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Original Article

The impact of different Al concentrations on the structural and optical characterization of ZnS Nanostructured thin films by SILAR method

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Abstract *Al:ZnS thin films were grown utilizing SILAR method. Al:ZnS films were deposited employing various molar concentration of Al fabricated using 30 and 45 deposition cycle. XRD profile offers an increment crystal size with increment in molar concentration. whilst strain(E), dislocation density (δ), and number of crystal per unit (N) changes according to concentration. FESEM images shows porus nature of thin films. Energy dispersive x-ray spectroscopy (EDAX) confirm the presence of Zn, Al, S within binding energy range of 0 to 10 keV. The optical properties were studied by transmission spectra where found that for Al:ZnS films have high transmittance in visible area. The bandgap was found approximately 3.2 eV for Al:ZnS . These finding highlight the potential of Al doped ZnS thin films for Optoelectronic application, Solar Cell applications*

Keyword- *SILAR, XRD, FESEM, EDAX, UV-VIS, Al:ZnS thin films*

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Introduction

ZnS is II-VI semiconductor [1-4] Zinc Sulphide (ZnS) as nanoparticles materials was effectively used as significant materials for the application in photovoltaic devices [5]. The ZnS is non-toxic, plenty, environmentally friendly and chemically stable natural material [6]. On the other hand, ZnS semiconductor material appearance in two compound types of crystalline namely wurtzite in a high temperature and cubic zinc-blend (sphalerite) in a low temperature [7, 8]. In adding up, ZnS material displays a large bandgap in the immediacy of (3.54-3.91 eV) for the zinc blend and the wurtzite respectively [9, 10]. Furthermore, the physical properties of ZnS can be tainted by dopant concentration [10-12]. ZnS doped with impurities are the most significant process and thus exhibit different properties. Elements like, gallium (Ga), aluminum (Al), chromium (Cr), boron (B), fluorine (F), Indium (In), copper (Cu), manganese (Mn) and chlorine (Cl) with a variety of doping levels can be functional to tailored properties of ZnS [13-17]. Among these impurities, aluminum doped ZnS exhibits the excellent properties [18, 19]. As such, it is inevitability to study the characteristics of ZnS nanomaterials under Al dopant concentration. Irrespective, the literature offers limited research focusing on the effects of under Al dopant concentration on the properties of ZnS nanomaterials deposited onto glass substrate. The several techniques used to prepare ZnS thin films, which offer them a diversity of appealing physical properties. These techniques include: electron beam deposition, sputtering, sol-gel, thermal evaporation, pulsed laser deposition and chemical bath deposition [18, 20-26]. In this work we focus on the effect of concentration and number of cycle's variation on the structural, surface morphological and optical properties of Al doped ZnS thin films.

Experimental

Aluminium doped Zinc Sulphide thin Films were done with zinc sulphate using SILAR method. The number of deposition cycles for ZnS and Al was adjusted to obtain various compositions of Al:ZnS thin films were prepared by using SILAR method at room temperature. A commercial glass substrate (75 mm × 25 mm × 1 mm) is considered to deposit ZnS film. Prior to deposition, the substrate was degreased in ethanol for 10 min, followed by ultrasonic cleaning with doubly distilled water for another 10 min, rinsed in deionized water and finally air dried in. To obtained Al doped ZnS thin film, 0.2 M and 0.4 M aluminium chloride ($AlCl_2$, $2H_2O$) was added in proper ratio with the solution. Zinc sulphate and aluminium chloride were dissolved in deionized water to prepare solutions. (cationic precursor). Aqueous solution of sodium sulphide (Na_2S) was the anionic precursor.

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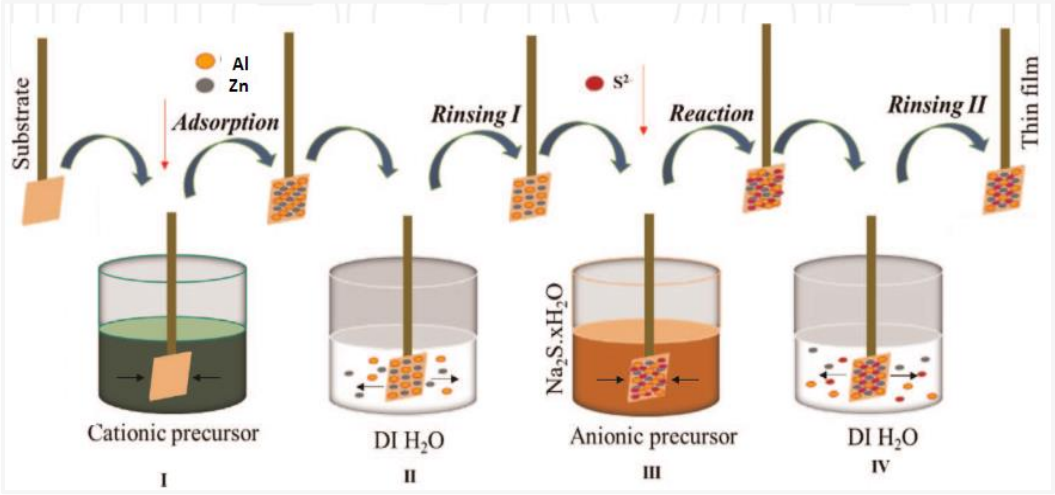

Fig. 1: Schematic representation of mechanism behind SILAR

The term 'adsorption' relates to cohesive or Vander walls forces between the ions in the solution and surface of the substrate, which help to hold the atom on the surface of the substrate. The adsorption phase results into the layer of positively and negatively charged cations also known as Helmholtz electric double layer. The rinsing allows the removal of loosely bonded atoms from the surface after adsorption process.

In reaction stage, the anionic precursor solution introduces the anion on the cationic layer and then again rinsing is performed to remove the loosely bonded anionic atoms on the surface. The process completes one cycle. The numbers of cycles are performed to form the layer of desired thickness.

Result and discussion

XRD Analysis

Fig. 2 shows the XRD pattern of Al: ZnS thin film prepared at substrate temperature of 303K with different dopant concentrations and dipping cycles, the XRD spectra were recorded with scanning angle ranging from $10^0 - 80^0$. Crystallographic, micro structural properties of Al:ZnS thin film on glass substrate have been studied in a coordinated manner within the thin films of different aluminium concentrations of 0.2 M and 0.4 M for 30 cycles and 45 cycles . XRD line profile, cross sectional microstructure and pole figures from orientation distribution analysis concurrently indicated a growth of Al:ZnS on glass substrate with its cubic (zinc blende) crystal structure and it was found to be polycrystalline structure. The 2θ peak observed at 29.2^0, $47.5^0$$57.1^0$exhibit the formation of the cubic zinc blende phase of Al:ZnS which correspond to the (111)(220) (311) planes of reflections. It was observed that the grain size increases as the concentration of the film deposited increases. A shift in the peak positions was noticed with the increase of doping concentration. This is mainly due to the smaller atomic radius of Al^{3+}ion (0.54 A) compared toZn^{2+}ion (0.74 A), resulting in the development of strain in the films The observed d-values and lattice parameter are in good agreement with the standard values for the cubic zinc blend structure. Lattice parameters: The lattice parameters would be slightly modified due to the doping of aluminum ions (Al^{3+}) into the ZnS lattice.

The average grain size is evaluated by well known Scherrer's formula and found to be 80 nm – 120.4 nm.

$$D = \frac{0.94\,\lambda}{\beta\, cos\, cos\, \theta} \ldots\ldots (1)$$

Where, λ the wavelength of X-ray used (λ = 1.54060Å), β is full width at half maxima (29.2^0).

The lattice parameters a in the prepared thin films have been determined as a = 3.10 Å respectively and are in good agreement with the values listed by the American society for testing materials (ASTM).

The average dislocation density was found to be 0.1562 $X10^{14}$ lines/m^2 calculated by:

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

The number of crystallites per unit area (N) and the strain (ε) of the films were determined by following relations:

$$N = \frac{t}{D^3} \quad \ldots (3)$$

$$\varepsilon = \frac{\beta\, cos\, cos\, \theta}{4} \quad \ldots (4)$$

Where, t is the thickness of the film. The calculated structural parameters are N = 0.2343 X 10^{14},ε = 0.0324 $lines^{-2}m^{-4}$. The small values of δ obtained in the present study confirm the good crystalline of thin films fabricated by the SILAR technique.

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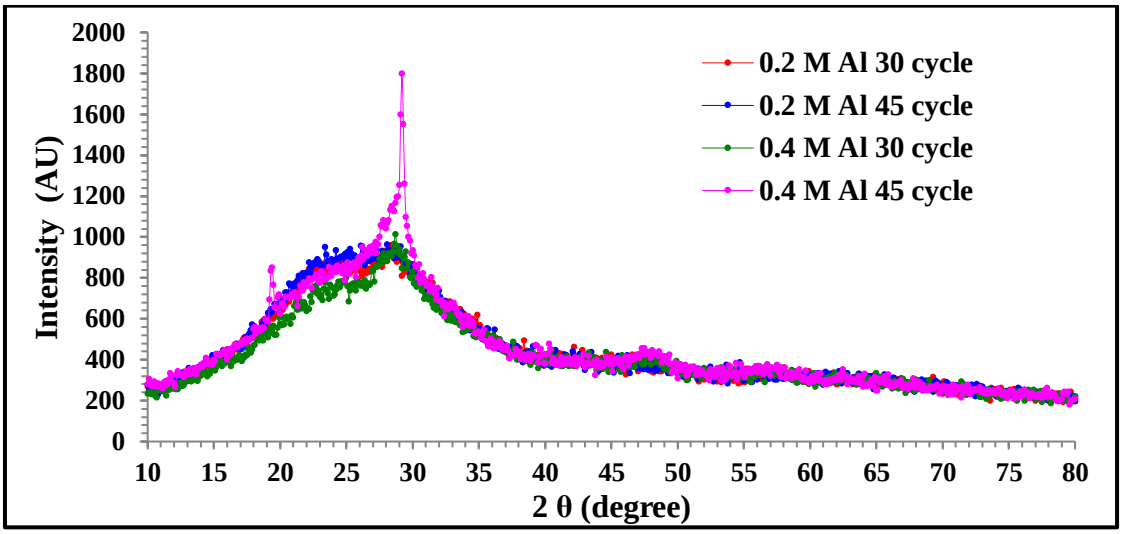


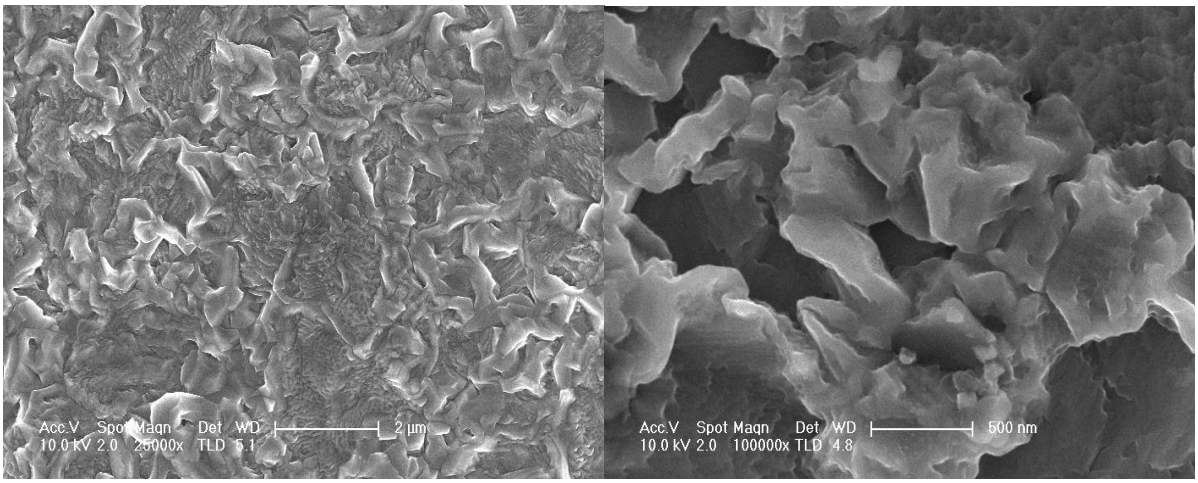
Figure 2: X-ray diffractograms of Al:ZnS thin films

Table 1: Crystalline Parameters of the Al:ZnS Thin Films

Parameter	
Crystal Size (D)	80 – 120.4 nm
Dislocation Density (δ) lines/m²	0.1562 X10¹⁴
Number of Crystals Per Unit (N)	0.2343 X 10¹⁴
Micro Strain (E)	0.0324

FESEM Studies

Figure 3 (a, b, c) shows FESEM images of Al:ZnS thin film with various magnifications 25K, 100K and 200K for 0.2 M Al concentration 30 cycles. FESEM results showed that the sizes of grain were in the nanometric range. The grain size of the Al:ZnS films is observed to be 160 nm. From FESEM results particle particles are uniformly deposited. The micrograph shows spores nature of material. According to the surface morphology, it could be seen that the thin films had porous surface.



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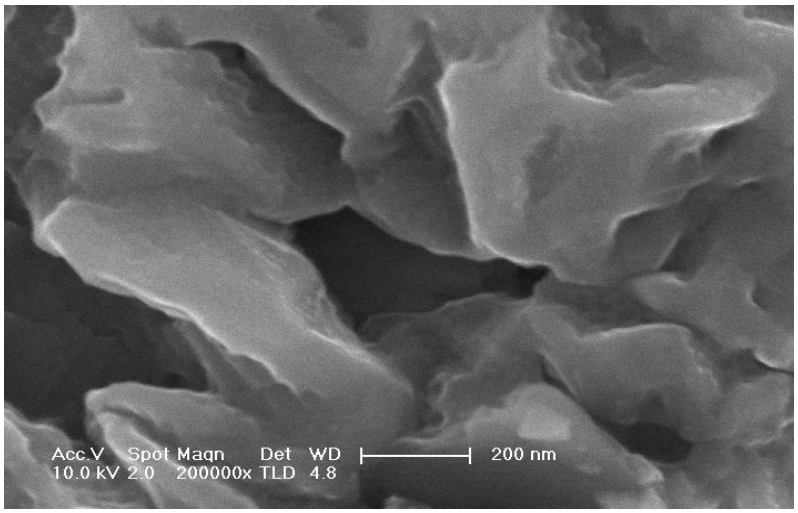

Fig. 3 (a - c): FESEM image of Al:ZnS (0.2 M, 30 cycles) thin film

Figure 4 (a, b, c) shows FESEM images of Al:ZnS thin film with various magnifications 25K, 100K and 200K for 0.4 M Al concentration 30 cycles. FESEM results showed that the sizes of grain were in the nanometric range. The grain size of the Al:ZnS films is observed to be 80-140 nm. From FESEM results particle of different sizes were uniformly distributed over the surface. The micrograph shows porous nature of material. According to the surface morphology, it could be seen that the thin films had porous surface.

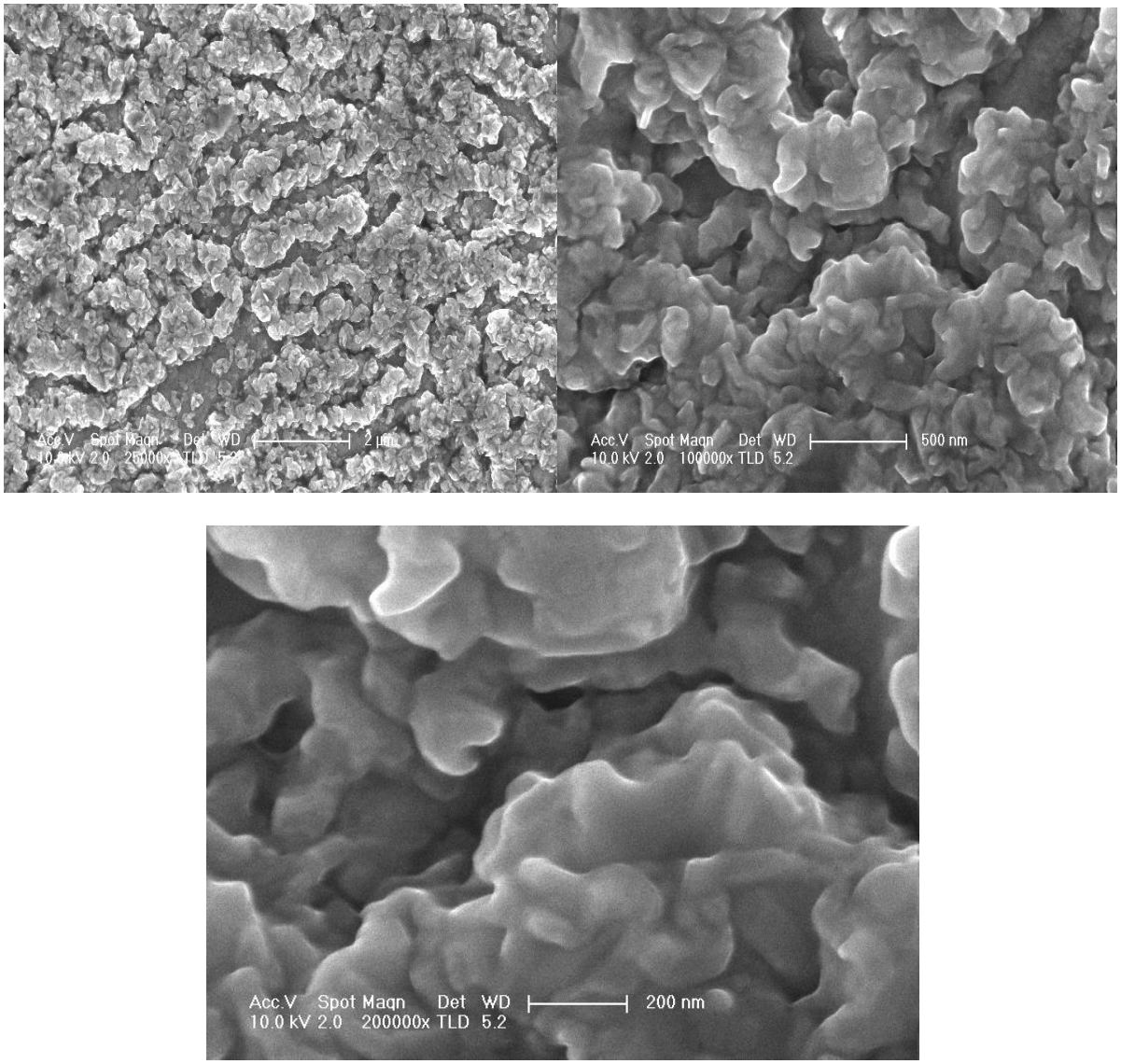

Fig. 4(a - c): FESEM image of Al:ZnS (0.4 M, 30 cycles) thin film

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EDAX

The elemental analysis of Zn, Al and S has been carried out by EDAX in the binding energy region between 0 to 10 KeV shown in Figure – 5 (a, b) This spectra shows the excepted elements detected. The spectrum peak reveals presence of Zn, Al and Sat 0.4, 3.6, 1.6 and 11.2 KeV which confirms the presence of Zn, Al and S. Also there was no evidence for the appreciable amounts of impurities. The atomic percentage of Zn, Al and S were found to be 24.39%, 2.81 % and 72.80 % respectively.

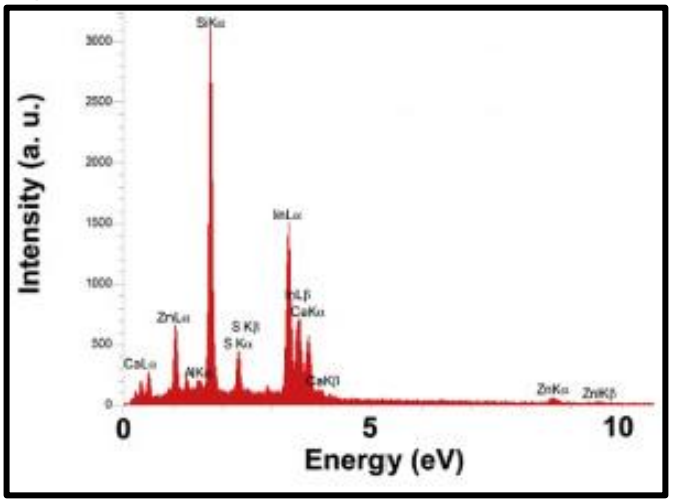

Fig 5 (a)

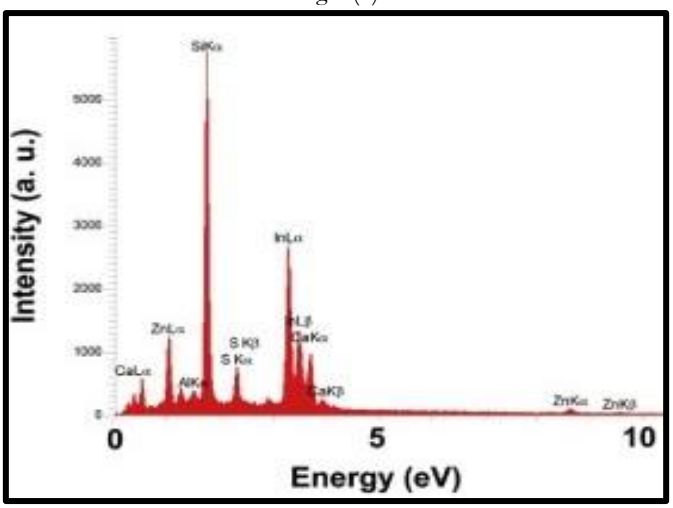

Fig 5 (b)

Fig. 5 (a, b): EDAX spectrums of Al:ZnS

UV – VIS Spectroscopy

The optical absorption spectra were obtained in the 300 nm – 1100 nm wavelength range by employing a Shimadzu 2450 UV-Visible model of the spectrophotometer. The spectra displayed in Fig. 6 shows the absorbance spectra. The estimated band gap values were obtained as 3.2 eV for Al:ZnS. Hence the Al:ZnS can be used in development of efficient photovoltaic application.

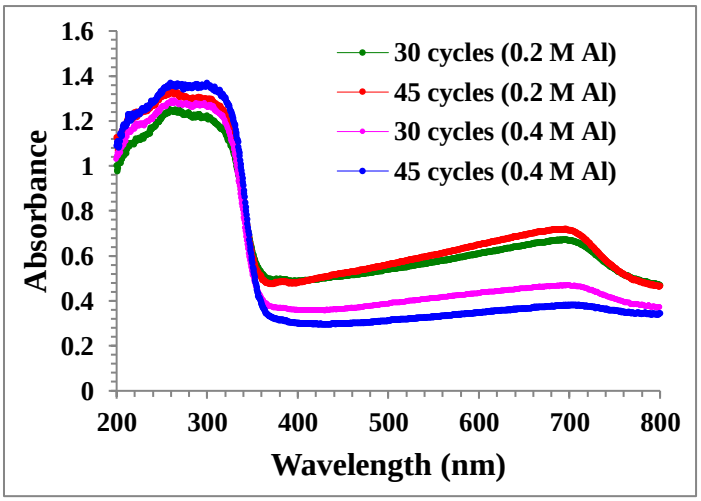

Fig. 6: Absorbance Spectra of Al:ZnS Thin Film

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Conclusion

Al:ZnS thin film was grown utilising by SILAR method. From the X-ray diffraction analysis indicated a growth of Al:ZnS on glass substrate with its cubic crystal structure the grain size increases as the concentration of the film deposited increases. FESEM shows that particles are uniformly deposited and thin films has porous surface. The estimated band gap value obtained as 3.2 eV for Al:ZnS For above conclusion Al:ZnS can be used in development of Optoelectronics, Photovoltaic and Solar Cell applications.

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Conflicts of interest

The authors declare that there are no conflicts of interest regarding the publication of thesis paper.

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