Journal of the Nigerian Association of Mathematical Physics
Volume33,(January, 2016), pp147 – 154

Effects of Bath Composition on the Optical and Electrical Properties of Zinc Sulphide (ZnS) Thin Filmsusing Electrodeposition Technique

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Abstract

Electrodeposition Technique was used to deposit thin films of Zinc Sulphide (ZnS) on fluorine doped Tin Oxide (FTO) glass substrate. The absorbance of the deposited films was studied using M501 UV-VIS spectrophotometerin the range of 300-900nm using a step size of 20. Investigation reveals that the absorbance of the deposited films increased with the bath composition. The grown films showed low absorbance value in the range of 0-2.3 and a high transmittance value in the range of 0-0.9 for all the deposited films. The absorbance of the deposited films decreased as the wavelength and the photon increased. The average optical band gap energy of the film was found to be 2.8eV.

Keywords: Optical properties, Thin Film, Fluorine doped Tin oxide (FTO),Electrodeposition, ZnS

1.0 Introduction

Zinc sulphide (ZnS) is found in nature as Zinc blende (also called Sphalerite or β-ZnS and with a cubic structure) and wurtzite (α-ZnS, which is a hexagonal structure). The names of these minerals are used to designate the corresponding crystal structures. Zinc sulphide is an important II–VI compound semiconductor material and is commercially used in solar cells [1], infrared windows [2, 3], and phosphor materials by doping with transition or rare-earth metals [4, 5]. There has been growing interest in developing techniques to prepare semiconductor ZnS thin films. ZincSulphide semiconductor with a wide band gap energy which is suitable for applications in solar cells, solar selective decorative coatings, UV light emitting diode, photo catalysis and phosphors in flat panel displays. ZnS thin films are nontoxic to human body, very cheap and abundant. Thesemiconductor thin films deposition from aqueous solution [6-10] becomes increasingly popular because it has advantages of economical and capability of large area deposition. Various techniques have been employed to prepare ZnS thin films including successive ionic adsorptionreaction method [5], electrodeposition[6], chemical bath deposition [11], spray pyrolysis [12], vacuum evaporation [13] and pulsed laser deposition [14]. Electrodeposition offers several advantages: it is relatively economical; it can be used on a large scale; and it is conducted at low-temperature. Although there has recently been a growing interest in the electrodeposition of ZnS film due to these advantages, two issues have concerned us. The first is that heat-treatment is necessary after deposition in order to adjust the ZnS stoichiometry, thus forfeiting the advantages of a low-temperature process. The second is that electrodeposition is often performed at a relatively negative potential, indicating that a sub-reaction of hydrogen evolution reduction could arise, leading to a reduction in current efficiency [15]. For these reasons, we have been strongly interested in achieving a single electrodeposition of ZnS films at a low over potential (a more positive potential) and without heat-treatment.

In this paper electrodeposition method is used to deposit ZnS thin films onto substrate (FTO) to study the effect of bath composition on the optical properties of ZnS. Several researchers have grown Zinc sulphide (ZnS) by varying many growth parameters and using different techniques as well. However, the several author's reports are often silent on the effect of bath composition on the results obtained.

2.0 Materials and Methods

ZnS thin films were prepared on the glass substrates Fluorine doped Tin Oxide (FTO) by electrodeposition technique. The substrates were cleaned ultrasonically by detergent solution, acetone, and deionized water, respectively, to ensure the

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complete cleanness. The reaction bath for the deposition of Zinc Sulphide (ZnS) was composed of four electrolyte Zinc Chloride ($ZnCl_2$), hydrated Sodium Sulphide ($Na_2S.H_2O$), Potassium tetraoxosulphate VI (K_2SO_4) and Tetraoxosulphate VI acid (H_2SO_4). The growth of ZnS films were determined with respect to the different bath parameters which includes time of deposition and substrate for the deposition, the concentration and the pH of the solution were kept constant throughout the experiment. The pH value was maintained at 2.5 while the concentration of the compounds were maintained as prepared i.e **0.10M** $ZnCl_2$, **0.10M** $Na_2S.H_2O$**, 0.10M** K_2SO_4, and **0.10M** H_2SO_4 with the following reactions;

$$ZnCl_{2(aq)} + Na_2S.H_2O_{(aq)} \rightarrow ZnS_{(s)} + 2NaCl_{(aq)} + H_2O \quad (1)$$

$20cm^3$ each of $ZnCl_2$ and $Na_2S.H_2O$ was measured into $100cm^3$ beaker using burette. $20cm^3$ of K_2SO_4 was measured into the same $100cm^3$ beaker containing $ZnCl_2$ and $Na_2S.H_2O$ respectively to serve as the inert electrolyte which helps to dissociate the Zn from the $ZnCl_2$ and S from the $Na_2S.H_2O$ to form the required ZnS film on the substrate and the solution was acidified with $5.00cm^3$ of dilute H_2SO_4 which serves to adjust the P^H value. The entire mixture was stirred with the glass rod to achieve uniformity.

In each of the reaction baths prepared, a glass substrate and carbon electrode were connected to a DC power supply source and the time was maintained at **90(s)** for different contraction of **K_2SO_4**

Table 1: Preparation of ZnS Thin Films

Slide No	Volume of $Zn(NO_3)_2.6H_2O$ (cm^3)	Bath composition of $Zn(NO_3)_2.6H_2O$ (M)	Volume of K_2SO_4 (cm^3)	Bath composition of K_2SO_4 (M)	Deposition time (s)	Deposition voltage (v)	Volume of H_2SO_4 (cm^3)
A	20.00	0.10	20.00	0.10	90.00	3.00	5.00
H	20.00	0.20	20.00	0.10	90.00	3.00	5.00
I	20.00	0.30	20.00	0.10	90.00	3.00	5.00

2.1 Optical Characterization

The absorbance of ZnS thin film was obtained by computerized monochromatic beam spectrophotometer (M501) at wavelength range of 300-900nm in the step of 20nm. The base of the thin film deposited glass substrates was mounted vertically on a rotating holder at sample compartment respectively and scanned to obtain the absorbance of the film. The wavelength from 300nm-400nm falls in the UV region, 400nm-700nm falls in the VIS region and 700nm-900nm falls in the NIR region. Other properties which include: transmittance, reflectance, refractive index, optical thickness, coefficient of absorption, extinction coefficient, optical conductivity and dielectric constant were derived using the formula below

From the law of conservation of energy we obtained,

$$A+T+R=1 \quad (2)$$

Where A is the absorbance, R is the Reflectance, and T is the transmittance, give by

$$T = 10^{-A} \quad (3)$$

Refractive index n and the 0ptical thickness t are given in [12]

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2}} - K^2 \quad (4)$$

$$t = \frac{In(\frac{1-R^2}{T})}{\alpha} \quad (5)$$

Coefficient of absorption α and photon energy E are given by

$$\alpha = \frac{A}{\lambda} \quad (6)$$

$$E = \frac{hc}{\lambda} \quad (7)$$

Extinction coefficient k and Optical conductivity σ are given by

$$K = \frac{\alpha\lambda}{4\pi} \quad (8)$$

$$\sigma = \frac{\alpha nc}{4\pi} \quad (9)$$

Real dielectric constant ε_r and Imaginary dielectric constant ε_i[13]

$$\varepsilon_r = n^2 - k^2 \quad (10)$$

$\varepsilon_i = 2nk$

3.0 Discussion of Results

Figure1 shows the plot of absorbance as a function of wavelength of the films deposited at constant time of 3min and voltage of 3V respectively. From the graph, it is observed that at 0.1M, 0.2M, and 0.3M respectively, the absorbance falls at the

range of 0.2-0.1, 2.1-1.1, and 2.2-1.2 respectively. The deposited films show high absorbance in high photon energy and low absorbance in low photon energy. The absorbance of the deposited films also increased with increased inbath composition. The high absorbance in the UV region makes ZnS useful in forming p-n junction solar cell with other suitable material for photovoltaic application, in the other hand a low absorbance of 0.2-0.1 alsomake ZnS thin film useful for optical component in high laser window application [16].

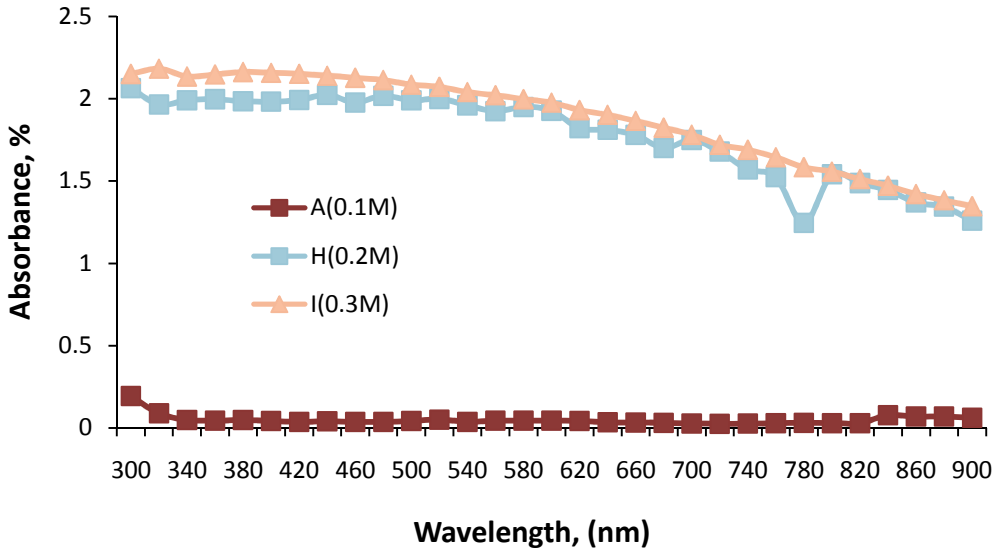

Figure 1: Plot of absorbance as a function of wavelength

Figure 2 Shows plot of transmittance as a function of wavelength, At 0.1M, the transmittance tend to be very high which increases at the range of 0.52-0.7 while at 0.2M and 0.3M respectively the transmittance range obtained was at 0.01-0.07 respectively and at a wavelength range of 300nm-900nm. The high transmittance makes ZnS thin film a useful material for pyroelectric detector, while low transmittance makes it useful for double glazed windowing.

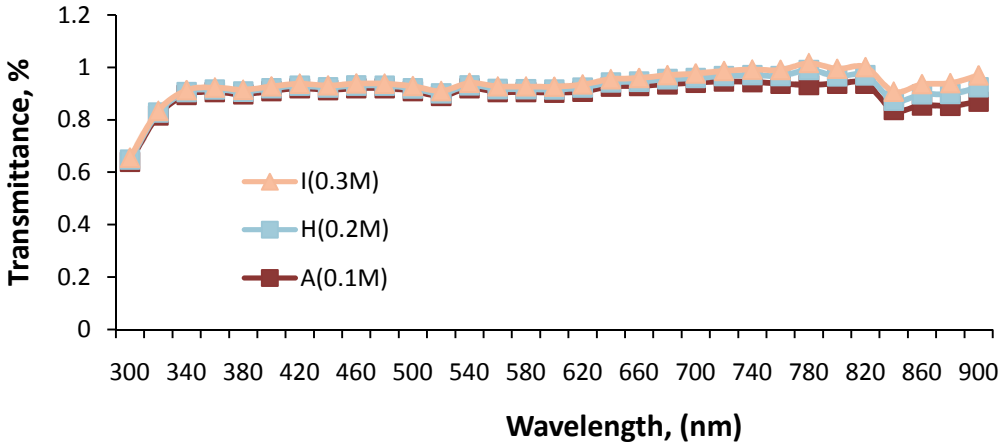

Figure 2: Plot of transmittance as a function of wavelength

The plot reflectance as a function wavelength figure 3 shows that at 0.1M a good thin film of about 0.2-0.09 is deposited on the glass substrate but an increase in bath composition of 0.2M, and 0.3M respectively gives a negative value between -1.2 to -0.3 respectively at wavelength of 300nm-900nm, 300nm-800nm and 300nm-900nm respectively. Investigation reveals that high reflectance of 0.2-0.09 can be used as a photosynthetic radiation device and as a sensor.

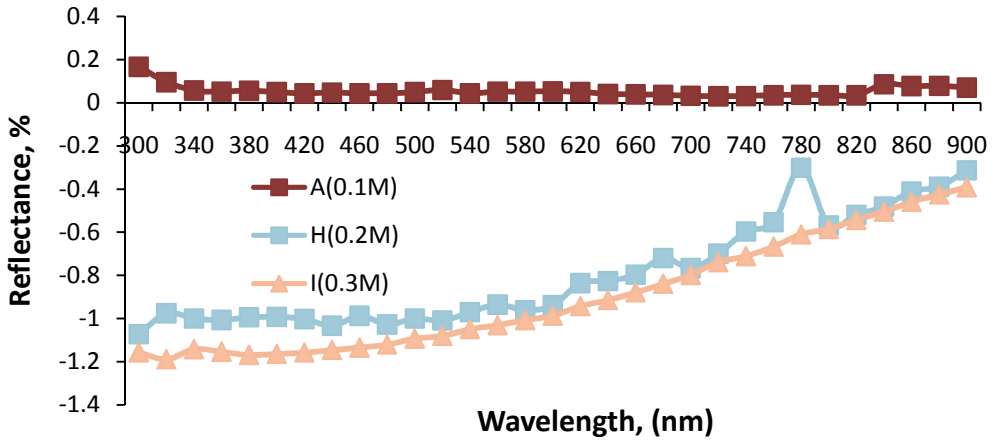

Figure 3: Plot of reflectance as a function of wavelength

Figure 4 shows the optical conductivity as a function of photon energy. At 0.1M, the optical conductivity is relatively constant while at 0.2M and 0.3M, the optical conductivity gives a value of 5.6E-8 and 5.4E-8 respectively.

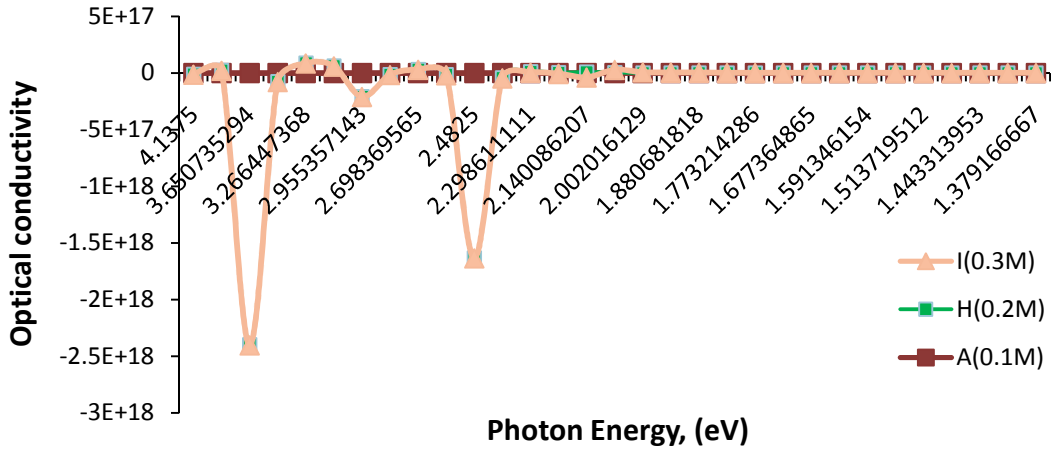

Figure 4: Plot of optical conductivity as a function of photon energy

Figure 5-7 shows the plots of absorption coefficient square as a function of photon energy for slide A at 0.1M a band gap was observed to be 3.6eV, 0.2M a band gap of 2.3eV for Slide H is obtained and the band gap energy of 2.5eV at 0.3M for Slide I. Investigation reveals that ZnS thin film is useful in functional layer materials [16]. This also makes ZnS useful for p-type conductivity as a semiconductor material. It means that absorption coefficient square as functionphoton energy also depend on the bath composition of thin film deposited as showed.

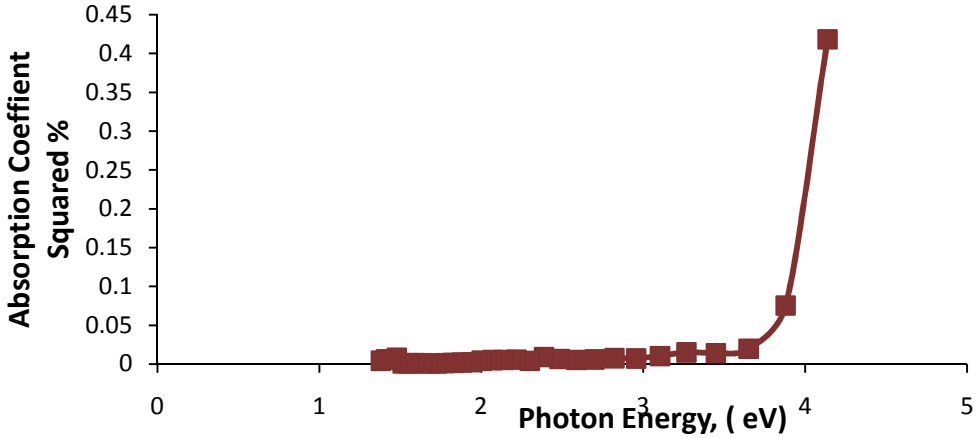

Figure 5: Plot of absorption coefficient square as a function of photon energy (Slide A)

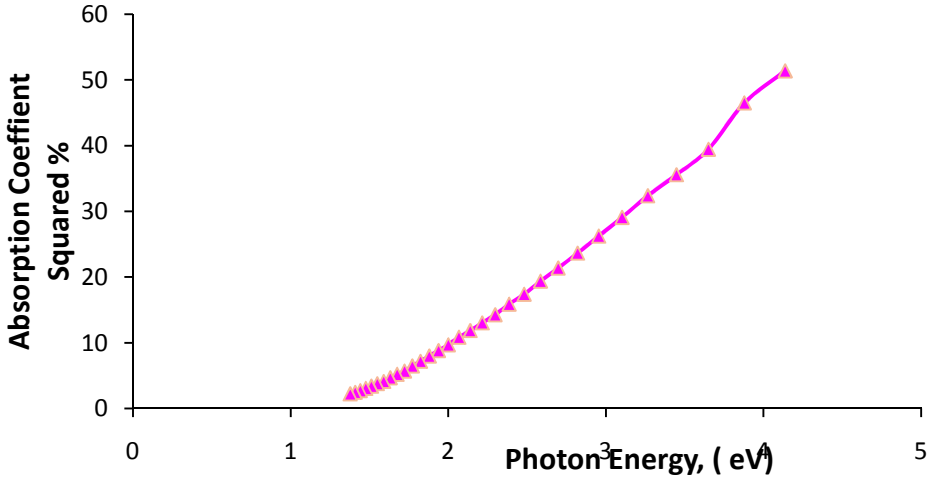

Figure 6: Plot of absorption coefficient square as a function of photon energy (Slide H)

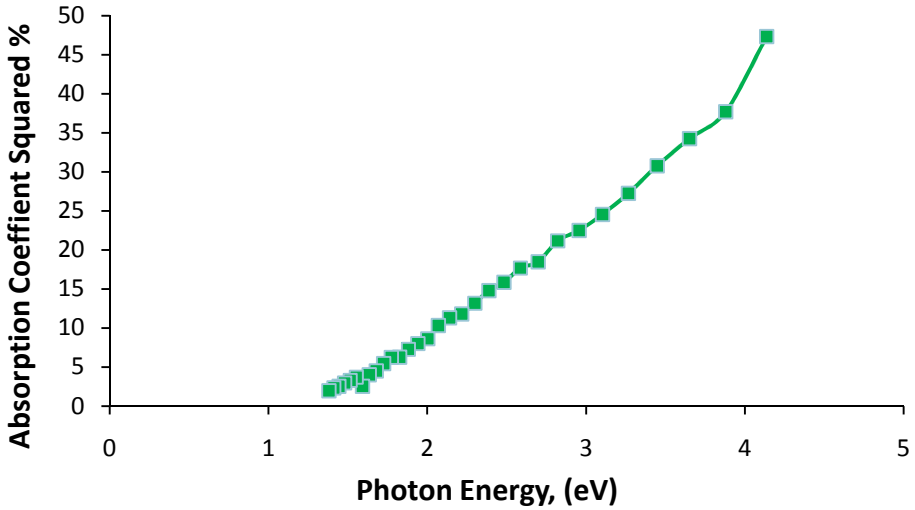

Figure 7: Plot of absorption coefficient square as a function of photon energy (Slide I)

Figure 8 shows the plot of refractive index as a function of photon energy. It is reveal that at 0.1M, the refractive index is zero, when there is increase in thephoton energy from 1.3–4.0 while at 0.2M and 0.3M, the refractive index decreases downward from 0 to -1.7, as the photon energy increases from 2.3-2.5 and 3.5–3.8. This kind of material can be used in optical components and multispectral applications.

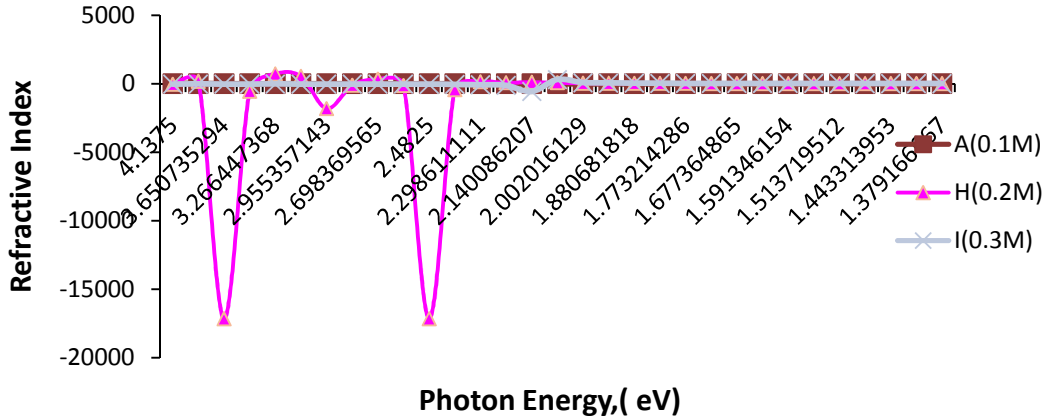

Figure 8: Plot of refractive index as a function of photon energy

Figure 9 shows the plot of extinction coefficient as function photon energy. At 0.1M there was a slit increase from 0.009-0.02 in the UV region to the VIS region while at 0.2M and 0.3M, we have an increase from 0.9 - 0.15 and 0.9 - 0.15 respectively. Investigation reveals that this low extinction coefficient can be useful in incandescent lamp dome exposure. Therefore ZnS thin film is applicable.

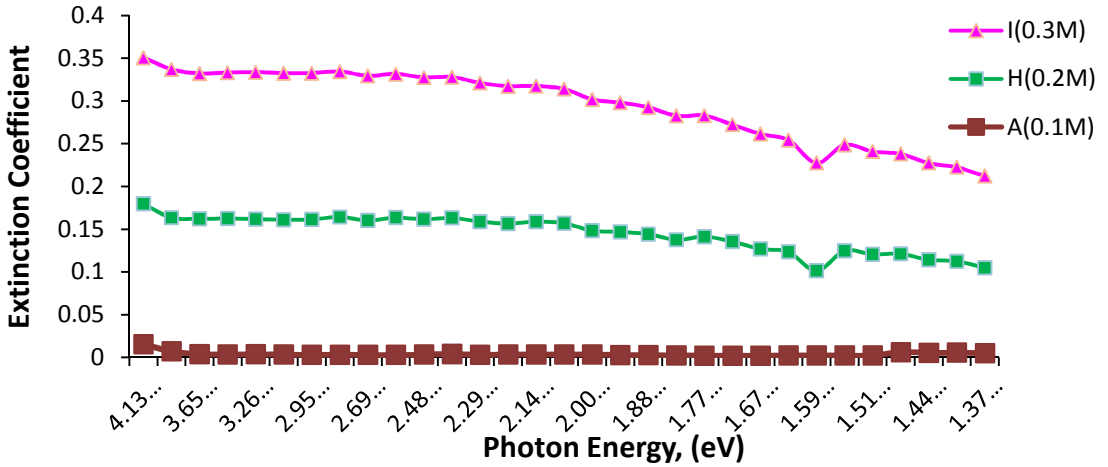

Figure 9: Plot of extinction coefficient as a function of photon energy

Figure 10 shows the plot of real dielectric constant as a function of photon energy, at 0.1M, the real dielectric constantis zero while at 0.2M and 0.3M the real dielectric increases in VIS region. This reveals that ZnS has a good dielectric thin film as a result of increase in thebath composition which is useful in the fabrication of capacitors and storage of energy. This shows that increase in thebath composition increases the dielectric material of thin films deposited.

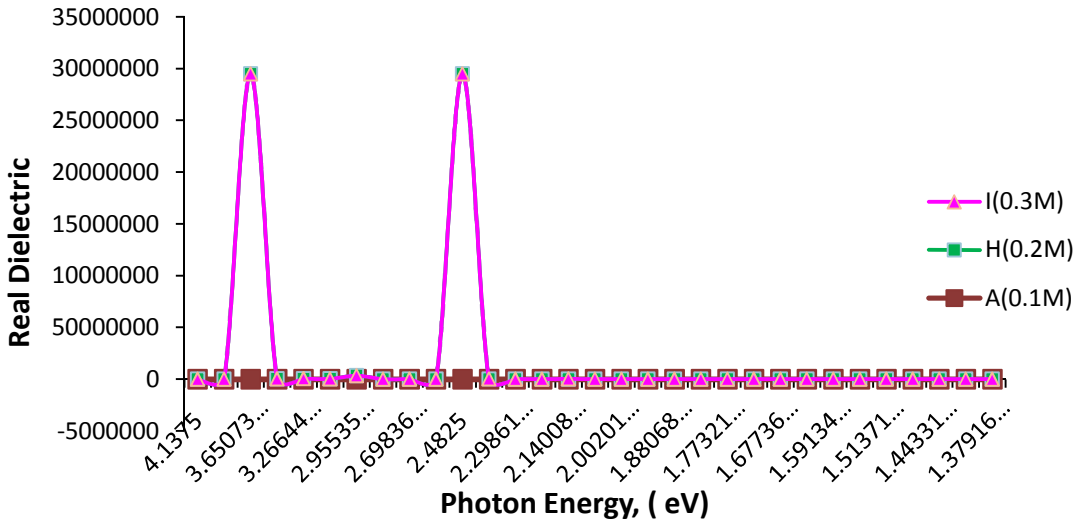

Figure 10: Plot of real dielectric constant as a function of photon energy

Figure 11 shows the plot of imaginary dielectric constant as a function of photon energy, at 0.1M the imaginary dielectric constant is zero. At 0.2M and 0.3M gives zero while there was an increase in the photon energy from 2.4–2.6eV and 3.4–3.8eV.

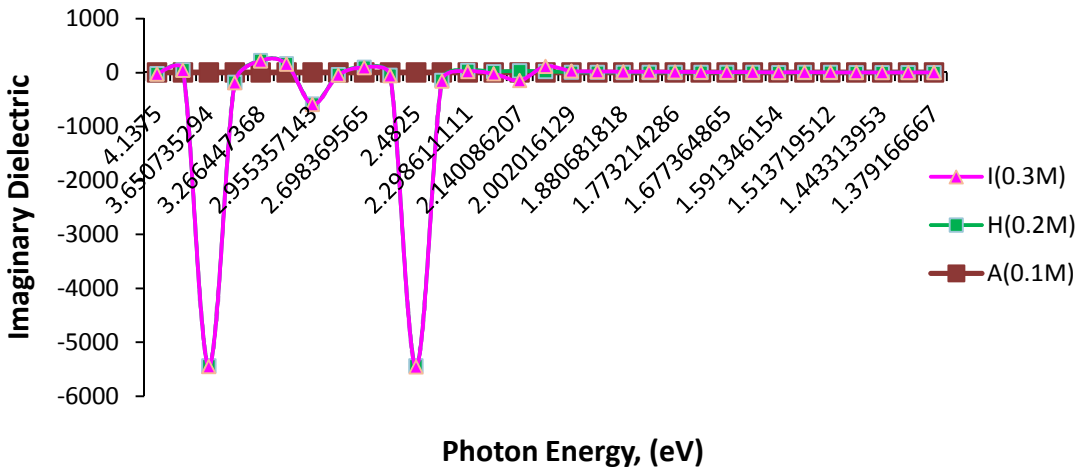

Figure 11: Plot of imaginary dielectric constant as a function of photon energy

4.0 Electrical Properties of CuSe Thin Films

The electrical properties of the deposited copper selenide films were studied using a standard four point probe technique. The arrangement was made in such a way that the voltage across the transverse distance of the films was measured using silver paste on top of the coated slide to ensure good ohmic contact to the film. The four point probes were arranged such that the two outer probes were connected to current supply and the two inner probes to a voltage supply. As current flows between the two outer probes, voltage drop across the inner probes was measured. The sheet resistivity of the thin film depends on the current, voltage and thickness values of prepared thin film. Equations:

$$\ell = \frac{\pi}{In2}\frac{V}{I} = 4.523t \quad (11)$$

$$R_s = \frac{resistivity}{4.523\ xthickness} = \frac{\ell}{4.523t} \quad (12)$$

$$\sigma = \frac{1}{\ell} \quad (13)$$

Table 2: Electrical Property of CuSe Films

SAMPLE	AVERAGE VOLTAGE (V)	AVERAGE CURRENT (A)	THICKNESS (Ω/m)	SHEET RESISTIVITY (Ω/m)	SHEET RESISTANCE (Ω)	ELECTRICAL CONDUCTIVITY (Ω/m)
A	$2.13x10^4$	$4.30x10^6$	168	$3.43x10^5$	14.22	$7.29x10^{-7}$
H	$2.15x10^4$	$4.36x10^6$	178	$3.54x10^5$	14.24	$8.36x10^{-7}$
I	$2.10x10^4$	$4.39x10^6$	179	$3.64x10^5$	14.26	$8.43x10^{-7}$

5.0 Conclusion

Zinc Sulphide thin films have been successfully prepared by electrodeposition technique.The absorbance of the deposited films falls at the range of 0.2-0.1, 2.1-1.1, and 2.2-1.2 respectively. The deposited films show high absorbance in high photon energy and low absorbance in low photon energy. The absorbance of the deposited films also increased with increased inbath composition.The transmittance tend to be very high which increases from the range of 0.52-0.7 while at 0.2M and 0.3M respectively the transmittance range obtained was at 0.01-0.07.The transmittance of the ZnS films increases at the visible and near infrared region, this make ZnS a good candidate to be used as antireflection coatings. The value of refractive index remain nearly constant in the wavelength range 400-900nm; this behavior represents an optical stability within this spectral range.

6.0 References

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