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Effects of Annealing Temperature on the Dual Solution Synthesis and Optical Characterization of AlS: ZnS Thin Films

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Abstract: SnS: ZnS alloyed thin films were successfully deposited on glass substrates using two solutions-based methods: SOLUTION GROWTH and technique at room temperature. Aluminium sulphate ($AlSO_4.7H_20$) was the source of Al, Zinc sulphate ($ZnSO_4.7H_20$) was the source of Zn, sodium thiosulphate ($Na_2S_2S0_3$) served as the source of S. Ethylene DiamineTetraacetic Acid (EDTA) was used as the complexing agent. The effect of variations in annealing temperature was studied. The optical and solid state properties of the film like Reflectance (R), Absorbance(A), Transmittance (T), Refractive Index (n), Extinction Coefficient (K), Refractive index (n), Absorbance Spectra (A), and Transmittance Spectra T (%) were determined. These properties make AlS suitable for solar cell fabrication, and architectural design to reduce exposure to skin cancer, cataracts and impaired immune system due to UV rays. The band gap of the film suggested that the material is a semiconducting thin film. In recommendation, this material has high transmittance and is capable of absorbing UV rays, urgent development of this technology is recommended to lenses and mirror manufacturers.

Keywords: ***Annealing, temperature, alloy, thin films, als:zns, characterization***

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1.0 Introduction

The energy band gap of semiconductors is the most distinct property of semiconductors from insulators and metals. It determines wavelengths of light that can be absorbed or emitted by the semiconductors (Bahaman and Saroja, 2016; Eddy *et al*., 2022, 2024). The iconicity becomes even larger and more important in the II-VI compounds such as ZnS. As a result, most of the II-VI compound semiconductors have band gaps larger than 1 eV. The exceptions are compounds containing the heavy element mercury (Hg). Mercury Telluride (HgTe) is a zero band gap semiconductor (or a semi-metal) similar to grey tin (Berger, 2017). While the large band gap II-VI compound semiconductors have potential applications for displays and lasers, the smaller band gap II-VI semiconductors are important materials for the fabrication of infrared detectors (Dissanayaka and Samarasekara, 2018).

Recently, there have been many advances enabled by thin film deposition techniques in a wide range of technological applications: laser diodes, solar cells, electroluminescent displays etc. The main advantages of using ZnS, include thin film coating in the optical and microelectronic industries ii) ZnS reduces engenders toxicity to our environment when compared with CdS because of its high toxicity, and iii) the use of the wide band gap material ZnS (3.7 eV) as a buffer layer could decrease the window absorption losses and improve the short-circuit current of the cells and can be replaced by CdS (2.4 eV) thereby increasing the current generated (Kumar *et al.,* 2016a). To obtain its full behaviour of conductivity, the electrical resistivity needs to be reduced since un-doped ZnS films have very high electrical resistivity (typically 107 Ωcm). This is possible by doping these layers with suitable impurity atoms without affecting the optical properties of the layers too much (Eid *et al.*,2010).

Aluminium sulphide (AlS) has a wurtzite-like crystal structure, existing in several forms. The thin films of aluminium sulphide can be used in optoelectronic industries solar cell production and other applications in electronic industries (Hossain *et al.,* 2019). Aluminium sulphides are versatile materials that can exhibit exceptional electrical, optical, and structural properties, aluminium sulphides have been incorporated into a broad range of devices; including, heterogeneous catalysts, energy conversion and energy storage devices, transistors, photodetectors, and gas sensors.

Zinc sulphide (ZnS) is one of the direct–VI semiconductor compounds with a large band gap energy of ~3.65 eV at room temperature. The material crystallizes in both cubic and hexagonal forms and is a material of reference to test several theoretical models in condensed matter physics (Altaf, 2015). The material has huge potential applications in both bulk and thin film forms in various photovoltaic and optoelectronic devices (Elidriss*et al.,* 2019). It is used as the key material for solar control coating, optoelectronic devices, electroluminescence devices, sensors and others.

ZnS thin film is mostly suitable as a window layer in heterojunction photovoltaic solar cells; because the wide band gap reduces the window absorption losses and improves the short circuit current of the cell (Kumar *et al.,* 2015). Research has shown that ZnS is transparent to visible light and opaque to ultraviolet radiation and near-infrared radiation (Osiele in Oluwatoyin, 2020). ZnS materials could also be used in radio frequency field-spattered films such as CdZnS and modified ZnS/CdS (Oladejiand Chow in Oluwatoyin, 2020). Different techniques have been used to fabricate ZnS thin films, like sputtering (Shao *et al.*in Oluwatoyin, 2020), molecular beam epitaxy (Kavanagh and Cameron 2011), spray pyrolysis (Elidrissi*et al.,* 2015), successive ionic layer adsorption and reaction technique (Nicolau in Oluwatoyin, 2020), pulsed-laser deposition (Yano *et al.* in Oluwatoyin, 2020), chemical bath deposition (Fukarova-Juruskovska *et al.* in Oluwatoyin, 2020), chemical vapour deposition (Kashani in Oluwatoyin, 2020), liquid phase atomic layer expitaxy (Lindroos*et al.* in Oluwatoyin, 2020) and spin coating (Kumar *et al.,* 2015). Among these, the spin coating technique is an attractive method for thin film deposition for various reasons: it is less hazardous, less costly, progressively more uniform as it thins, fast operating system and is therefore capable of easy scaling up. Additionally, the growth of the films occurs at a relatively low temperature, compatible with flexible organic substrates. As such, there is no need for the use of metal catalysts, and thus it can be integrated with well-developed silicon technologies. Also, there are varieties of parameters (spin speed, time of spin, acceleration, fume exhaust, etc.) that can be adjusted to effectively control the morphologies and properties of the final product (Tyona, 2013). In this study, Al-doped ZnS films have been deposited by a simple chemical bath deposition (CBD) method. This method has been successfully used to deposit a variety of metal chalcogenides and oxides as this method is expected to dope the films uniformly. However, this study aims to understand the effects of annealing temperature on the growth and characterization of AlS: ZnS thin films.

2.0 Materials and Methods

2.1 Preparation of AlS: ZnS alloy thin films

2.1.1 Substrate preparation

The substrates (glass slides) were degreased in HCL for two hours, washed in cold water with detergent and then rinsed with distilled water and allowed to drip dry in air. The degreased cleansed surface has the advantage of providing nucleation centres for the growth of the films, hence yielding adhesives and uniformly deposited films (Ezema et al., 2017).

2.1.2 Deposition of sulphide alloy thin films using dual solution synthesis (SGT AND SIMILAR)

In this research work, compounds were deposited using solution growth and the SILAR technique. Aluminium sulphide alloy thin films (AlS, ZnS) were deposited using SILAR after which it is dipped into a bath of ZnS prepared by solution growth technique respectively. In the end, there were four basic deposited thin films using the two techniques with variations in annealing temperature.

2.2 Characterization of deposited thin films

The XRD analysis was carried out using an X-ray diffractometer modelled GBC Enhanced Mini Material Analyzer (EMMA), The XRD pattern gives information relative to the nature and structure of the alloyed thin films of CuS: ZnS. The crystallite sizes given in Table 1 are obtained using Debye-Scherer's equation expressed as equation 1 (Onwuemeka and Ekpunobi, 2018; Osuwa and Anusionwu, 2011; Offiah*et al.*, 2012; Nwaokorongwu*et al.*, 2018).

$$D = k\lambda\beta cos\theta \qquad (1)$$

where k is the shape factor (k=0.9), D is the grain size or average crystallite size, λ is the wavelength of Cukα radiation used (λ =1.54A≡0.154nm), β is the experimentally observed diffraction peak with width at half maximum intensity (Full Width at Half Maximum FWHM) and θ is the Bragg's diffraction angle. The microstructure of the thin films of SnS: ZnS were determined using a surface electron microscope. The elemental compositions and thicknesses of the samples were determined using Rutherford backscattering spectroscopy (RBS).

3.0 Results and Discussion

3.1 Spectral and solid state properties of AlS: ZnSThin Films

The variations in absorbance/transmittance and reflectance for varying annealing temperatures at normal incidence wavelength ranges between 350nm - 700nm of the films were obtained. The thickness of the films was obtained. Table 4.1 below shows the identification of samples of AlS: ZnSthin films with variations in annealing temperature. The plot of the solid-state properties including, energy band gap, extinction coefficient, refractive index, absorbance spectra, transmittance spectra and reflectance spectra against their corresponding photon energies are shown in Fig.s 1- 7. As contained in Table 4.2, there are variations in the solid state properties of the chemical bath deposited glass/AlS: ZnS for different annealing temperatures. The result shows that the annealing temperature has a significant effect on the transmittance of chemical bath deposited AlS: ZnS thin film.

Table 1: Identification of samples ofAlS: ZnS thin films with variations in annealing temperature

Bath sample	Annealing temperature (K)
R0	As grown sample
R2	373
R3	423
R4	532
R5	473

3.1.1 Spectral absorbance

Fig.1 shows the spectral absorbance value of chemical bath deposited AlS: ZnS thin films deposited and annealed at different temperatures of 373K, 423K, 532 and 473K. The as-grown sample was used as a reference for annealing temperature. The spectral absorbance of sample R2 annealed at 373K showed a maximum value of about 0.8, sample R3 annealed at 423K showed a maximum value of about 0.7, sample R4 annealed at 523K showed a maximum value of about 0.1, R5 annealed at 473 showed the maximum of 0.32, while the as-grown sample R0 showed 0.38 all corresponding to the wavelength of range of 350nm - 700nm in the UV-VIS region of the electromagnetic spectrum. The result shows that the annealing temperature has a significant effect on the absorbance of the chemical bath deposited AlS:ZnS thin film. This makes them useful for window coating for those living in hot climates like Nigeria in the sense that the radiation will be absorbed by such films and the inside is kept cool.

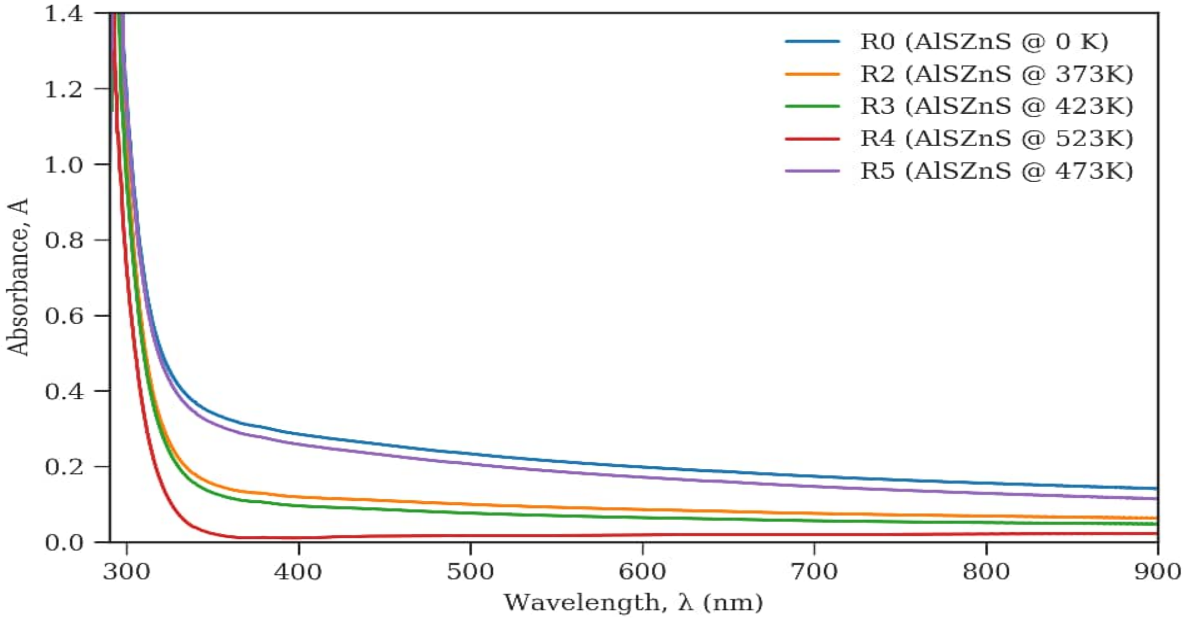

Fig. 1: Absorbance spectra of AlS: ZnS thin film annealed at different temperatures

3.1.2 Spectral transmittance

Fig. 2 shows the spectral transmittance value of chemical bath deposited AlS: ZnS thin films deposited and annealed at different temperatures of 373, 423, 532 and 473 K. The as-grown sample was used as a reference for annealing; temperature. The spectral transmittance of sample R2 annealed at 373K showed a maximum value of about 70.0%, sample R3 annealed at 423K showed a maximum value of about 72.0% of sample R4 annealed at 532K showed a maximum value of about 98.0% R5 annealed at 473 showed the maximum value of 48.0%, while the as-grown sample R0 showed 44.0% all corresponding to the wavelength of range of 350nm - 700nm in the UV- VIS region of the electromagnetic spectrum. The result shows that the annealing temperature has a significant effect on the transmittance of chemical bath deposited AlS: ZnS thin film. The transmittance showed that the films annealed, have greater transmittance in the region studied. The transmittance properties exhibited make the film good material for screening of the UV portion of the electromagnetic spectrum which is dangerous to human health and as well harmful to domestic animals. The film can be used for coating eyeglasses for protection from sunburn caused by UV radiation(Asogwa, 2010).

Fig.3 shows the reflectance value of chemical bath deposited AlS: ZnS thin films deposited and annealed at different temperatures of 373K, 423K, 532K and 473K. The as-grown sample was used as a reference for annealing; temperature. The spectral transmittance of sample R2 annealed at 373K showed a maximum value of about 3.82%, sample R3 annealed at 423 K showed a maximum value of about 1.30% of sample R4 annealed at 532K showed a maximum value of about 1.29% R5 annealed at 473 showed a maximum value of 1.25%, while the as-grown sample R0 showed 3.81% all corresponding to the wavelength of range of 350nm - 700nm in the UV- VIS region of the electromagnetic spectrum. The result shows that the annealing temperature has a significant effect on the transmittance of chemical bath deposited AlS: ZnS thin film.

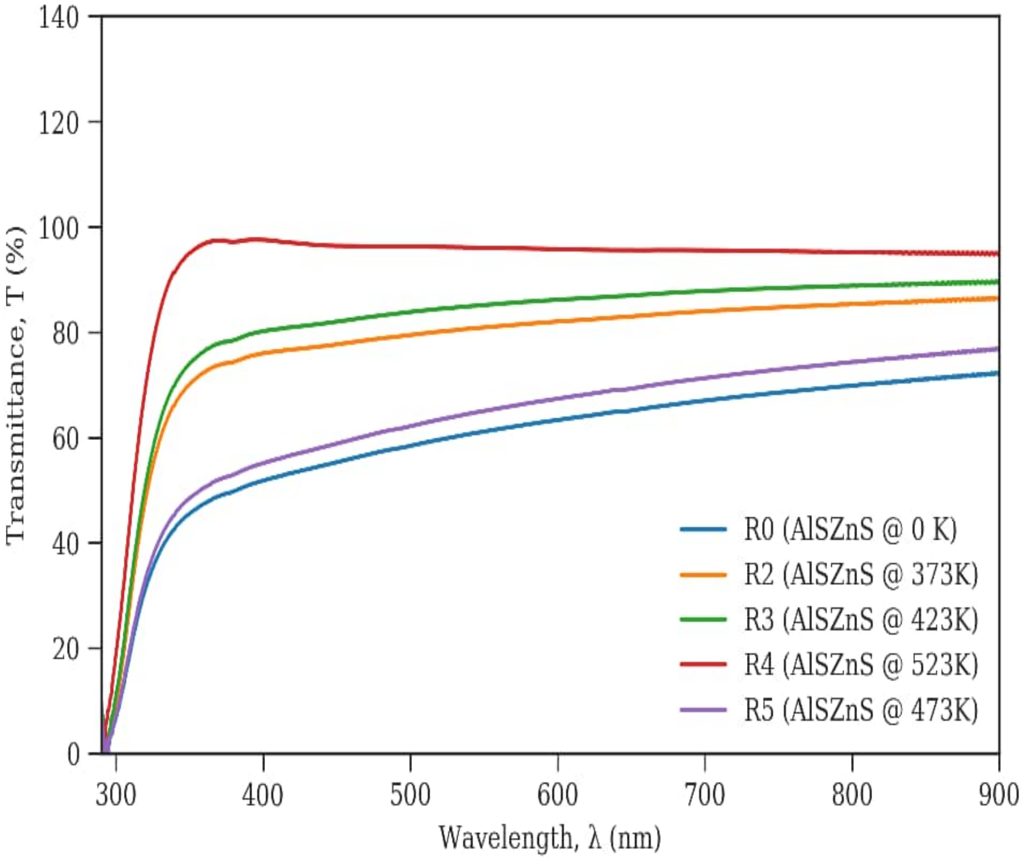

Fig.2: Transmittance spectra of AlS: ZnS thin film annealed at different temperatures.

3.1.3 The Reflectance (R)

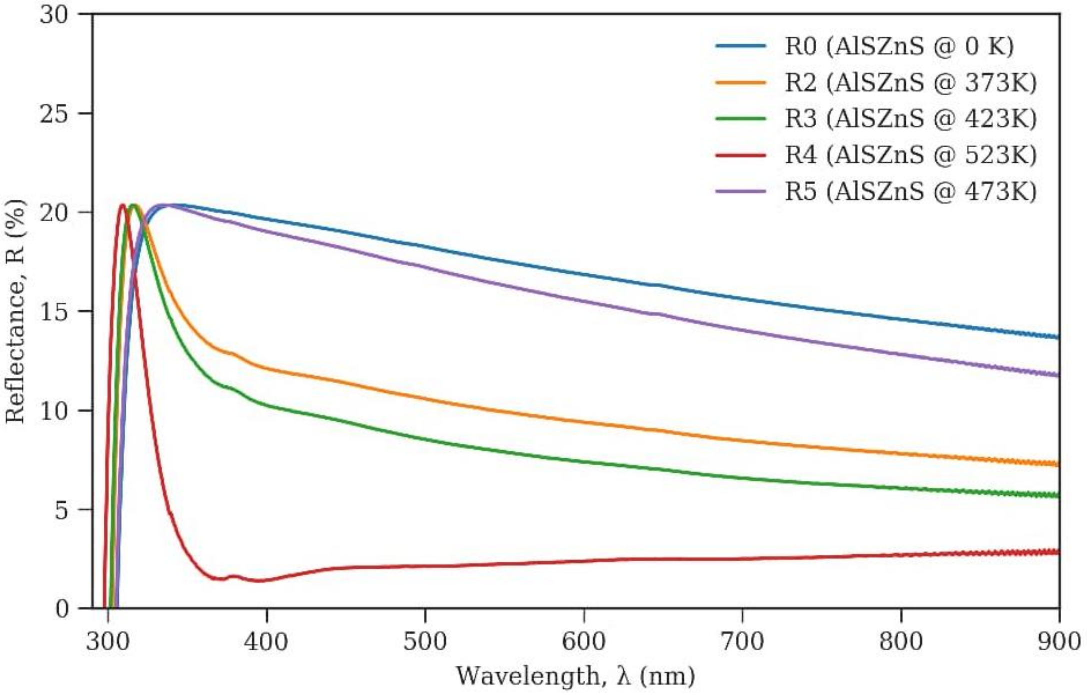

Fig. 3: Reflectance spectra of AlS: ZnS thin film annealed at different temperatures

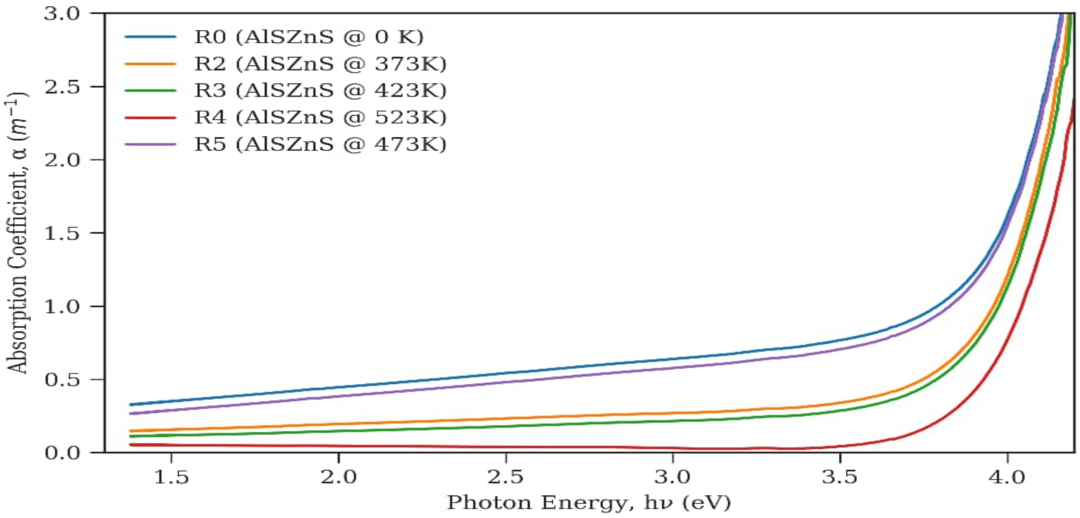

Fig.4: Absorption coefficient spectra of AlS: ZnS thin film annealed at different temperatures

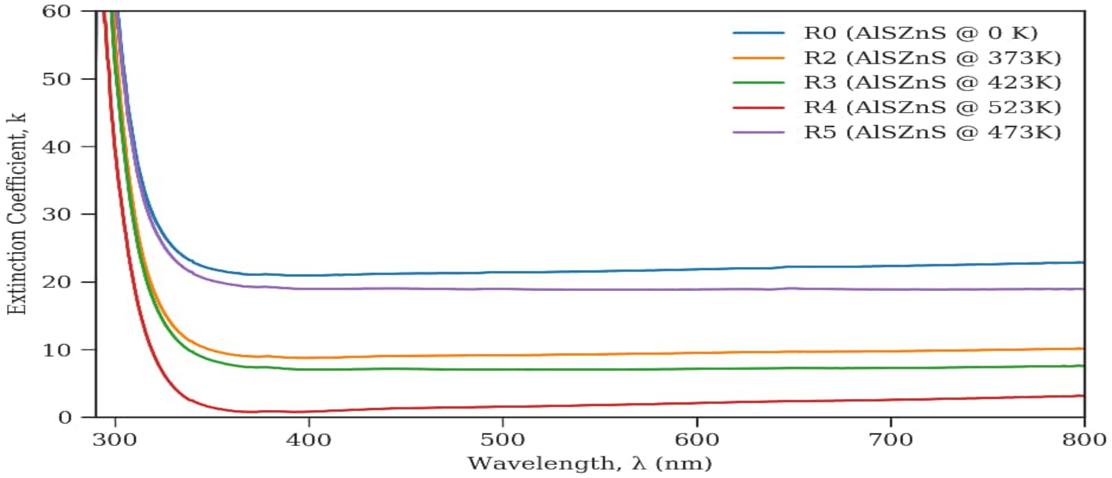

Fig.5: Extinction coefficient spectra of AlS: ZnS thin film annealed at different temperatures.

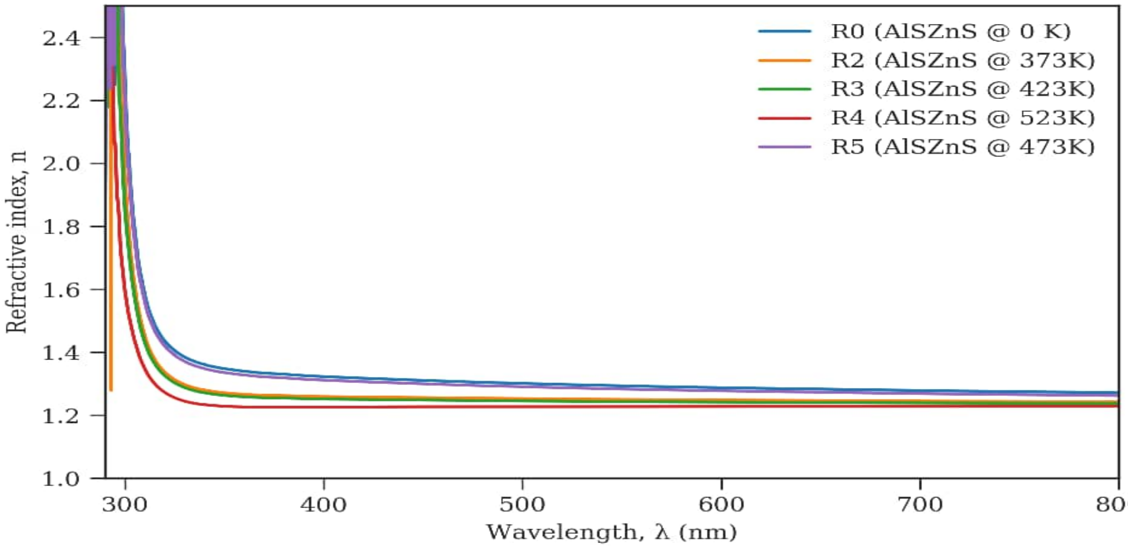

Fig.6: Refractive index spectra of AlS: ZnS thin film annealed at different temperatures

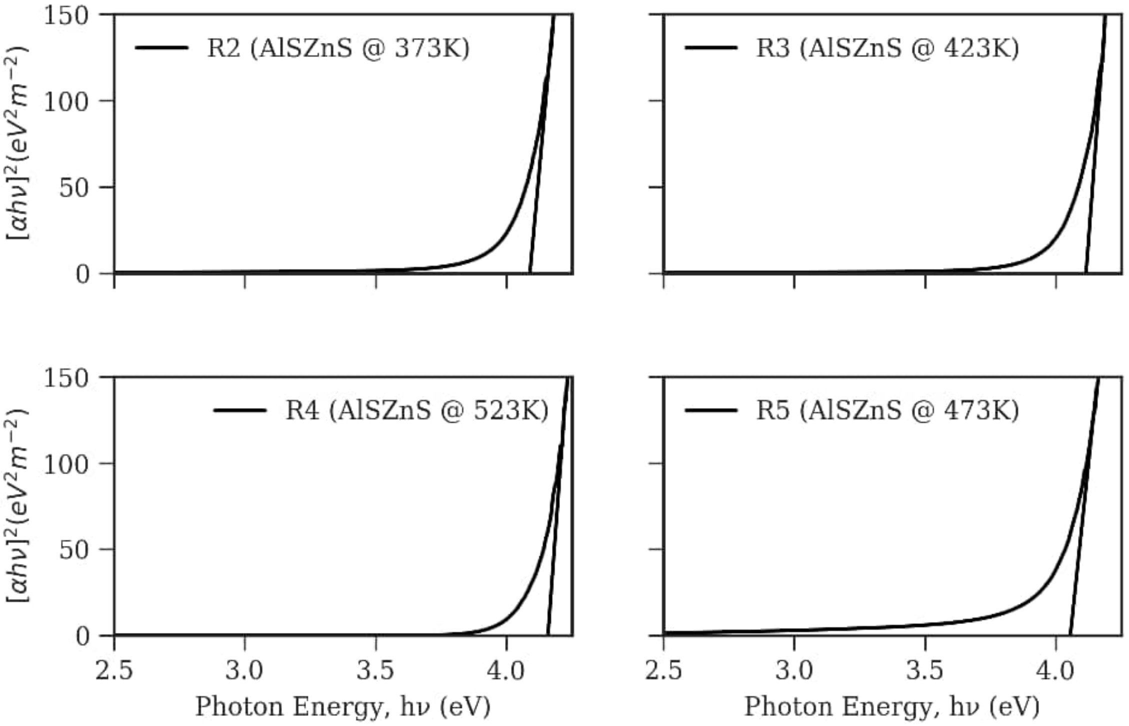

Fig.7: (α $h\nu$)^2 versus photon energy (eV) of AlS: ZnS thin film annealed at different temperatures.

Table 2:Values of maximum optical and solid state properties of chemical bath deposited AlS: ZnS thin films.

Bath Sample	A$_C$(m^2/ mol)	E$_{BG}$ (eV)	|E$_c$(m$^-$ ^{1}cm-^{1})	n	A(AU)	%T	%R
R0	0.38	80.0	24.0	20.00	0.50	44.0	3.82
R2	0.80	72.0	10.0	13.50	0.25	70.0	1.30
R3	0.70	70.0	9.0	12.50	0.20	78.0	1.29
R4	0.10	75.0	4.0	2.00	0.18	98.0	1.25
R5	0.32	78.0	20.1	19.50	0.19	50.0	3.81

****k = Extinction Coefficient, A = absorbance, n = refractive index, T = percentage transmittance, %R = percentage reflectance, A$_C$= absorption coefficient**

4.0 Conclusion

SnS: ZnS alloyed thin films were successfully deposited on glass substrates using two solutions-based methods: SOLUTION GROWTH and SILAR technique at room temperature. Aluminium sulphate (AlSO$_4$.7H$_2$0) was the source of Al, Zinc sulphate (ZnSO$_4$.7H$_2$0) was the source of Zn, sodium thiosulphate (Na$_2$S$_2$S0$_3$) served as the source of S. Ethylene DiamineTetraacetic Acid (EDTA) was used as the complexing agent. The band gap of the film suggested that the material is a semiconducting thin film. The optical and solid-state properties such as reflectance (R), absorbance e (A), transmittance (T), refractive index (n), extinction coefficient (K), Refractive index (n), Absorbance spectra (A), and Transmittance Spectra T (%) determined showed that the material could be used as:

(i) Photovoltaic: In the fabrication of solar panels.
(ii) Automobile: In the car industry such as anti-dazzling on the window screen.
(iii)Architectural design to reduce exposure to skin cancer, cataracts and the impaired immune -system due to UV rays.

(iv) In the agricultural industry, to reduce the greenhouse effect

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Compliance with Ethical Standards Declarations

The authors declare that they have no conflict of interest.

Data availability

All data used in this study will be readily available to the public.

Consent for publication

Not Applicable

Availability of data and materials

The publisher has the right to make the data public.

Competing interests

The authors declared no conflict of interest.

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Authors' Contributions

ECN and PUK-O: Methodology and graphical plots. ECN: Writing an original draft, editing, data analysis and manuscript handling. UJ: proofreading and initial correction. All the authors read and approved the final manuscript.