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Research Article

Effects of Annealing Treatments on the Properties of Zinc Antimony Sulphide Thin Films

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ABSTRACT: *The effects of high temperature heat treatment on freshly grown zinc antimony sulphide thin films have been studied with the aim of improving the film electrical and optical properties. Such heat treatments were carried out less than 30 minutes after the ternary compound was co-deposited on plane glass substrates using a two-step chemical deposition technique of first growing binary ZnS and* Sb_2S_3 *separately and subsequently depositing one on top of the other to enable interfacial diffusion of atoms take place in the bi-layer stack that resulted in ternary zinc antimony sulphide,* $Zn_{1-x}Sb_xS$ $(0 < x < 1)$*, of variable stoichiometry across the junction. Such films however exhibited low crystal order which however became significantly improved after annealing at temperature of 250 ℃. The heat treatment also increased film optical transmittance from 31 % to 71 %, decreased the absorption coefficient from* $9.8x10^5$ m^{-1} *to* $3.1x10^5 m^{-1}$ *and increased conductivity from 0.0014* $\Omega^{-1}m^{-1}$ to 0.0016 $\Omega^{-1}m^{-1}$ *such that could render the films applicable in some optoelectronic technologies.*

KEYWORDS: *Zinc antimony sulphide, Annealing, Optical propertie, Absorption coefficient.*

I. INTRODUCTION

The interest in fabricating several ternary thin films has grown in recent years despite marked difficulties in fabricating good grades [1];[2];[3];[4];[5]. Ternary films often derive good characteristics from the two binary components that they are made of. For example, zinc antimony sulphide thin film has band gap of 2.20 eV – 3.10 eV [6], different from 1.50 eV – 1.80 eV obtained for antimony sulphide (Sb_2S_3) [7] and 3.60 eV for zinc sulphide (ZnS) in their bulk [8] but closer to the 2.20 eV obtained for thin film Sb_2S_3 [9]. Good grades of zinc antimony sulphide thin films have been reported to have electrical semiconductivity of 0.0014 - 0.0016 $\Omega^{-1}m^{-1}$ at small but optimum thickness of 344 nm [6]. This is useful in maintaining low series resistance and hence the compound could be applicable in integrated electronic circuitry. In this work, the lowest of such resistance was obtained at a treatment temperature of 250 ℃. The growth technique used in this work was the chemical bath deposition (CBD) which normally employs a liquid precursor, usually a solution of organic metallic powder dissolved in an organic solvent and kept in a reaction bath, where reaction takes place. When the ionic product (IP) exceeds the solubility product (SP), precipitation of compound takes place in the bath. If a suitable substrate, which can be metallic or not, is dipped in the bath, this precipitation on its surface results in growth of good stoichiometric thin film [10]. A one-step direct growth of stable zinc antimony sulphide of useful crystalline quality from same precursor solution containing ions of Zn, Sb and S was not possible in this

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work and has not been reported elsewhere. Hence a two-step chemical deposition technique was adopted by first depositing binary ZnS and Sb_2S_3 separately and subsequently depositing one on top of the other to form a composite ZnS-Sb_2S_3 stack deposit. Interfacial diffusion of atoms took place in the bilayer stack that resulted in ternary zinc antimony sulphide, $Zn_{1-x}Sb_xS$ ($0 < x < 1$), of variable stoichiometry. This co-deposited ternary film was annealed to enhance the formation of a single composite ternary nanofilm. In this work the substrate of choice was plane soda lime glass which has very good sticking coefficient to zinc sulphide.

II. EXPERIMENTAL DETAILS

Two reaction baths A and B were set up to grow ZnS and Sb_2S_3 respectively. Bath A contained 0.6g of $SbCl_3$ dissolved in 5ml of acetone, 10 ml of 1.0 M $Na_2S_2O_3$ (sodium thiosulphate) and 30ml of distilled water, the solution being stirred vigorously in a 50ml beaker. The glass substrate was dipped into the bath which was left for 13 minutes at room temperature and at a pH of 7. Acetone (CH_3COCH_3) acted as a complexant to enable slow release of Sb_2S_3 as follows [11]:

$$2SbCl_3 + CH_3COCH_3 \rightarrow 2Sb(CH_3COCH_3)^{3+} + 3Cl_2$$
$$Sb_2(CH_3COCH_3)^{3+} \rightarrow Sb^{3+} + CH_3COCH_3$$
$$Na_2S_2O_3 + OH^- \rightarrow Na_2SO_4 + HS^-$$
$$HS^- + OH^- \rightarrow H_2O + S^{2-}$$
$$2Sb^{3+} + 3S^{2-} \rightarrow Sb_2S_3$$

Bath B contained 3ml of 1.0 M$ZnCl_2$, 10 ml of 10.0 MNH_3, 5 ml of 1.0 MNH_2CSNH_2 and 20ml of distilled water. The pH of the solution was 11.0. The substrate was dipped and the bath was left at 51°C for 18 h during which grayish ZnS film deposited on the substrate following reactions complexed by ammonia as follows:

$$ZnCl_2 + 4NH_3 \rightarrow Zn(NH_3)_4^{2+} + 2Cl^-$$
$$Zn(NH_3)_4^{2+} \rightarrow Zn^{2+} + 4NH_3$$
$$NH_2CSNH_2 + OH^- \rightarrow CH_2N_2 + H_2O + HS^-$$
$$HS^- + OH^- \rightarrow H_2O + S^{2-}$$
$$Zn^{2+} + S^{2-} \rightarrow ZnS$$

The ZnS grown in bath B was removed, rinsed with plenty of distilled water, and transferred to a fresh bath of A for the stack growth of Sb_2S_3 on the ZnS. After 18 hrs, the ternary stack bilayer is removed, rinsed in plenty of distilled water, drip dried in dust-free environment and labelled 24A. The fabrication exercise was repeated but the as-grown deposits was annealed shortly (less than 30 min) after drying and labeled 24B. The heat treatment was for an hour at a temperature of 150 °C. Similar processes were carried out three additional times except that the deposits were annealed each for an hour at temperatures of 200 °C, 250 °C and 300 °C respectively and deposits labeled 24C, 24D and 24E respectively. Sticking quality consideration favoured stacking Sb_2S_3 on ZnS as against first growing Sb_2S_3 on the glass substrate and subsequently depositing ZnS on Sb_2S_3 layer.

The absorbance data of the films were obtained using UNICO-UV-2012PC spectrometer on the 200 – 1100 nm range of light at normal incidence to the samples. The electrical resistivity and sheet resistivity of thin films were measured using a QUADPRO, model 301 auto calculating four point probe and the thicknesses of films were deduced in Rutherford backscattering (RBS) analysis. The as-grown film as well as the heat treated films were subjected to X-ray diffraction (XRD) using Phillips X'pert PRO Diffractometer that applied Cu Kα

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radiator as choice X-rays of λ = 0.15406 nm to scan films continuously from 2θ = 10 – 99° in step size of 0.2° at room temperature of 288 K. This enabled the effect of heat treatment on the crystallinity of samples to be deciphered. From the absorbance data, the spectral transmittance, reflectance, refractive index, extinction coefficient and absorption coefficient were calculated using the well established relationships between them [12]. To enhance orderly crystal growth, the substrate surfaces were extensively pre-cleaned before deposition. They were dipped in hydrochloric acid for an hour, washed with distilled water and drip dried before use.

III. RESULTS AND DISCUSSIONS

3.1 RBS Results

The Rutherford backscattering analysis results for the as-grown film as well as that of film annealed at optimum temperature of 250°C. were as shown in Fig.1 and Fig.2 respectively. They reveal the thicknesses and percentage elements abundance in layer 1 (deposit) and layer 2 (substrate glass). It could be seen that annealing had deoxygenated the deposit while decreasing film thickness from 350 to 342nm. The substrate glasses were unaffected in their thicknesses and elemental composition. The variation of film thickness with annealing temperature was as shown in Fig.3. Beyond this optimum annealing temperature of 250°C, the thickness rose again. It appears that thermal oxidation had set in, beyond this temperature that would lead to the burning of the films.

3.2 X-ray Diffraction Results

The XRD analysis results carried out on the as-deposited sample and samples annealed for an hour at the temperatures already listed were consistent with the previous but recent work by this researcher [13] which revealed poor crystal order for as-deposited films but clear diffraction peaks and patterns for annealed deposits which pattern matched ICDD card no. 06-065-0309. Scherrer's formula [14];[15];[16] was applied to calculate the average size, D of crystal grain as:

$$D = \frac{0.89\lambda}{\beta \cos\theta} \tag{1}$$

where the X-ray wavelength used was λ, the angle of diffraction is θ and the radiation peak of X-rays of highest intensity has full width at half maximum β. The XRD analysis thus revealed average grain size of film to be 30.980 nm.

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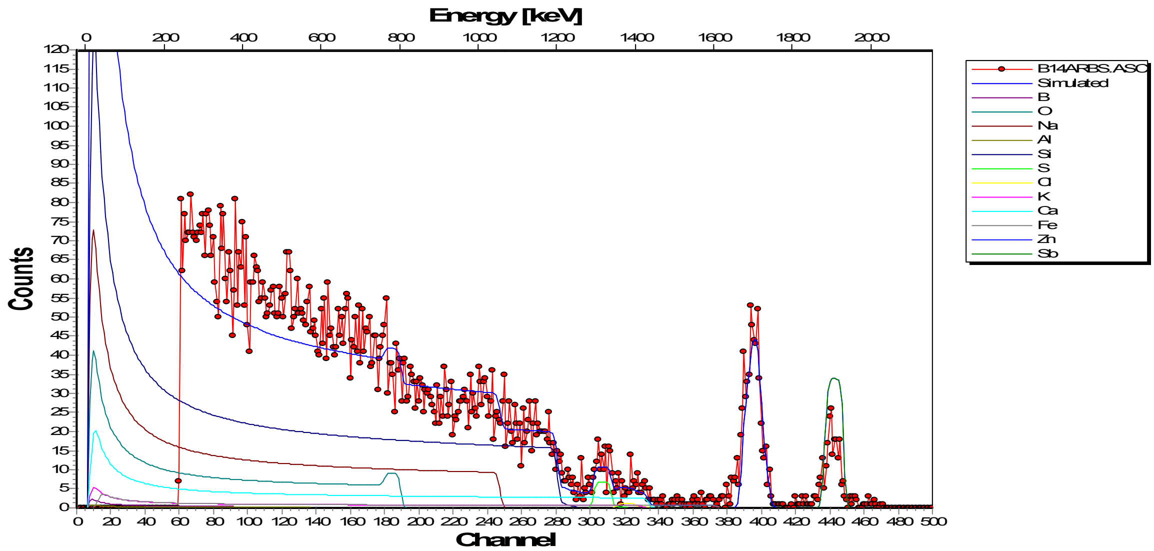

Fig.1: RBS Results for As-grown Zinc Antimony Sulphide Thin Film. Layer 1: Thickness. 350 nm. Composition: Zn 61.25 %, Sb 10.15 %, S 27.33 %, O 12.23 %. Layer 2: Thickness. 954740 nm. Compo: Si 31.97 %, O 32.89 %, Na 25.85 %, Ca 1.64 %, Al 0.25 %, K 1.05 %, Fe 0.38 %, B 5.89 %.

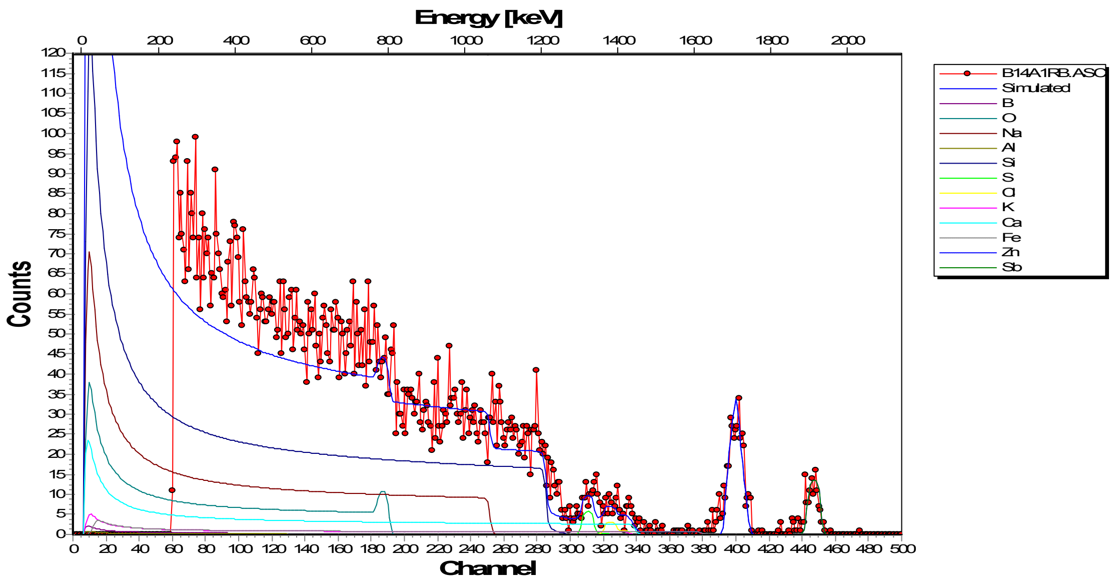

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Fig. 2: RBS Results for Zinc Antimony Sulphide Thin Film Annealed at 250 °C. Layer 1: Thickness 342 nm. Compo: Zn 55.87 %. Sb 12.46 %, S 31.63 %, O 0 %. Layer 2: Thickness. 954740 nm. Compo: Si 31.97 %, O 32.89 %, Na 25.85 %, Ca 1.64 %, Al 0.25 %, K 1.05 %, Fe 0.38 %, B 5.89 %.

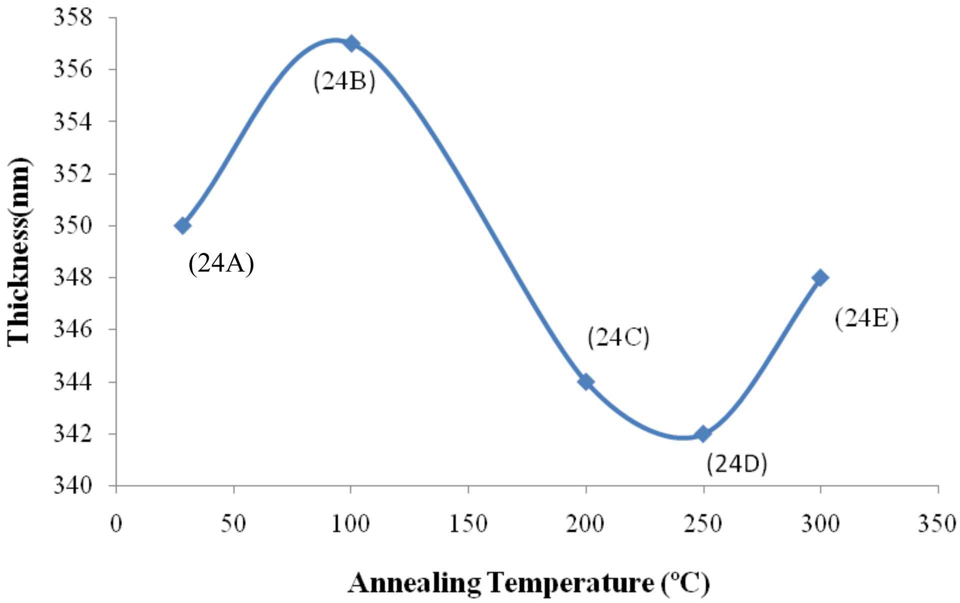

Fig. 3: Thickness Vs Annealing Temperature for Zinc Antimony Sulphide

3.3. Optical Results

The absorbance results are as shown in Fig. 4 while those of estimated transmittance, reflectance, refractive index , extinction coefficient and absorption coefficient, are as shown in Figs. 5, 6, 7, 8 and 9 respectively for samples 24A, 24B, 24C and 24D. The absorbance values which varied from 0.15 to 0.4 in the visible frequencies became fairly stable at 0.23 from yellow to near infra red ranges but became very high from violet toward ultra violet region. The transmittance was higher (71 %) in heat treated films than (31 %) in as-grown film. The reflectance was as low as 14 % for treated films but as high as 21 % for as-deposited film. The same trend followed for refractive index, extinction coefficient and absorption coefficient which was found to be high ($9.8x10^5$ m^{-1}) for as-deposited film but very low ($3.1x10^5$ m^{-1}) for treated film.

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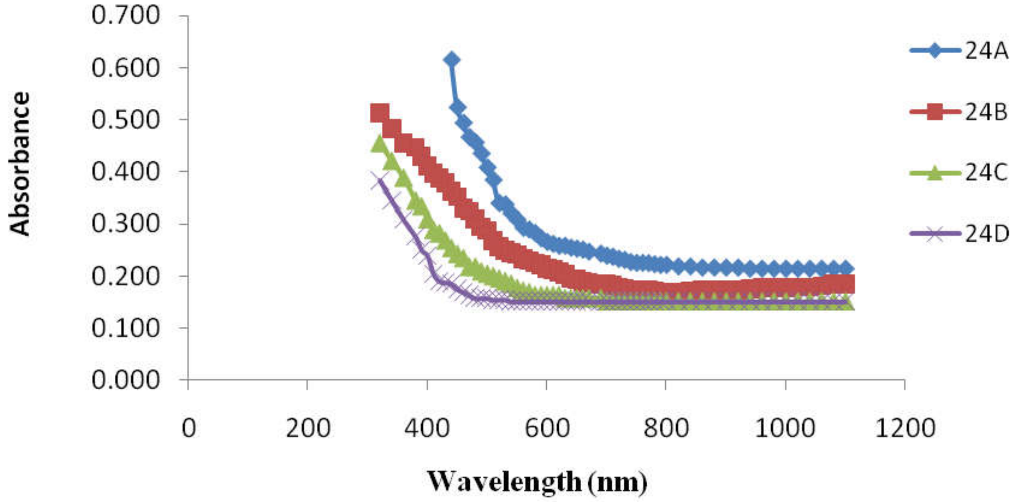

Fig. 4: Spectral Absorbance of Zinc Antimony Sulphide Annealed at Various Temperatures

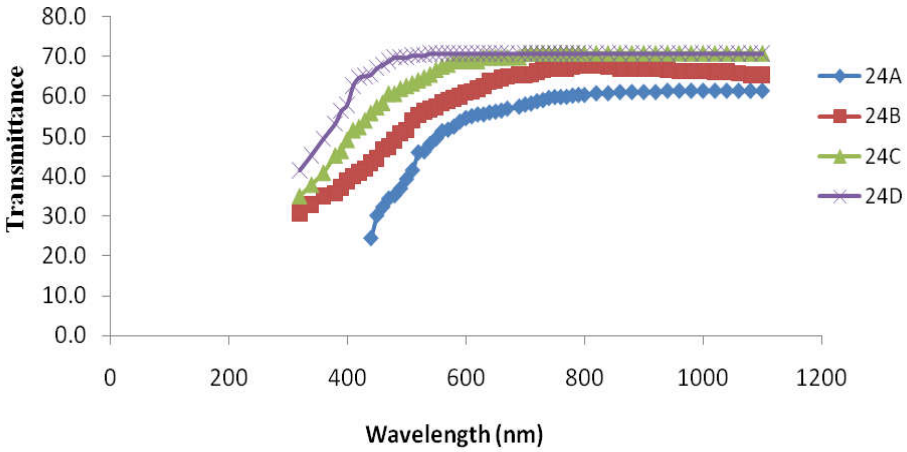

Fig.5: Transmittance Spectra of Zinc Antimony Sulphide Thin Films Annealed at Various Temperatures

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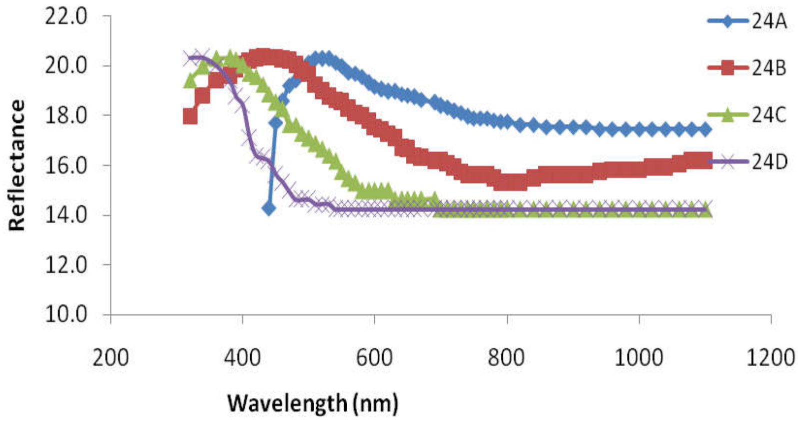

Fig.6: Reflectance Spectra of Zinc Antimony Sulphide Thin Films Annealed at Various Temperatures

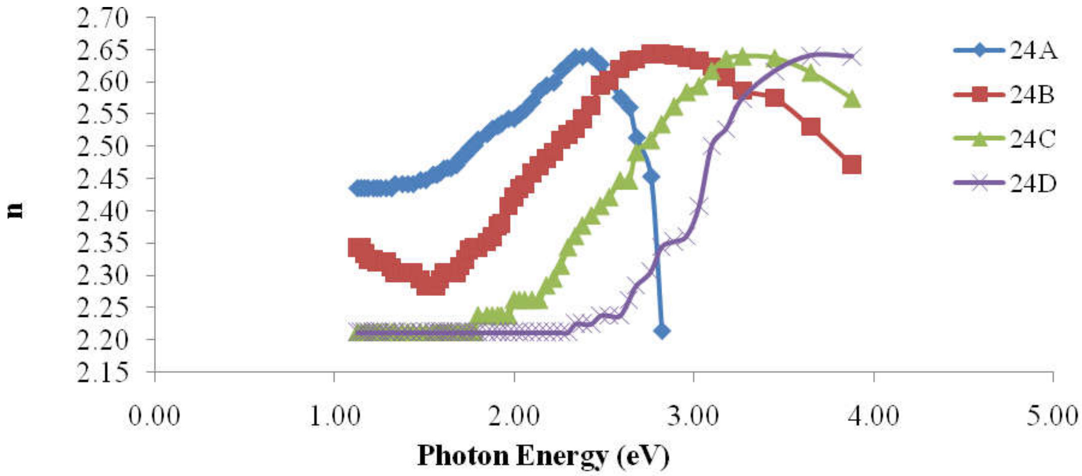

Fig. 7: Refractive Index Vs Photon Energy for Zinc Antimony Sulphide Annealed at Various Temperatures

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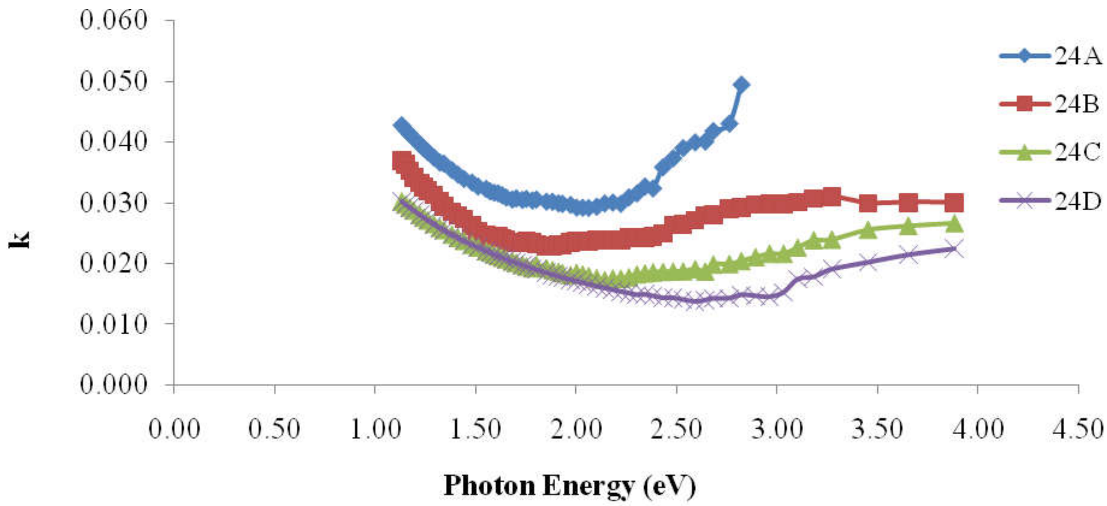

Fig. 8: Extinction Coefficient Vs Photon Energy for Zinc Antimony Sulphide Annealed at Various Temperatures

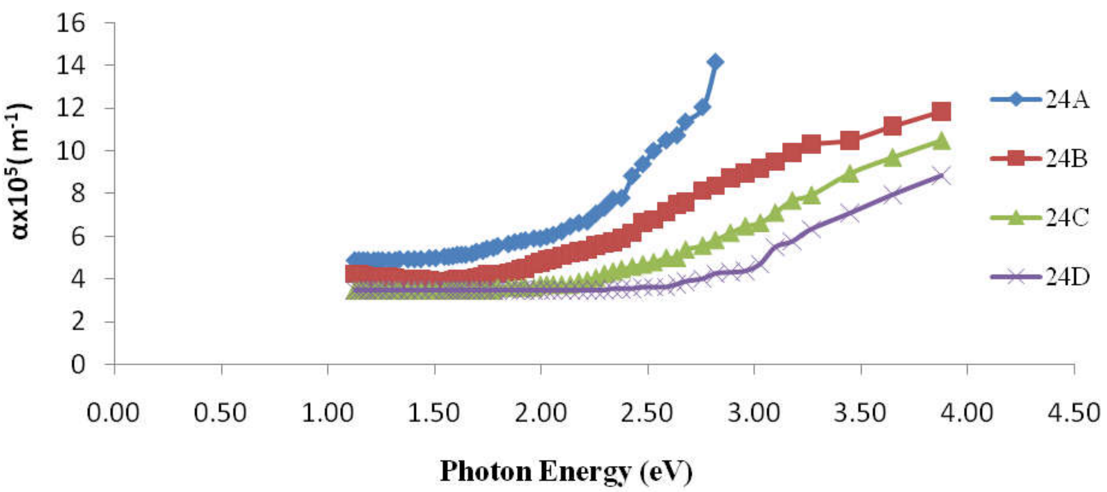

Fig. 9: Absorption Coefficient Vs Photon Energy for Zinc Antimony Sulphide Annealed at Various Temperatures

3.4 Four Point Probe Results

Research Article

The QUADPRO model 301 auto calculating four point probe analysis of resistivity profile carried on the surface of fabricated films revealed the electrical properties of films as given in Table 1. The heat treatment increased film electrical conductivity.

Table 1. Electrical Propertiies of as-deposited and Annealed Films

	Resistivity (Ωm)	Sheet resistance (x10^8 Ωsq)	Conductivity ($Ω^{-1}m^{-1}$)
As-deposited film	702	20.35	0.0014
Film annealed at 250 °C	625	18.44	0.0016

IV. CONCLUSION

The effects of annealing treatments on the optical properties of freshly deposited stack ZnS-Sb_2S_3 thin films have been investigated. The co-deposition CBD technique used produced nanofilms of grain sizes 30.98nm. The as-deposited film was amorphous while film annealed at 250°C showed reasonable crystalline order. The RBS results revealed a thermal de-oxygenation of films and annealing enabled formation of films of thickness 342 nm, resistivity 625Ωm, absorption coefficient 3.1x 10^5 m^{-1} and transmittance 71%. The effects of these heat treatments on energy gaps of film samples are currently being studied but the possible applications of zinc antimony sulphide as series resistors in electronics and as optical windows in solar cells are suggested.

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