GROWTH AND CHARACTERIZATION OF ALUMINIUM ZINC SULPHIDE TERNARY THIN FILMS FOR DEVICE APPLICATIONS

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ABSTRACT

Aluminum zinc sulphide (Al_2ZnS_4) ternary thin films were successfully deposited on glass substrates using solution growth technique at bath temperatures 298 K and 333K. The films were characterized for structural properties using GBC enhanced mini-material analyzer x-ray diffractometer with a wavelength of 1.5418 $\mathring{A}$. The structural characterization revealed that the films exhibited polycrystalline structure. The optical characterization was done using UV-VIS-NIR Spectrophotometer. Transmittance was found to vary from 32-90 % and 42-95 %for films deposited at bath temperatures of 298 K and 333K respectively while the optical band gap of 3.40-3.85 eV was observed. The high transmittance in the visible region and wide band gap energy exhibited by the films suggest that the films could be used as window layers in heterojunction solar cell as well as in optoelectronic applications.

Keywords: *transmittance, thin films, band gap, solution growth, characterization*.

I. INTRODUCTION

New ternary thin films of aluminum zinc sulphide belongs to group II-VI compounds materials with hexagonal structure. The properties and applications of ternary thin films in light-emitting diodes, solar cells and non-linear optical devices have increased in recent years [1]. Ternary thin films have been recommended as good materials for window layer solar cells [2] while Some of the ternary compounds have been examined for specific applications in super ionic conducting materials [3]. The preparation of ternary thin films have been achieved using both simple and advanced deposition techniques. Simple deposition techniques such as chemical bath deposition [4-7], spray pyrolysis [8] have been reported while advanced techniques such as sputtering has been reported [9, 10].However, in third world countries, these advanced techniques have not been widely utilized because of their complexity and the poverty of the third world countries. Hence, the growing interest in developing simple and cheap techniques of depositing thin films. The chemical bath deposition technique offers the simplest, cheapest, most economical and affordable method of depositing thin films of various kinds.In this work, we present the characterization of chemically deposited aluminum zinc sulphide (Al_2ZnS_4) ternary thin films.

II. MATERIALS AND METHODS

Before the deposition, the substrates (slides) were degreased by putting them in flask filled with concentrated HNO_3 for 24 hours. Thereafter, the decreased substrates were taken out from the flask, washed with detergent, rinsed with de-ionized water and dried in air. The reason for degreasing was to provide nucleation centers for the growth of the films, thereby producing highly adhesive and uniformly deposited films. The reaction bath constitutes a mixture of 16mls of 0.1-0.5M of A1CI_3, 16mls of 0.1-0.5M of $ZnSO_4$, l0mls of 0.1M of $CS(NH_2)_2$ and l0mls of concentrated aqueous ammonia (NH_3) solution in a 100ml beaker. The mixture was stirred with magnetic stirrer for the uniformity of the solution. Ethylene diamine tetraacetic and ammonia were used as the complexing agents to prevent spontaneous precipitation and ensure film deposition for the growth of Al_2ZnS_4. The deposition was done at two different bath temperatures 298 K and 333K for 24 hours and 2 hours respectively. The substrates were dipped vertically into the reaction baths with the help of the perforated synthetic foam. The substrates were allowed to stay in the bath for different dip times. The films were washed in distilled water and dried in air, after each deposition. The above was repeated for each of the different temperatures used. After the deposition, a GBC enhanced mini-material analyzer (EMMA) X-ray diffractometer with a Cuka radiation of wavelength $\lambda = 1.5418A^o$ was used to characterized for the crystal structure of the thin films while the optical characterization was done using the UV-

VIS-NIR spectrophotometer to determine the transmittance (T) versus wavelength measurements spanning 300 nm-1000 nm.

III. RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction profiles of aluminum zinc sulphide ternary thin films at concentration of 0.1 M of the films grown at different bath temperatures 298 K and 333K while Figures 2 and 3 depict the x-ray diffraction profiles of aluminum zinc sulphide ternary thin films at concentrations of 0.3 Mand 0.5M respectively at different bath temperature. The films were polycrystalline in nature because of the presence of multiple x-ray diffraction peaks as shown in Figures 1-3. From fig.1,several peaks orientation of the crystal growth were observed which are short but stronger with slightly preferred orientation at (2θ = 41.443° and 47.621°) corresponding to diffraction lines produced by (104) and (105) planes respectively for AlZnS films deposited at bath temperature of 298 K while the XRD pattern for AlZnS films deposited at 333K is characterized with several peaks having preferred orientation at (2θ = 32.172° and 37.441°) corresponding to diffraction lines produced by (102) and (105) planes respectively. From fig.2,the films grown at 298 K has preferred orientation at 2θ = 14.59° and 22.038° corresponding to (002) and (003) planes respectively while the film grown at 333K has preferred orientation at 2θ = 28.401° and 36.085° which corresponds to (100) and (103) planes respectively. Figure 3 shows that the films grownat 298 K depicts prominent peaks at (2θ= 7.180°) which corresponds to (001) plane and (2θ = 14.581°) which corresponds to (002) plane with JCPDS: 00-040-1074.The effect of concentration and bath temperature on the structural properties of the films can be seen. The intensity of diffraction peaks increased with both parametric variation of concentration and bath temperature.This is an indication that the crystallinity of the deposited films increased with increase in the parameters of growth. The lattice parameter, crystallite sizes and micro strain were calculated using equations (1), (2) and (3) respectively [11]. The summary of the structural parameters are shown in tables 1 and 2 for AlZnS thin films deposited at 298K and 333K respectively.

$$d_{hkl} = \frac{a_o}{\sqrt{h^2 + k^2 + l^2}} \quad (1)$$

Where d_{hkl} is the interplanar spacing, a_o is the lattice parameter while hkl are miller indices.

$$D = \frac{k\lambda}{\beta cos\theta} \quad (2)$$

Where λ is the wavelength of the x-ray radiation, β is the full width half maximum of the diffraction peaks of preferred orientation, k is the scherrer constant which accounts for the shape of the particle with the value of 0.9 [12]and θ is the diffraction Bragg's angle.

$$\mu = \frac{\beta \cos\theta}{4} \quad (3)$$

μ is the micro strain while other parameters retain their usual meaning.

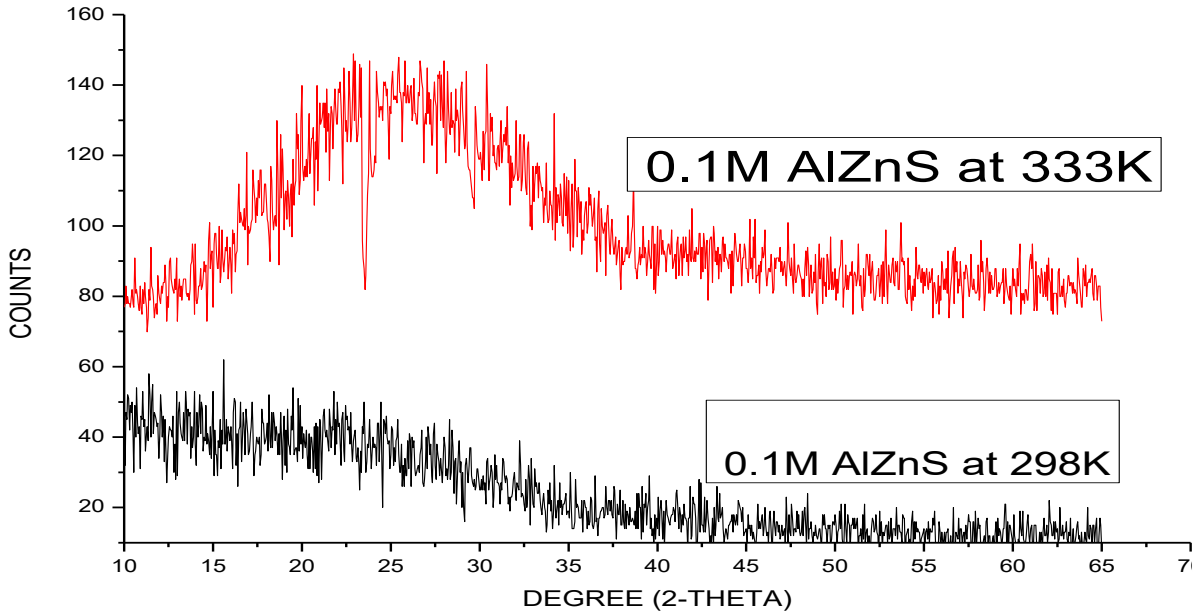

Fig.1: X-ray diffraction profiles of AlZnS thin films for 0.1M at different bath temperatures

Table 1: Structural parameters of AlZnS thin films at varied concentrations for 300K

Conc (M)	Lattice constant (a_o)	Crystallite size (D)	Micro strain (μ) x10^{-2}
0.1	9.353	12.491	2.776
0.3	12.115	11.710	2.961
0.5	7.615	11.845	2.927

Table 2: Structural parameters of AlZnS thin films at varied concentrations for 333K

Conc (M)	Lattice constant (a_o)	Crystallite size (D)	Micro strain (μ) x10^{-2}
0.1	6.904	12.113	2.862
0.3	5.503	12.035	2.880
0.5	12.220	11.845	2.985

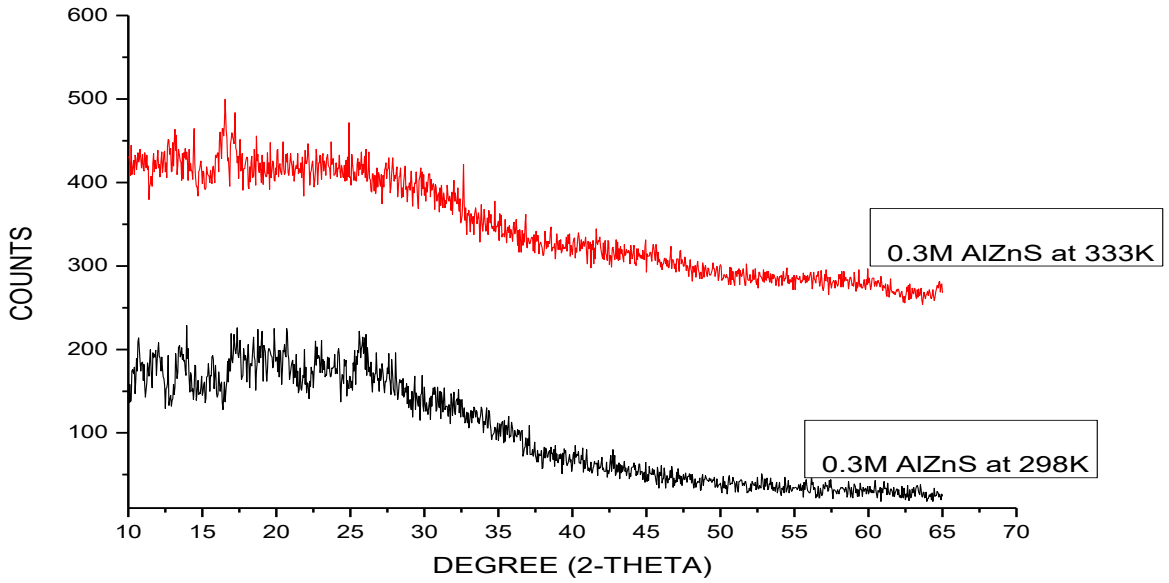

Fig.2: X-ray diffraction profiles of AlZnS thin films for 0.3M at different bath temperatures

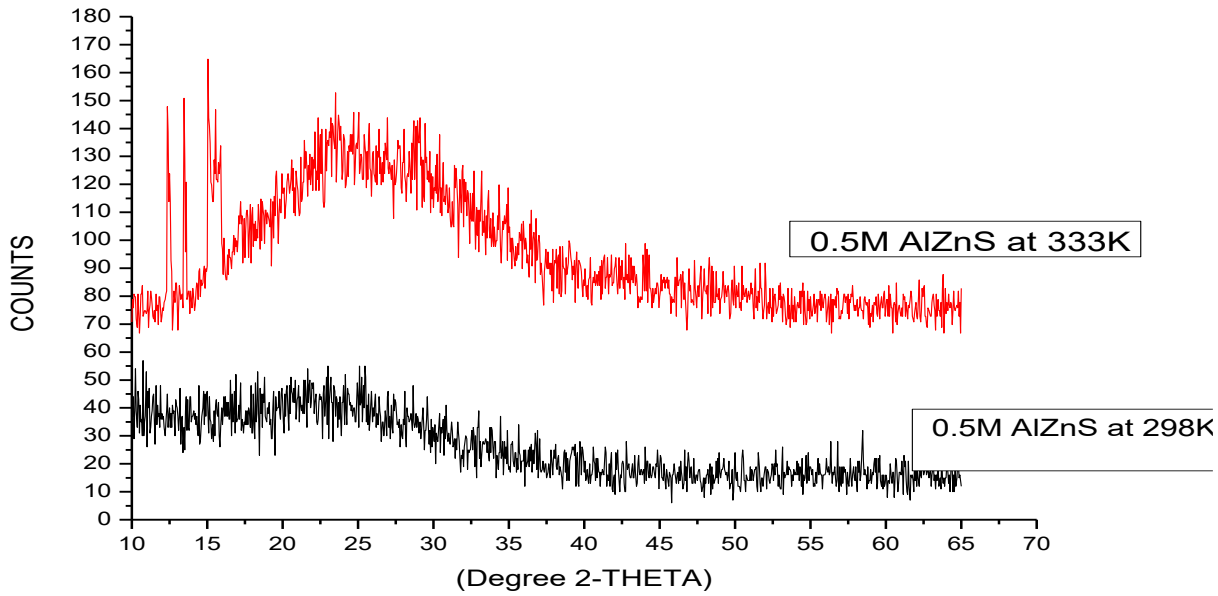

Fig.3: X-ray diffraction profiles of AlZnS thin films for 0.5M at different bath temperatures

The plots of transmittance against wavelength at different concentrations of Al_2ZnS_4 thin films deposited at 298K and 333K are shown in Figures 4 and 5 respectively. From fig.4, the transmittance spectra for films deposited at 298K indicates that the transmittance increases with concentration exhibiting a maximum for 0.5M layer. The transmittance varies from 32-75%, 55-85% and 84-90% for 0.1M, 0.3M and 0.5M respectively. From fig.5, the transmittance fluctuates with wavelength for 0.1M and 0.3M layers while the transmittance increases with wavelength for 0.5M layer. The influence of bath temperature on the transmittance of the films can be observed. When the bath was maintained at 298K, the transmittance of the films rose to about 90% for 0.5M layer (fig.4) and

reduces to 84.5% at bath temperature of 333K (Fig.5). Other layers (0.1M and 0.3M) showed similar variations in transmittance with bath temperatures. At bath temperature of 298K, the transmittance increases with concentration and showed opposite behavior for bath temperature of 333K. The average transmittance of AlZnS thin films is above 50% except for 0.1M layer (fig.4) and 0.5M layer (fig.5). Human eye is sensitive only to the range 400-700 nm and is peaked at 500 nm [13]. This is an important factor in window coatings and is met in these films. AlZnS thin films deposited in the work is therefore suitable for window coating. Generally, the transmittance of the films deposited in this work is very high with a maximum of 90% and 96% for films deposited at bath temperatures of 298K and 333K respectively. In the infrared region, the high transmittance of the thin films are high enough for coating of the roofs and walls of poultry houses. This will provide the needed heat required for warming of young chicks and has the potential to reduce the cost of energy consumption associated with the use of electric bulbs, stoves and lambs to produce the needed heat to warm young birds. These findings are in agreement with the report of other authors [14-17].The transmittance of thin films are greatly modified by deposition parameters. In the literature, the influence of growth parameters such as concentration [18-23], annealing temperature [14-17, 24-26], deposition time [27-30] and P^{H}[31] on the transmittance of thin films have been reported.

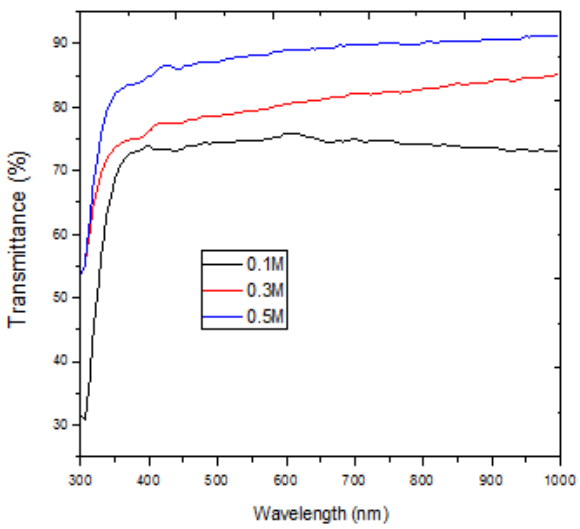

Fig.4: Plot of T against λ at different concentrations for 300K

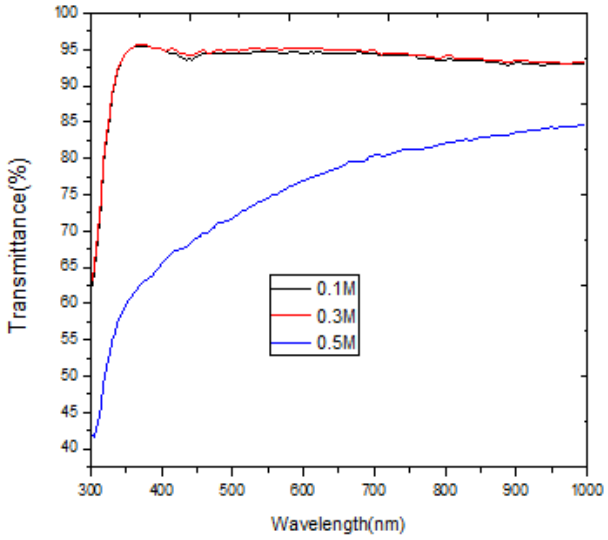

Fig.5: Plot of T against λ at different concentrations for 333K

The plots of absorption coefficient against photon energy is shown in Fig. 6 for AlZnS thin films deposited at 298K, and Fig.7 for AlZnS thin films deposited at 333K. From figure 6, the absorption coefficient increased with concentration exhibiting a maximum for 0.5M layer. Similar trend was observed for AlZnS thin films deposited at 333K. Our values are in similar other of magnitude with the values reported elsewhere [5-7].

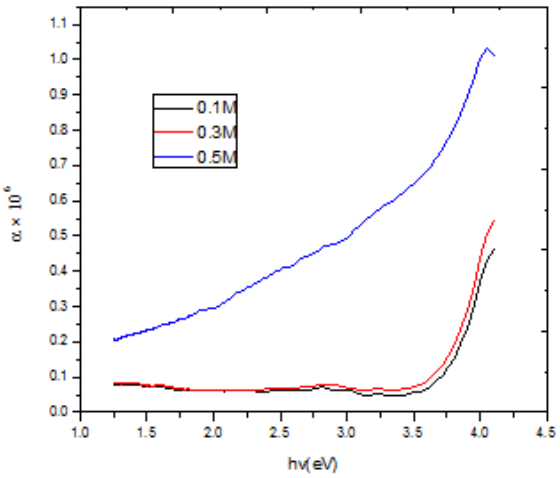

Fig.6: Plot of α against hv at different concentrations for 300K

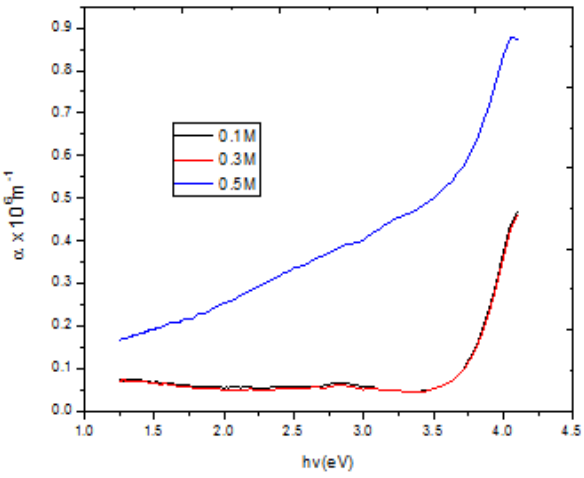

Fig.7: Plot of α against hv at different concentrations for 333K

Fig.8 shows the plots of $(\alpha hv)^2$ versus hv for the determination of band gap of AlZnS thin films deposited at 298K while fig.9 depicts the plot of $(\alpha hv)^2$ versus hv for the determination of band gap of AlZnS thin films deposited at 333K. From fig.8, the direct energy band gap values are 3.80eV, 3.70eV and 3.40eV for 0.1M, 0.3M and 0.5M respectively. Clearly, a band gap narrowing can be observed with increase in concentration. As observed in fig.9, the band gap vary in the same manner, decreasing from 3.85eV for 0.1M to 3.80eV for 0.3M and 3.65eV for 0.5M. With respect to bath temperature changes, the band gap energy increases from3.80 eV to 3.85 eV for 0.1M layer, 3.70 eV to 3.80 eV for 0.3M layer and 3.40 eV to 3.65 eV for 0.5M layer. These band gap values are higher compared to that of Uhuegbu (2007) for CuZnS and FeZnS thin films [32], Orori et al (2014) for $Cd_xZn_{1-x}S$ [5], Rojas and Oliva (2013) for $Cd_xZn_{1-x}S$ thin films [6]. However, they are in agreement with that of Kumar et al (2008), Shinde et al (2011), and Igweoke et al(2018) for binary ZnS thin films [21,33, 34].The variations in the energy band gap with parametric investigation involving concentration and annealing temperature suggest that the energy band can be tailored to suite specific application by varying growth parameters. The high transparency in the visible region and wide direct band gap energy exhibited by these films make them ideal for use as window layer in a heterojunction solar cells. The use of wide band gap materials as window layers in solar cell fabrications is to minimize the recombination loss prevalent in direct band gap semiconductors thereby admitting a maximum amount of light to the junction region and the absorber layer. CdS thin films are widely used as window layer in CIGS solar cells. However, there are great concern about the toxicity of Cd in this architecture [35] and so; several alternative window layers are currently being investigated to replace CdS. In our view, AlZnS thin films stand high for possible incorporation in CIGS solar cell.

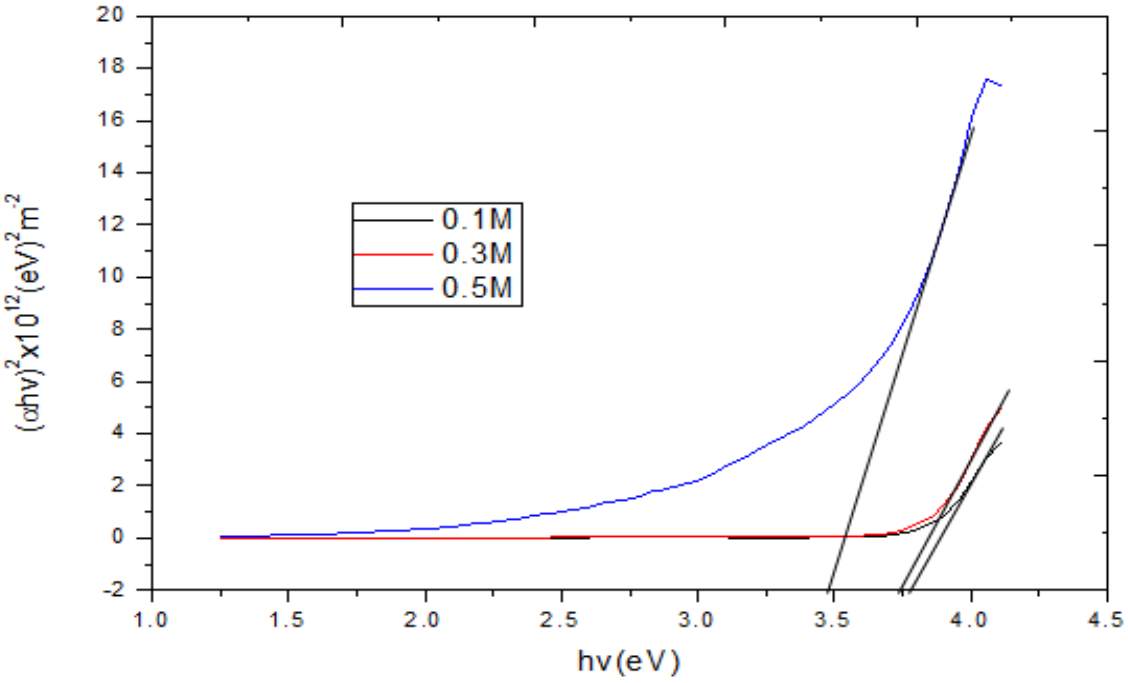

Fig.8: Plot of $(\alpha hv)^2$ against hv at different concentrations for 300K

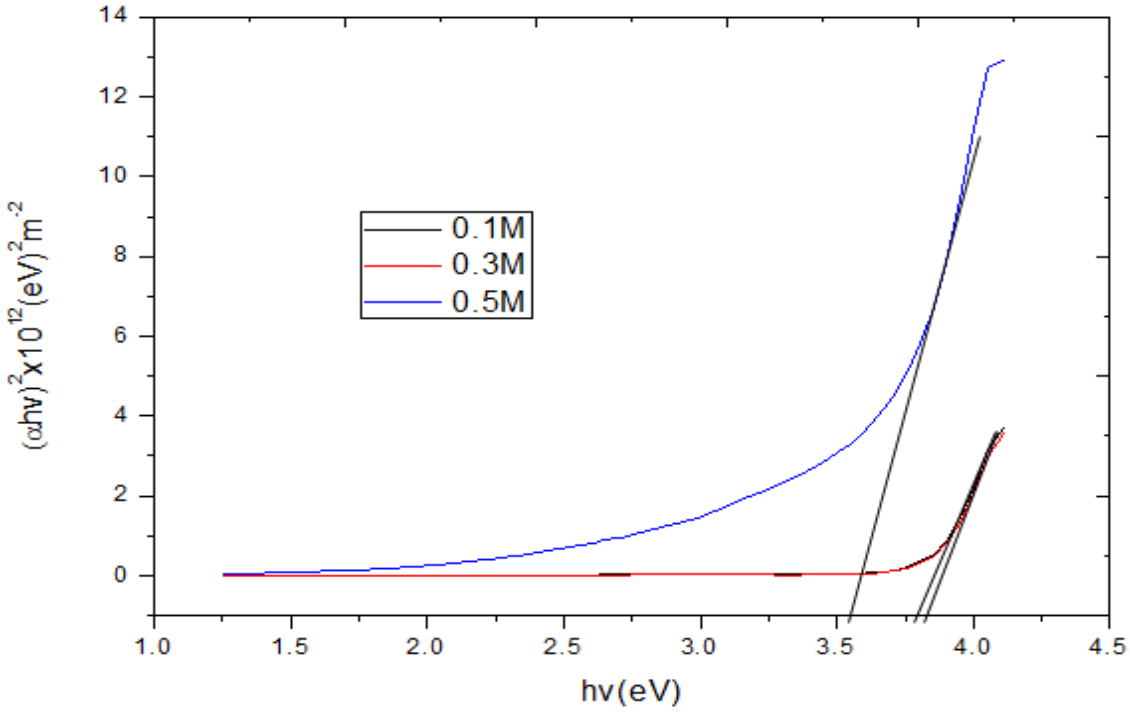

Fig.9: Plot of $(\alpha hv)^2$ against hv at different concentrations for 333K

IV. CONCLUSION

New ternary thin films of Aluminum Zinc Sulphide grown have been successfully deposited on glass substrate using solution growth technique (SGT). The structural characterization was carried out using GBC enhanced mini material analyzed (EMMA) X–ray diffractometer while optical characterization was done using UV-VIS –NIR Spectrophotometer. The results of both XRD and optical parameters showed considerable variation with growth parameters. The high transparency in the visible region and wide energy band gap of the films suggest that AlZnS thin films deposited at different bath temperature and concentration are suitable for photovoltaic and optoelectronic applications.

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