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EFFECT OF VARYING pH ON THE OPTICAL AND ELECTRICAL PROPERTIES OF ELECTRODEPOSITED ZnS THIN FILMS.

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ABSTRACT

The effect of varying pH on the optical and electrical properties of electrodeposited ZnS has been studied. The electrical parameter were studied using the Photoelectrochemical (PEC) cell while the optical parameters were studied using the UV-Visible spectrophotometry technique for wavelength range 400 – 1900 nm. Visual examination revealed that the colour of the ZnS thin films became lighter as the pH reduced. High transmittance, which decreases with increase in the pH were observed at the visible and near infrared regions. The values of the energy bandgaps decreases as the pH values decrease, an indication that the transmittance of the ZnS thin film decreased with decreased pH. The average current density and thickness of the thin films decreased with increasing pH while the thin films were all p-type in electrical conductivity which shows that variation in the pH did not have any significant effect on the conductivity type of the films.

1. INTRODUCTION

Zinc sulphide (ZnS) belongs to group II-VI direct bandgap semiconductor [1,2], normally occurring in two crystalline forms viz;. cubic or zincblende (ZB) structure and hexagonal or wurtzite (WZ) structure [3 – 5]. It has a high melting point, refractive index and transmittance in the visible region, making the material useful as reflector and dielectric filter [5 – 9]. ZnS has shown remarkable application capabilities in various technological areas like flat panel displays, field emitters, laser, photonics, solar cells, electroluminescent devices etc due to its wide bandgap energy of ~3.7 eV [7, 10 – 11]. The ability of ZnS to be synthesized in various dimensions and shapes necessitated its wide application in electronics, optoelectronic, health and safety devices. In solar cell application, it has been found to be a better buffer layer substitute in a CIGS solar cells because it is non-toxic and environmental friendly [12-14].

Several parameters have been shown to affect the structural and optical properties of ZnS,The transmission of ZnS deposited by chemical bath deposition is noted to increase as the pH increased for wavelength range of 300 – 1800 nm. Bandgap reduction with increased pH was also report in [15].

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According to {16], thebandgap of chemical bath deposited ZnS varied with variation in the pH. The bandgap varied from 3.84 to 3.93 eV as the pH varied from 10 to 10.6. Elsewhere in [17], it was reported that the transmission values of the spectral range of300 – 1800 nm increased with increase in pH for ZnS deposited using chemical bath deposition method. Also a decrease in pH leads to the increase in the thickness of the ZnS thin films. ZnS thin films prepared at a pH of 10.55 using a chemical bath deposition method showed a transparency of 66 – 87 % and energy bandgap ranging from 3.79 – 3.9 3 eV [18]. Despite the number of information on the effect of pH on ZnSthin films, report of films obtained via the electrodeposition route is scarce. This work studied the effect of varying pH on the electrical and optical properties of ZnS thin films grown using the eletrodeposition method.

2. MATERIALS AND METHOD

The ZnS thin films were deposited on fluorine-doped tin oxide (FTO) substrates using the electrodeposition technique. The FTO substrates were cleaned with de-ionized water, liquid soap and methanol. The FTO served as the cathode in a two electrodes set-up with carbon rod as the counter electrode. The electrolyte was prepared by mixing solutions of $ZnSO_4.7H_2O$ (0.15M) and $Na_2S_2O_3.5H_2O$ (0.015M) in double distilled aqueous bath. The pH of electrolyte solution was adjusted to 4.00 by using diluted H_2SO_4 acid and was maintained at room temperature while stirred using magnetic stirrer. The cathode and anode electrodes are immersed in the electrolyte bath concentration, and are connected to negative and positive terminals of the power supply respectively. The distance between the electrodes was kept constant during deposition, and then connected to a potentiostat at a cathodic voltage of 1450 mV. Subsequent ZnS films were deposited at pH of 3.00 and 2.00. The ZnS thin films deposited at electrolytic bath pH of 4, 3 and 2 were labelled M_4, M_3 and M_2, respectively.

Photoelectrochemical (PEC) cell measurement was carried out to determine the electrical conductivity type of the thin films and UV-Visible Spectroscopy was also done to determine the optical properties of the deposited films for the wavelength range from 400 – 1900 nm. The following optical properties were studied for the deposited ZnS thin films: absorbance (A), transmittance (T), reflectance (R) and the bandgap energy.

3. RESULTS AND DISCUSSION

The visual appearances of the ZnS thin films grown at different pH are shown in Figure 1. It can be observed that the colour of the ZnS thin films became lighter as the pH was reduced from 4 to 2. Figure 2 shows the variation of the average current density and thickness with pH. It can be seen that the both the average current density and thickness of the ZnS thin films decreased as the pH increased, in accordance with the report of [17]. The variation of the PEC signal with the electrolytic pH of the bath is shown in Figure 3. The PEC signal of the ZnS thin film increased with increasing pH and all the grown ZnS thin films were of p-type in electrical conductivity.

The transmittance spectra of electrodeposited ZnS layers in wavelength range 300 nm to 900 nm are shown in Figure 4. The transmittance increases with increase in incident photon from the visible to the near infrared region. It was observed that the transmittance decreased with decrease in pH of the material. This is in agreement with previous researches [15, 17]. The absorbance decreased as the wavelength of the incident photon increased and reduced as the pH of the bath increased (Figure 5). The reflectance spectra of the thin film layer deposited at different pH are plotted in Figure 6. It was observed that ZnSthin films have very low reflectance in direct contrast to their transmittance. The reflectance reduced with increase in the incident photon wavelength from the visible to the near-infrared region and the reflectance reduced as the pH of the bath increased. The summary of the optical parameters for the electrodeposited ZnS layers are shown in Table 1.

The energy bandgap (E_g) of the electrodeposited ZnS layers was estimated from the graph of $(\alpha h\nu)^2$ against photon energy by extrapolating the straight-line portion of the graph with the photon energy axis where$(\alpha h\nu)^2 = 0$ in Figure 7. Energy bandgaps of 3.40 eV, 3.30 eV, and 3.20 eV were obtained at electrolytic bath pH of 4, 3, and 2 respectively. The energy bandgap for the electrodeposited layers increased as the pH of electrolytic bath increased. This is in line with the report of [16] but contradicts the report [15] in which the band gap energy decreased from 3.78 eV to 3.67 eV when the pH increased from 10 to 11.5.

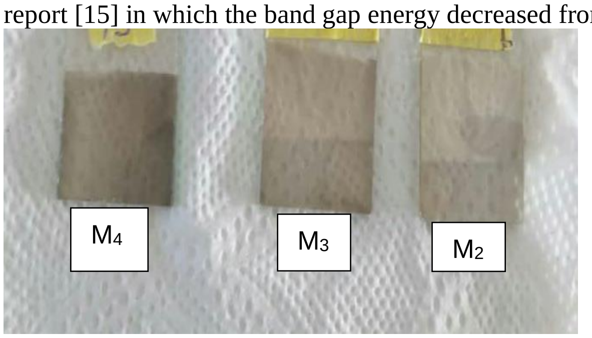

Fig 1: Visual appearance of the ZnS thin films grown at different temperature.

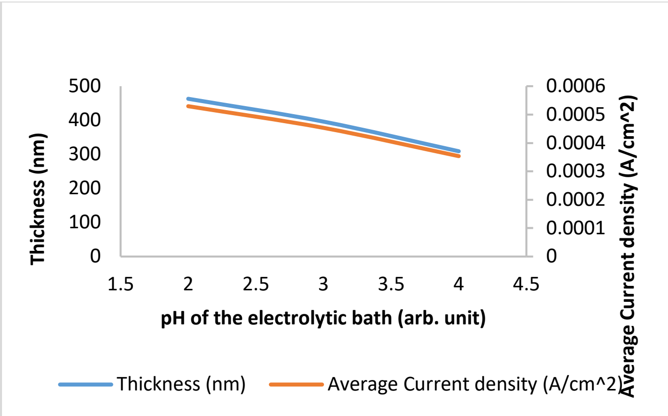

Fig 2: Variation of thickness and average current density with pH.

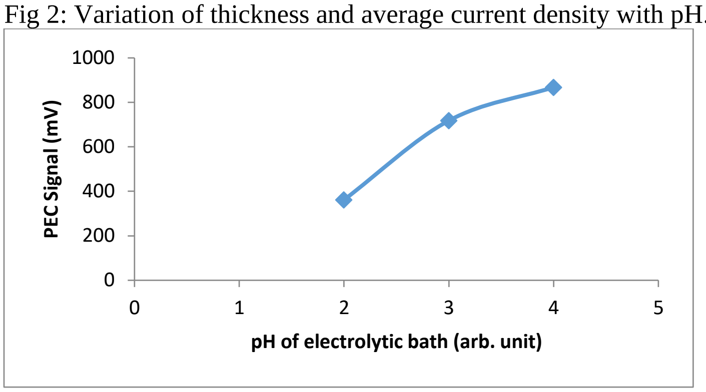

Fig 3: Variation of PEC signal against the pH of the electrolytic bath

Table 1: Summary of optical properties of electrodeposited ZnS thin film

Sample ID	Time (sec.)	Band gap (eV)	Average Transmittance	Average Reflectance	Average Absorbance	PEC values (mV)
M_4	1200	3.40	0.81	0.10	0.18	+868
M_3	1200	3.30	0.61	0.17	0.22	+718
M_2	1200	3.20	0.55	0.18	0.27	+362

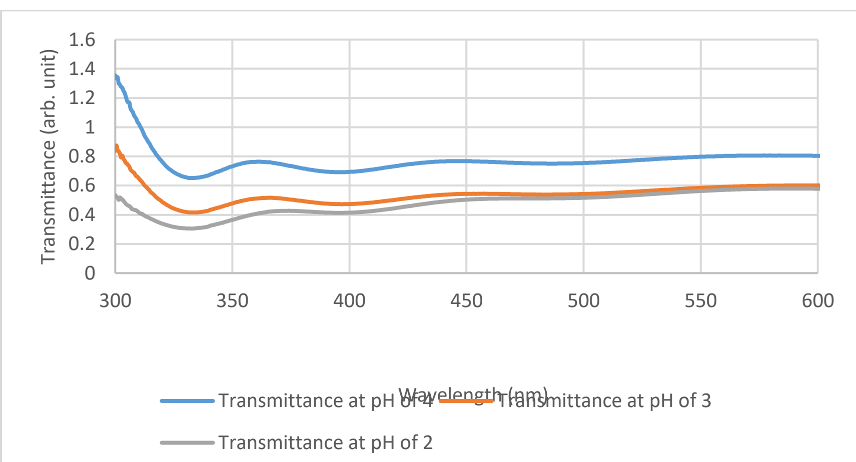

Fig 4: Variation of transmittance against wavelength of the electrodeposited ZnS layers

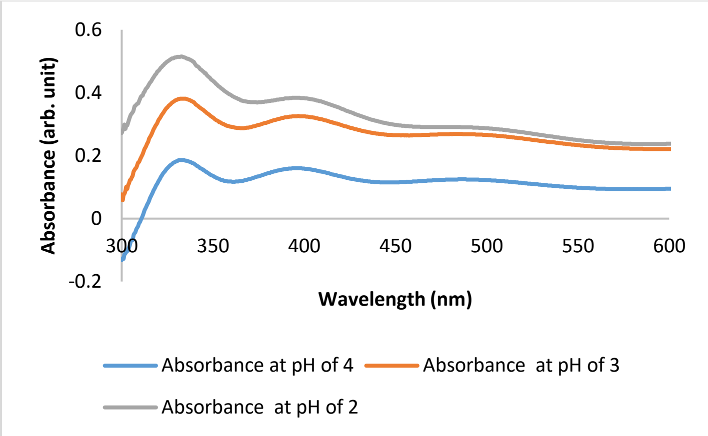

Fig 5: Variation of absorbance against wavelength of the electrodeposited ZnSlayers

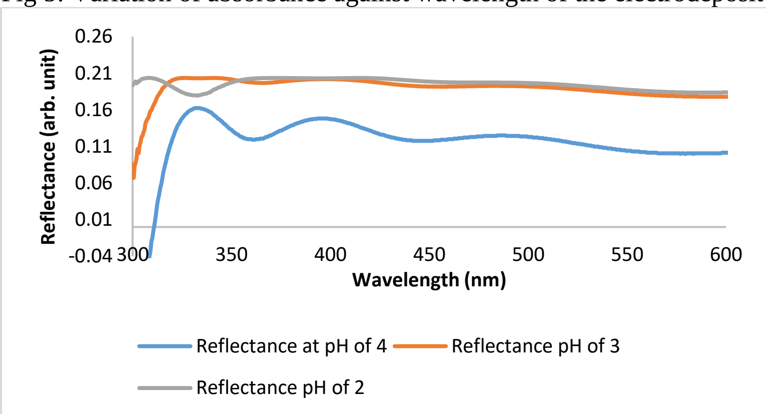

Fig 6: Variation of reflectance against wavelength of the electrodeposited ZnS layers

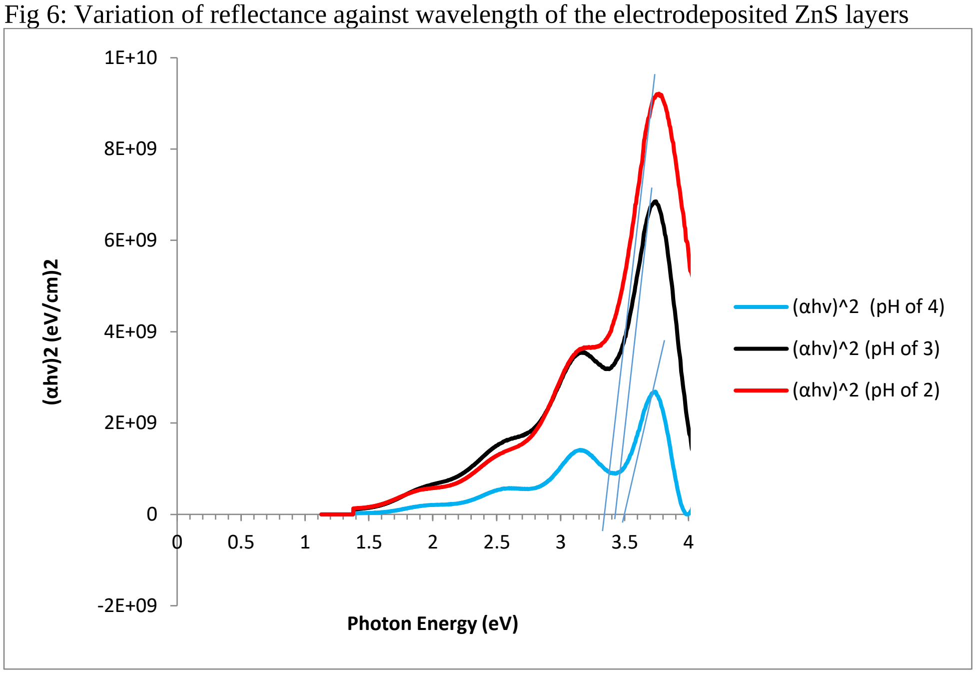

Fig 7: Variation of $(\alpha h\nu)^2$ against photon energy of the electrodeposited ZnS layers

4. CONCLUSION

The electrical and optical properties of electrodeposited ZnS thin film were studied for varying pH values. The thin films were all p-type in electrical conductivity. The average current density and thickness of the thin films decreased with increasing pH. The films showed high transmittance at the visible and near infrared regions. The energy bandgapZnS thin films obtained are comparable to the values reported in literature. The research revealed that varying pH has effect on the optical and electrical properties of ZnS thin films prepared via the electrodeposition method. However, changes in the pH do not have significant effect on the conductivity type of ZnS thin film.

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