) and the ZnS's (1.6387) c/a ratios (Sher, 1995). This observed outcome on the c/a ratio of the prepared CdZnS film samples and its binary constituents indicate that planes of the atoms are closely stacked, which is in good agreement with the literature (Abza et al. 2018; Ahamed Ikbali et al., 2020).

Additional analysis was theoretically performed in determining the films' lattice constants using the composition dependent Vegard's relations (equations (19) and (20)), so as to get more information about the prepared ternary alloy structure. Vegard's empirical relation

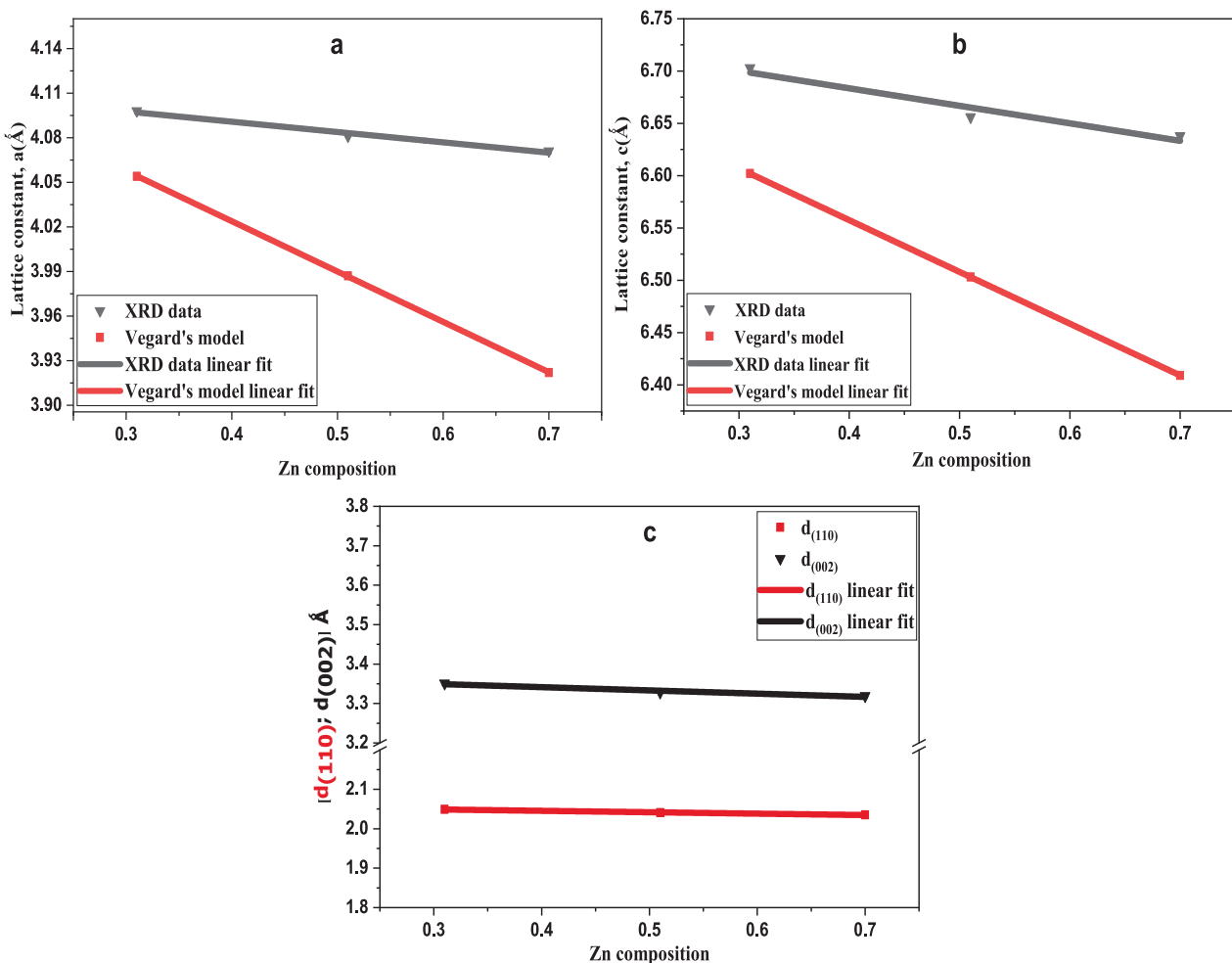


Fig. 4. Variation of the lattice constants (a) “a” and (b) “c” as a function of x in $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ calculated from XRD data and Vegard's model (c) Variation of d-spacing for (110) and (002) planes with Zn composition.

revealed that at constant temperature, a linear connection occurs between the crystal lattice constant of an alloy and the composition of its constituent elements or in the case of higher order alloys, constituent compounds (Vegard, 1921; Denton and Ashcroft, 1991; Rodriguez et al, 2016). This law is largely believed to be valid for the lattice constant variation with composition (Alam et al, 2020).

$$a_{Cd(1-x)ZnS} = (1-x)a_{CdS} + (x)a_{ZnS} \quad (19)$$

and

$$c_{Cd(1-x)ZnS} = (1-x)c_{CdS} + (x)c_{ZnS} \quad (20)$$

where $a_{Cd(1-x)ZnS}$, a_{CdS} , a_{ZnS} , $c_{Cd(1-x)ZnS}$, c_{CdS} , and c_{ZnS} are the lattice constants for the ternary alloy- $Cd_{(1-x)}Zn_xS$ and its binary constituents- CdS and ZnS . Substituting the values of the standard lattice constants for the binary constituent into the relations produce the following equations:

$$a_{Cd(1-x)ZnS} = 4.16 - 0.34x, \text{ for ``a''} \quad (21)$$

and

$$c_{Cd(1-x)ZnS} = 6.756 - 0.496x, \text{ for ``c''} \quad (22)$$

In this study the values for a_{CdS} , a_{ZnS} , c_{CdS} and c_{ZnS} used are 0.4160 nm, 0.3820 nm, 0.6756 nm and 0.6260 nm respectively. x is the zinc composition in the ternary compound as obtained from the EDS measurement (as will be seen later). It is observed from Table 2 that the theoretically calculated lattice constants are approximately the same as the values obtained from the XRD measurements (Table 1).

Fig. 4 shows the plot of the lattice constants, “a” and “c” (experimental and Vegard’s law), as a function of the composition, x . It is obvious that both lattice parameters “a” and “c” calculated from the XRD data follows the same trend of linear decrease with increasing zinc composition as the Vegard’s plot. In both cases, it can be seen that the linear fit shows an insignificant deviation from exactness when compared with the Vegard’s plot. It has been reported that in some cases perfect linear behaviour are not observed (Kings, 1966). Nevertheless, it is frequently used in practice when experimental data are not available to estimate the lattice parameter for the system of interest. Thus the linearity observed in this plot depicts a consistency with Vegard’s law, and it is an indication of a homogeneous alloy structure. Similar linear decreasing behaviour has earlier been reported by Rodriguez et al (2016) on $CdZnS$ prepared using chemical bath technique, and it is chiefly attributed to the partial replacement of Cd^{2+} ions by Zn^{2+} ions, indicating a reduction in the lattice constant “a” and “c” as zinc composition increases (Thueman and Gaewdang, 2019).

3.2.2. Morphology

The SEM images for the samples taking at x4000 magnification are presented in Fig. 5. It is observed that the film covers the substrate well except for the CdS/ZnS -15 sample (Fig. b) that shows few pinholes. Observing the CdS/ZnS -20 sample (Fig. c), it is seen that the pinholes has disappeared and clustered grains presented. As the ZnS layer deposition time increases with an attendant increase in the Zn content, the SEM images reveals that the spherically shaped grains progressively reduce in sizes. Blue shift of the optical transition is one of the possible results of the reduction in grain sizes.

Table 2
Values of lattice constants calculated using Vegard’s law.

Samples	Composition, x	Lattice constant	
		a(nm)	c(nm)
CdS/ZnS -10	0.30	0.40546	0.660224
CdS/ZnS -15	0.51	0.39866	0.650304
CdS/ZnS -20	0.70	0.39220	0.640880

3.2.3. Elemental analysis

The EDS analysis was carried out to show the percentage elemental composition of the three studied samples. The presence of the expected elements, namely cadmium, zinc and sulphur are seen in the EDS spectra. Additionally, peaks associated to Si, O, Pt, C and Sn also showed in the films and these are reflections from the glass substrate (Hossaina et al., 2013). The atomic percent of each element is shown in table 3, from where the atomic percentage for Zn increases compared to that of Cd with the increasing ZnS layer deposition times, as verified by the continuous reduction in Cd/Zn ratio. The increase in atomic percent of Zn is due to the introduction of more Zn -contents into the bilayer structure as a result of the increasing deposition times of the ZnS layer. The zinc content (x) has been determined from the atomic percent of the element as expressed by the relation:

$$Zn/(Zn + Cd) \quad (23)$$

The calculated values of x together with the resulting ternary compounds according to x composition are shown in Table 3. High value of the atomic percentage of oxygen in the prepared films may be attributed to the incorporation of O from the surrounding air during post thermal annealing (Choudapura et al., 2019).

3.2.4. Optical properties

The optical transmission spectra within the wavelength range of 300 and 1000 nm for the thin film samples are shown in Fig. 6, where the observed maximum values of transmittance in the visible region for the CdS/ZnS -10, CdS/ZnS -15 and CdS/ZnS -20 samples are 86 %, 79 % and 76 % respectively. The reduction in percentage transmission is an indication of an increasing overall bilayer thickness as the deposition time increase (Zhou et al., 2011), which can be confirmed from the thickness calculation. An increase in film thickness always result in a dense structure, which enhances surface roughness, leading to high absorption and scattering of light, and an eventual reduction in percentage transmittance (Kumar et al., 2012). Films with similar percentage transmittance will always allow significant amount of light to reach the active portion of the solar cell and thereby improve the efficiency (Obaid et al., 2013).

The optical absorption coefficient (α) for the film samples, which refers to the extent to which light of a particular wavelength can penetrate into a material before it is absorbed, is plotted against wavelength and is presented in Fig. 7 (inset). From the figure, it is observed that all the thin film samples show an absorption coefficient values in the region of 10^4 cm^{-1} within the visible region. The same region of absorption coefficient has been reported by Ahamed et al, (2020) for $Cd_{1-x}Zn_xS$ thin films prepared by direct combination of Cd , Zn and S precursors with varying Zn precursor concentration. The absorption coefficient value is seen to increase with increasing ZnS layer deposition times, and invariably with increasing Zn contents. Films having similar value of absorption coefficient are recommended as a superior buffer material since low absorption coefficient gives minimum light decay in the buffer layer. This will permit more photons to arrive at the absorber layer thereby improving the short circuit current density (J_{sc}) as well as photoconversion efficiency (Ahamed Ikbali et al., 2020).

The determination of the samples’ band gap energy is achieved by extrapolating the linear portion of the graph of $(\alpha h\nu)^2$ against $h\nu$ to the energy axis at $(\alpha h\nu)^2 = 0$ as shown in Fig. 7, and the values obtained are presented in Table 4. Ravangane and Biradar (2013) have previously reported nearly the same range of band gap energy values for $Cd_{1-x}Zn_xS$ prepared by CBD technique, with Zn composition in the range of 0.4 to 0.8. It is observed from the table that the band gap energy values of the ternary compound increase with increasing ZnS layer deposition times. Increase in $Cd_{1-x}Zn_xS$ band gap energy with increasing Zn contents has been previously reported in literature (Nagamani et al.2012), and can be attributed to band gap enlargement caused by the introduction of additional ZnS compound, with higher band gap energy, into the

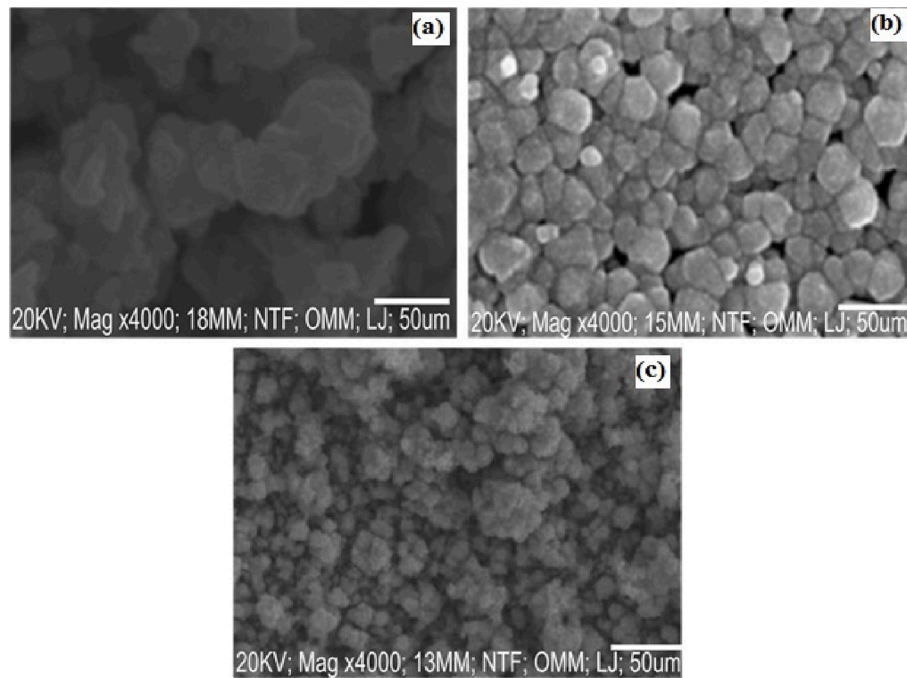


Fig. 5. SEM images for (a) CdS/ZnS-10 (b) CdS/ZnS-15 and (c) CdS/ZnS-20 thin film samples.

Table 3

EDS analysis for CdS/ZnS-10, CdS/ZnS-15 and CdS/ZnS-20 thin film samples.

	CdS/ZnS-10	CdS/ZnS-15	CdS/ZnS-20
Elements	At. (%)	At. (%)	At. (%)
Cd	26.39	26.01	12.13
Zn	11.90	26.59	28.63
S	9.83	5.43	6.82
O	48.63	36.13	32.84
Si	1.14	3.58	
Pt	1.10	0.64	
Sn	1.00	1.62	
C			19.58
Cd/Zn	2.22	0.98	0.42
Cd _{1-x} Zn _x S	Cd _{0.69} Zn _{0.31} S	Cd _{0.49} Zn _{0.51} S	Cd _{0.30} Zn _{0.70} S

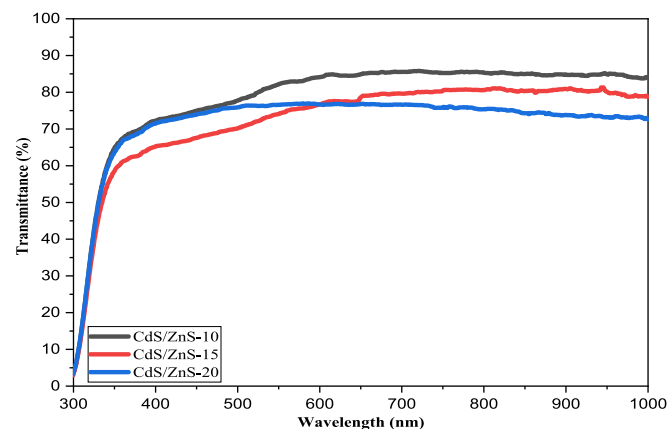


Fig. 6. Transmission and absorption spectra for CdS/ZnS-10, CdS/ZnS-15 and CdS/ZnS- 20 thin film samples.

structure as its deposition time increase. The tuning effect of the band gap energy as a result of the variation in ZnS layer deposition time and subsequent increase in Zn concentration favours Cd_{1-x}Zn_xS thin film as a better alternative for CdS and ZnS as buffer material in solar cell devices.

The variation of the band gap energies with Zn composition is shown in Fig. 8, from where a nonlinear behaviour is revealed. It is not unusual to observe a nonlinear variation of optical band gap energy with composition in alloys, as it has been observed in some classical semiconductor systems, such as AlInN and CdSe-CdTe (Berrah et al, 2008; Tit et al, 2009; Yamini et al., 2017).

A nonlinear variation of band gap energies with Zn composition has been previously reported by Azizi et al., (2016) for Cd_{1-x}Zn_xS thin films prepared by microwave radiation reaction technique. This deviation from linearity in semiconductors is due to a phenomenon known as the bowing effect, which has an associated bowing parameter that is described by a parabolic polynomial (Shi and Duan, 2008; Akhtar et al, 2011). Different alloys have their characteristic bowing parameters and it has been revealed that the bowing parameter of solid solution materials are influenced by various factors, such as solubility, electron potential, electronegativity, ionicity and crystal structure mismatch (Shi and Duan, 2008; Tit et al, 2009; Boukhris et al, 2011).

The bowing parameter in this case is determined empirically from a polynomial fitting of the band gap energy versus composition plot (Fig. 8), resulting in a quadratic expression represented in equation (23). From this equation, the bowing parameter is the coefficient of x², which is -0.33 eV, where the negative sign depicts an upward bowing or inverted nature of the parabola (Rockett, 2010). The value of the obtained bowing parameter is lower than the value reported on another Cd_{1-x}Zn_xS alloy prepared by Li et al., (2011) (b = 0.67 eV) via coevaporation technique, and very close to that prepared by Abza et al, (2018), using chemical bath technique with a bowing parameter of 0.2892 eV.

$$E_g(x) = (3.45 + 0.63x - 0.33x^2)eV \quad (24)$$

Theoretical calculation of the band gap energy E_g(x) of the Cd_{1-x}Zn_xS ternary alloy samples was additionally carried out. This is achieved by taking into cognizance its dependence on the band gap energy of its constituent compounds and zinc compositions, leading to a parabolic polynomial recognized as the Vegard's law (equation (24)) (Van Vechten and Bergstresser, 1970; Bao et al, 2016). This theoretical analysis was introduced in order to further corroborate the results of the band gap energy obtained from the plot of (αhν)² against hν. Because of

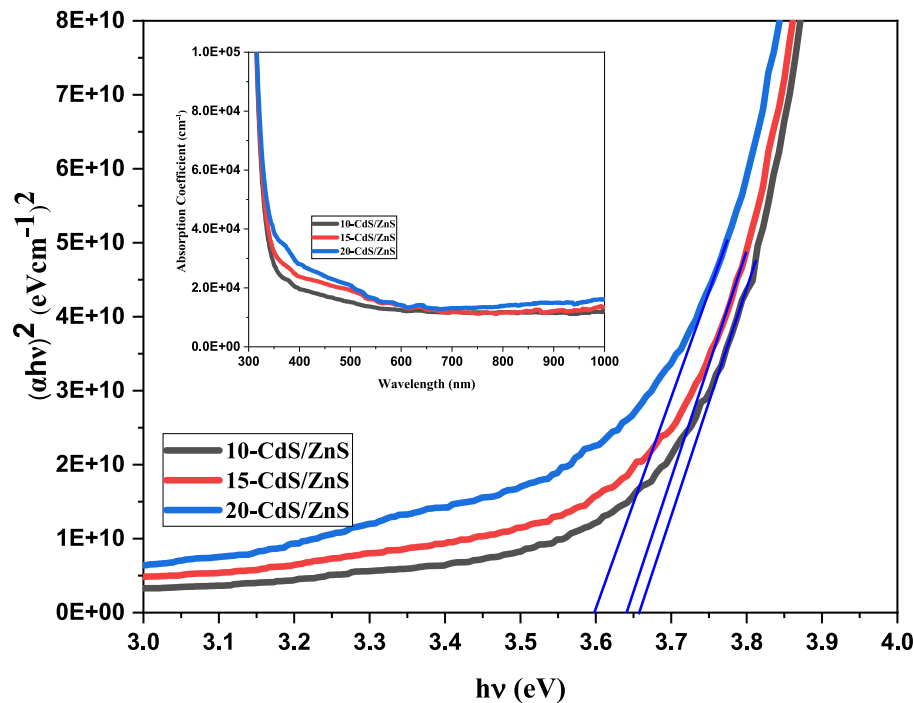


Fig. 7. Plot of $(\alpha hv)^2$ against hv for the thin film samples.

Table 4

Band gap energy values for the three thin film samples.

Samples	Composition, x in $Cd_{1-x}Zn_xS$	E_g (eV) (Vegard's Model)	E_g (eV) (Experimental result)
(Using obtained values for CdS & ZnS)			
CdS/ZnS-10	0.31	3.61	3.62
CdS/ZnS-15	0.51	3.69	3.68
CdS/ZnS-20	0.70	3.73	3.73

the usual nonlinear behaviour of the dependency, a term referred to as b (bowing parameter) which accounts for the degree of curvature, is always incorporated into the equation.

$$E_g(x) = xE_{g(ZnS)} + (1-x)E_{g(CdS)} - bx(1-x) \quad (25)$$

This equation can further be expressed in a general quadratic form as:

$$E_g(x) = E_{CdS} + (E_{g(ZnS)} - E_{g(CdS)} - b)x + bx^2 \quad (26)$$

The results of the calculated band gap energies using this equation are displayed in Table 4. Also included in the table, for comparison, are the values of the band gap energy calculated using the standard band gap energy for bulk CdS and ZnS binary constituents (2.42 eV and 3.75 eV respectively).

The table revealed that the values of the theoretically calculated and experimental band gap energies showed slight difference except for the CdS/ZnS-20 sample that are the same. This has further validated the formation of the CdZnS ternary alloy samples as well as confirming the correctness of the binary constituents' composition. The range of band gap energy values (3.6 to 3.7 eV) obtained from this study (experimental and theoretical) is observed to be narrow when compared with the range of increase of Zn composition in the alloy thin films. This outcome may be attributed to the high value of the CdS constituent (3.45 eV) obtained in this study. The band gap energy–composition plot is shown in Fig. 8, where the polynomial fit coincides exactly with that of the experimental

results. From here, it can be seen that it is possible to theoretically predict the band gap energy of a ternary alloy by knowing the constituents' band gap energy and their compositions. From the table it can be seen that the values of the band gap energy calculated using the band gap energy of the bulk binary constituents are lower than the ones gotten from this study for each Zn composition. This outcome may be connected to the unusually high value of the pure CdS band gap energy from this study, as explained earlier. The variation of the band gap energy with composition in this case is shown in Fig. 8 (inset).

3.2.5. Electrical property

The electrical resistivity of thin films is mostly significant to solar cell applications, and it is popularly known to depend strongly on the composition 'x' (Hossaina et al., 2013). The room temperature sheet resistance (R_s) and electrical resistivity (ρ) for the thin film samples are shown in Table 5. The table revealed that the sheet resistance as well as the electrical resistivity decrease with increasing ZnS layer thickness. The electrical resistivity reduction may be as a result of the attendant increase in Zn^{2+} concentration as the ZnS layer deposition time increases. Narasimman et al. (2016) reported the same outcome for CdZnS thin films prepared by doping CdS and quoted that the decrease in electrical resistivity may be attributed to the increase in the carrier concentration of the doped films due to the replacement of Cd^{2+} ions by Zn^{2+} ions. It has been revealed that films with wider band gap energy serves as a better buffer material for heterojunctions solar cells application, and an electrical resistivity value $< 10 \Omega\text{-m}$ ($< 10^2 \Omega\text{-cm}$) is commonly needed (Bakly et al., 2018).

4. Conclusion

This study presented results on the preparation of $Cd_{1-x}Zn_xS$ ternary alloy thin film (for $x = 0.31, 0.51$ and 0.70) through post thermal annealing of CdS/ZnS bilayer prepared by chemical bath deposition technique. The process has been seen as a substitute for the direct mixture of the appropriate precursors in the preparation of $Cd_xZn_{1-x}S$ using CBD method. In this case, different composition of the ternary compound having dissimilar properties can be realized in a more accurate way by altering the CdS/ZnS bilayer thickness ratio as a result of

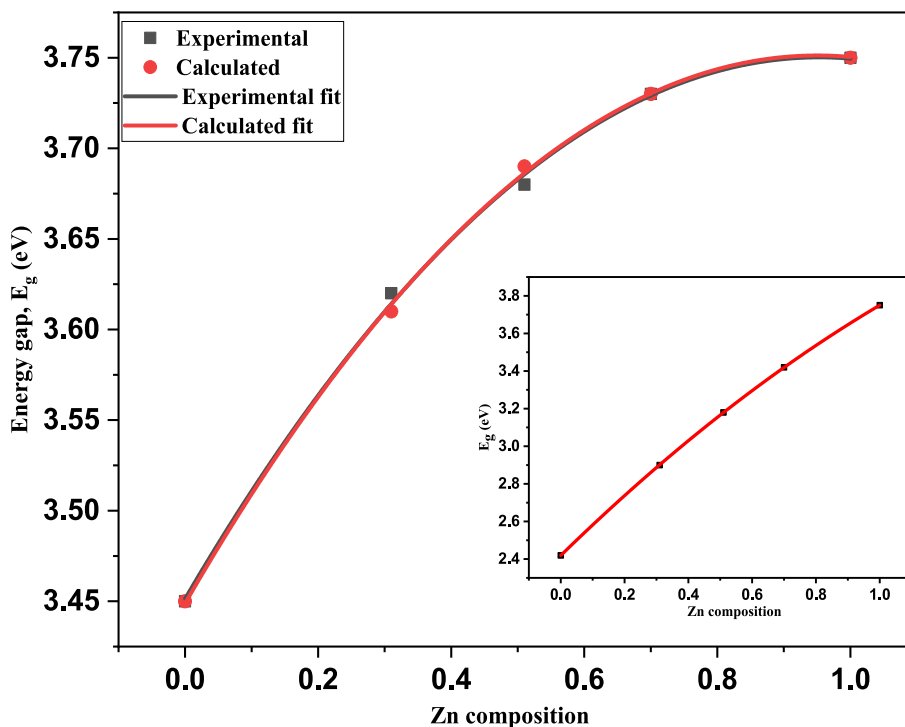


Fig. 8. Variation of band gap energy with Zn composition.

Table 5

Variation of electrical resistivity with zinc composition in the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin film.

Samples	Composition, x in $\text{Cd}_{1-x}\text{Zn}_x\text{S}$	sheet resistance R_s ($\Omega\text{m}/\text{sq}$)	resistivity ρ (Ωm)
CdS/ZnS-10	0.31	1.3×10^7	1.2×10^1
CdS/ZnS-15	0.51	2.6×10^5	3.4×10^{-2}
CdS/ZnS-20	0.70	1.8×10^4	2.1×10^{-3}

the variation in ZnS layer deposition time. The XRD spectra showed hexagonal structure with a noticeable continuous shift in the peaks position to the higher angles as the ZnS layer deposition time increases. Furthermore, lattice constant, interplanar spacing and crystallite size were observed to decrease with increasing ZnS layer deposition times as a result of the continuous introduction of Zn^{2+} with lower ionic radius into the crystal structure. The EDS spectra revealed that increasing deposition time of ZnS resulted in the introduction of more zinc content into the ternary compound structure. Reduction in the average transmission with increasing ZnS layer deposition times is also observed, which can be attributed to the increase in overall thickness of the bilayer. The band gap energy, which is within the range 3.62 and 3.73 eV continuously increase as the ZnS layer deposition time increases, and this may be as a result of the continuous inter diffusion of larger band gap energy ZnS with the lower band gap CdS. The band gap energy was also calculated theoretically using the composition dependent band gap energy as expressed by Vegard's law and the results obtained are the same with the experimental results. Four point probe measurement was used to determine the room temperature electrical resistivity with the highest value of $1.2 \times 10^1 \Omega\text{m}$ corresponding to thin film sample with zinc composition of 0.31.

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.

Data availability

Data will be made available on request.

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