OPTICAL PROPERTIES OF CHEMICAL BATH DEPOSITED CdS/PbS HETEROJUNCTION THIN FILMS: EFFECTS OF ANNEALING TREATMENTS

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Chemical bath deposition technique has been used to grow heterojunction thin films of CdS/PbS on soda lime plane glass substrates and the effects of high temperature annealing on the properties of films studied. A two-step deposition technique was adopted of first chemically depositing one binary components of the stack, that is, PbS on the substrate and subsequently growing CdS on top of PbS to form a stack CdS/PbS which when thermally annealed at sufficiently high temperatures, yielded $Cd_{1-x}Pb_xS$ ($0<x<1$). Such post-deposition heat treatment was done on thin films at various temperatures before they were subjected to elemental, structural and optical characterization using the techniques of Rutherford backscattering, X-ray diffraction and UV-VIS-NIR spectrophotometry respectively. It was found that heat treatment increased spectral absorbance. It also deoxygenated the films leaving the presence of only Cd, Pb and S in their various percentage abundances that resulted in thin films of hexagonal structure of average grain size 19.33 nm, band gap of 2.30 eV. and transmittance of up to 80 % suitable to apply in solar cells, protective coatings and photodetectors.

(Received March 28, 2018; Accepted May 16, 2018)

Keywords: Thin film, CdS/PbS stack, Chemical deposition, Band gap, Annealing

1. Introduction

A material becomes a thin film when it is built up as a thin layer on a substrate by controlled condensation of the individual atomic, molecular or ionic species either directly by a physical process or through a chemical and/or electrochemical reaction. Otherwise, it is a thick film [1-3]. Thin film semiconductors have attracted much interest for their expanding applications in electronic and optoelectronic devices due to their low production cost. Thin film can be made of single or multi-layer coatings on the substrates of different shapes and sizes [4]. Any two layers of semiconductors of different band gaps forms a heterojunction that can be either isotype or anisotype depending on the p or n conductivity type of the layers.

In this work, heterojunction CdS/PbS thin films were fabricated using a two-step chemical bath deposition technique (CBD) [5] of first growing PdS and CdS thin films separately on soda lime plane glass substrates and subsequently growing one on top of the other to form a stack of two layers that presented the heterojunction. The CBD technique has gained prominence in recent time for its simplicity, low cost and applicability for large area and irregular surface coverage and has been previously used successfully to deposit binary metal chalcogenides of PbS [6] and CdS [7,8] as well as ternary heterojunction nano films like CdS/CuS [9,10]. Various other techniques of fabricating thin films however also exist [11]. In this work, sticking coefficient consideration [12-14] required that PbS be first deposited to the substrate and subsequently CdS deposited on PbS.

It is known that Cadmium Sulphide (CdS) is a very promising II-VI thin film material because of its wide range of applications in various optoelectronic, piezo-electronic and semi-conducting devices [15]. Its wide direct band-gap (2.42 eV), refractive index 2.5 and n-type semiconductivity [16] makes it very useful as window material in CdTe devices for the fabrication of solar cells [17]. CdS has poor conductivity, usually as low as 10^{-8} $\Omega^{-1}m^{-1}$ [18]. On the other

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hand, PbS belongs to IV–VI group semiconductor with a direct narrow band gap (0.41 eV) suitable for infrared detection applications. It is also used as a photo resistance, laser diode, humidity and temperature sensors, decorative coatings and solar control coatings [19]. As both CdS and PbS are highly sensitive to light and in view of their practical applications, a study of their mixed thin films structure is expected to be of technical importance. It has been severally observed that the band gap of ternary thin films have values between those of binary components. Heat treatment enhances the formation of heterojunction when ternary films form from stacks of binary components. This research contributes in understanding the effect of such heat treatment in form of thermal annealing on the band gap and some other essential thin film properties.

2. Experimental details

The two-step co-deposition technique used in this work required that two chemical baths – bath A and bath B be used to deposit the binary film components: PbS and CdS respectively. The first step was to mix onto bath **A** 10.0 ml of 0.1 M $Pb(NO_3)_2$, 5.2 ml of 1.0 M NaOH, 6.0 ml of 0.6 M thiourea, the mixture being vigorously stirred. Distilled water was added to make the mixture up to 40.0 ml. Prepared microscope slides were loaded into the bath and left at room temperature for 20 minutes after which the glass, now covered by dark PbS deposits, were removed, rinsed in distilled water and left to drip-dry in dust-free air. Bath B was prepared by mixing onto it 4.0 ml of 0.8 M $CdCl_2$, 5.1 ml of NH_3 (aq) solution, 5.1 ml of 1.0 M thiourea $(NH_2)_2CS$, and 30.2 ml distilled water in a 50.0 ml beaker, these contents being vigorously stirred for 20 seconds. To grow CdS thin films, pre-cleaned glass substrates were vertically inserted in the solution and suspended from a synthetic foam which rested on top of the beaker. The bath was left for three hours at room temperature, after which the glass slides covered with yellowish CdS deposits were removed, rinsed in distilled water and left to drip-dry in dust-free air. Both films were deposited basically by the hydrolysis of thiourea in an alkaline solution containing lead (Bath A) and cadmium salts solution (Bath B). NaOH acted as a complexant in bath **A** while Ammonia (NH_3) did same in bath **B**. Stack CdS/PbS (labeled 14A) was achieved by dipping film product of bath A into fresh bath B. Formation of heterojunction continued up to two hours after the end of second deposition by the crossover of charge carriers across the junction. This carrier migration was enhanced by heat treatment of films. Hence similar growth processes were repeated as given above four other times except that each film was post deposition thermally annealed for an hour at a temperature of 100 ℃, 150 ℃, 200 ℃ and 250 ℃ and labeled 14B, 14C, 14D and 14E respectively.

Successfully grown films were subjected to Rutherford backscattering (RBS) using proton-induced X-ray emission (PIXE) scans from a Tandem Accelerator model 55DH by National Electrostatic Corporation (NEC) which deciphered the elements in both deposits and substrates. The RBS analysis also deciphered the thicknesses of deposits as well as substrates. The structure of films were obtained using X'Pert–Pro diffractometer which used Cu Kα radiator of $\lambda = 0.15406$ nm to scan films continuously as 2θ varied from 0 – 100^o at a step size of 0.02^o and at a scan step time of 0.2 s. A UV-VIS-NIR spectrophotometer was used to obtain the absorbance spectra of the films from where energy band gaps and other film spectral variations of transmittance, reflectance and refractive indices were deduced using their well known mathematical relationship with the absorbance [20,21].

3. Results and discussions

3.1 Elemental results

The Rutherford backscattering results for as-grown film and also film annealed at temperature of 150 ℃ were as shown in Figs. 1 and 2 respectively. It can be seen that the heat treatment had removed the small oxygen content seen in the as-grown film to reveal only Cd, Pb and S as in the annealed film. The heat treatment also reduced the thickness of deposit while leaving the substrate unchanged. The percentage abundances of the elements which were also deciphered in the backscattering were as shown in the figures.

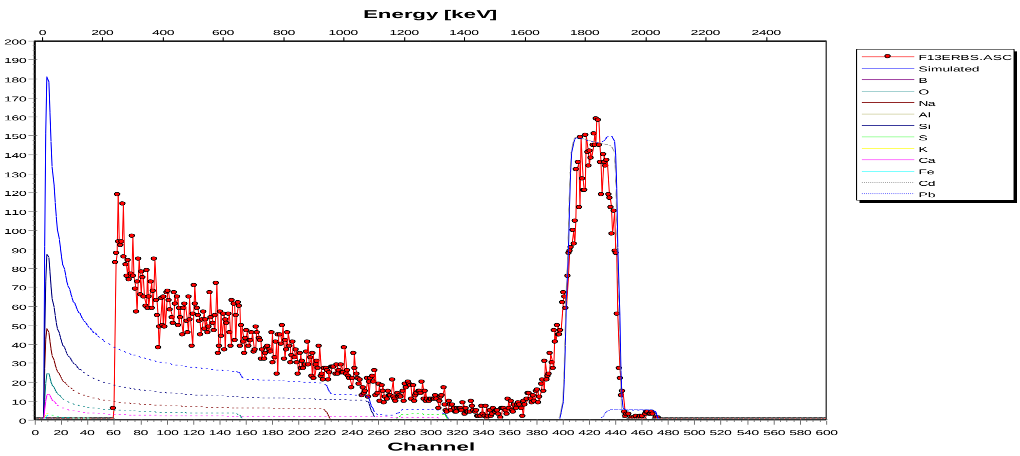

Fig. 1. RBS result for as-grown CdS/PbS thin film. Layer 1: Thickness: 440 nm. Compo: Cd 83.29 %. Pb 1.10 %. S 15.62 % O 0.16 %. Layer 2: Thickness 677899 nm, Compo: Si 31.97 % . O 32.89 %. Na 25.85 %. Ca 1.64 %. Al 0.25 %. K 1.05 %. Fe 0.38 %. B 5.89 %. Layer 1 refers to thin film sample while layer 2 refers to substrate.

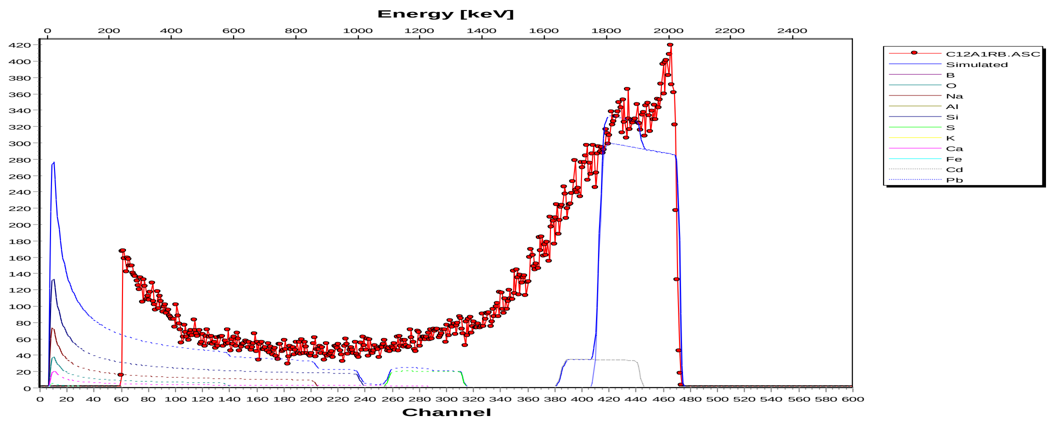

Fig. 2. RBS micrographs of annealed cadmium lead sulphide thin film. Layer 1: Thickness: 390 nm. Compo: Cd 83.31 %. Pb 1.10 %. S 15.62 %. Layer 2: Thickness 677899 nm, Compo: Si 31.97 % . O 32.89 %. Na 25.85 %. Ca 1.64 %. Al 0.25 %. K 1.05 %. Fe 0.38 %. B 5.89 %.

3.2 Structural results

The X-ray patterns of the as-deposited thin film and those deposited at annealing temperature of 150 °C were as given in Figs. 3 and 4. The as-deposited film at room temperature of 27 °C was clearly amorphous while the heat treated films were clearly crystalline with a phase that had prominent peaks and pattern that matched ICDD card no. 03-065-61623 which displayed for each angle 2θ such diffraction planes (hkl), of plane sizes d and full width at half maximum (FWHM) that are shown in table 1. The average grain sizes, D of the heterojunction films were obtained using Debye-Scherrer's formula [22-26].

$$D = \frac{0.9\lambda}{B\cos\theta} \tag{1}$$

where λ is the wavelength of X-rays = 0.15406 nm, B the full width at half maximum (FWHM) of the peak with the highest intensity and θ is the diffraction angle. Such average calculated grain size was 19.33 nm which revealed the film nanosize. Work is on going to determine details of other crystal phases all of which could conform to $Cd_{1-x}Pb_xS$ $(0<x<1)$.

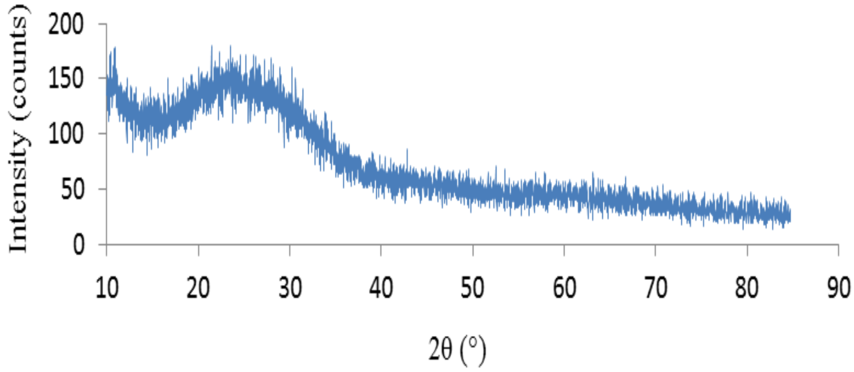

Fig. 3 XRD Pattern for As-deposited Zinc Antimony Sulphide Thin Film.

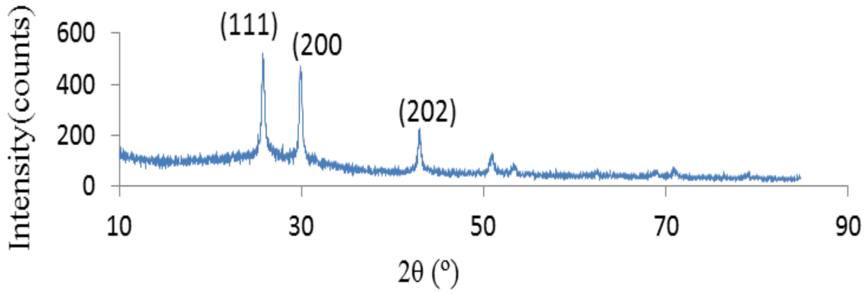

Fig. 4 XRD pattern of as-dposited CdS/PbS thin films.

Table 1. XRD Result for Cadmium Lead Sulphide, Card 03-065-61623.

h k l	d(A°)	2Theta (°)	FWHM	D(nm)
1 1 1	6.4732	26.07	0.7476	19.04
2 0 0	6.0731	30.25	0.7077	20.30
2 0 2	5.1355	43.08	0.7941	18.84

Average D: 19.33 nm

3.3 Optical analysis results

The spectral absorbance of the ternary cadmium lead sulphide film is as shown in Fig. 5 while those for transmittance, reflectance and refractive index are as shown in Figs. 6, 7 and 8 respectively. The absorbance was generally low, less than 0.05 in the NIR, between 0.09 – 0.25 in the VIS and very high n the UV. In most of the VIS (< 550 nm), the absorbance increased with annealing temperature. Conversely, the transmittance of heat treated films was high in the VIS (60 % – 80 %) but all good films converged to very high transmittance of between 86.8 and 90.8% in the UV frequencies. The removal of oxygen impurity and formation of ordered molecular arrangements as a result of heat treatment may have been responsible for these. The refractive index of the films (Fig. 8) which varied widely from 1.56 – 2.60 depended heavily on frequency rather than on heat treatment. This was also true for extinction coefficient which varied from 0.005 to 0.025 depending heavily on the frequency rather than on annealing temperature.

The film absorption coefficient, α is related to the transmittance, T as:

$$\alpha = \mathrm{Ln}T^{-1}x10^{6}(m^{-1}) \quad (1)$$

Absorption coefficient can be used to obtain the band gap Eg of thin film semiconductor film as [27,28].

$$\alpha h\nu = A(h\nu - E_g)^n \quad (2)$$

Hence,

$$\mathrm{Ln}\ \alpha h\nu = n\mathrm{Ln}\ (h\nu - E_g) + \mathrm{Ln}\ A \quad (3)$$

where h is the Planck's constant, ν the wavelength of radiation, A is a constant and n assumes values of 1/2, 2, 3/2 and 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. Equation 3 was used to obtain n to be 0.5 which suggested direct allowed transition.

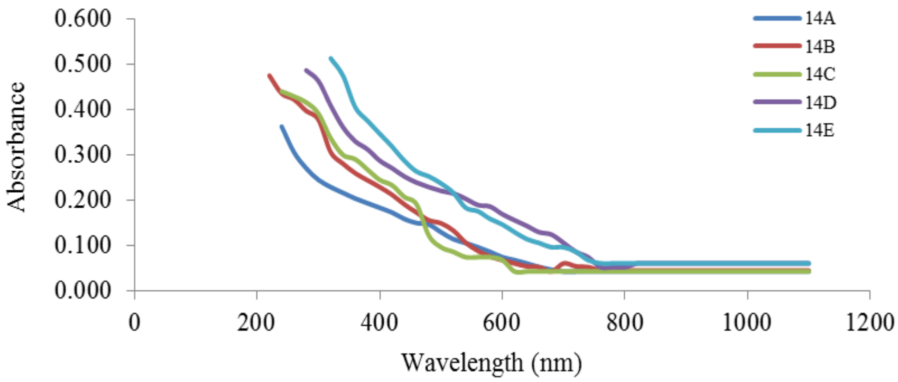

Fig. 5 Absorbance against wavelength for CdS/PbS

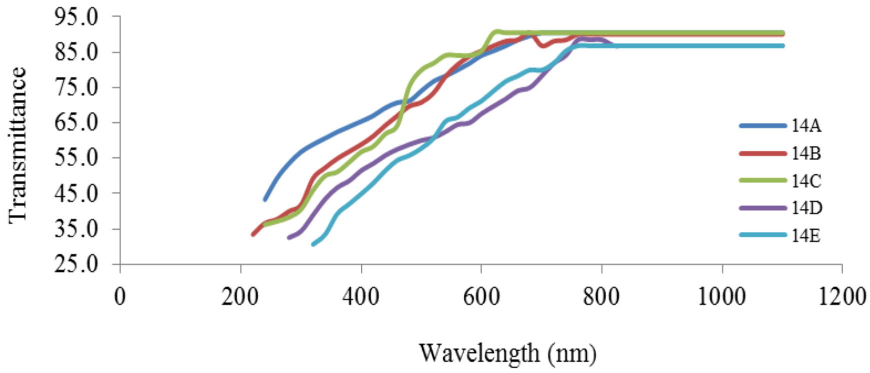

Fig. 6 Transmittance against wavelength for CdS/PbS thin films.

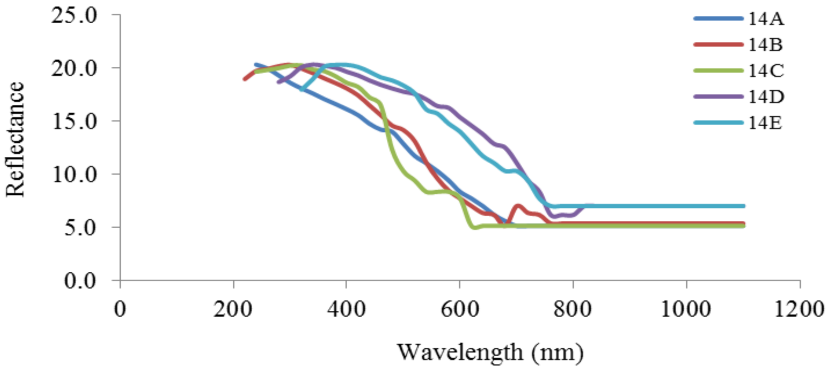

Fig. 7. Spectral reflectance of CdS/PbS thin films.

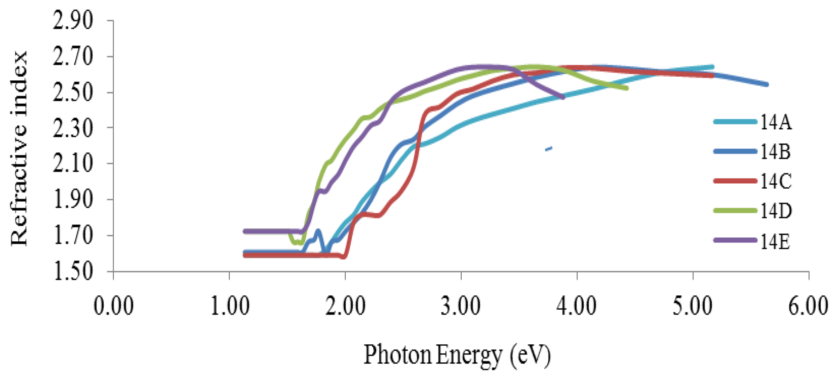

Fig. 8. Refractive index against photon energy for CdS/PbS thin films

For such direct allowed transition

$$(\alpha h\nu)^2 = A^2 (h\nu - E_g) \tag{4}$$

Plots of $(\alpha h\nu)^2$ against $h\nu$ were as shown in Fig. 9 from where the linear potions were extrapolated to the horizontal axis to reveal the band gap. The non linearity of the plots at low values of photon energy could be attributed to domination of other factors different from inter band transition in which equation 3 depends on. A close look at the Fig. 9 however shows non linearity for as-grown film and that thermally annealed at 100 ℃ throughout the energy spectrum covered which suggested very low crystal order of these samples. All the thermally annealed films had band gap of 2.3 eV. It therefore appeared that annealing at any temperature higher than 150 ℃ was unnecessary. However, in a similar study on thermal annealing effect carried out but on PVA-capped PbO thin film, Asogwa [26] reported that similar heat treatment resulted in decrease in band gap.

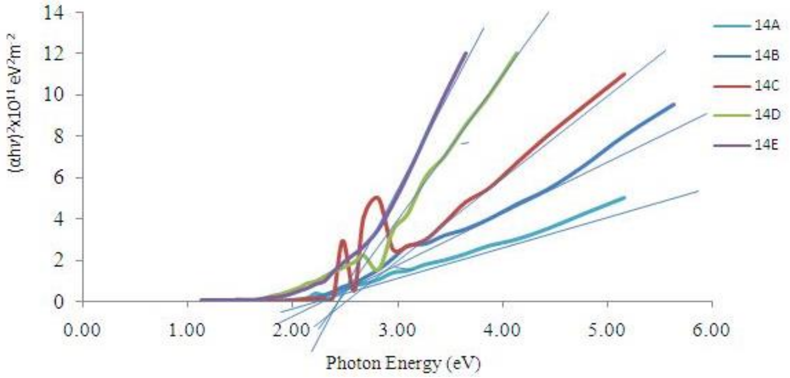

Fig. 9 (αhν)^2 agains photon energy for Cd/PbS thin films

4. Conclusions

The effects of thermal annealing treatments on the properties of chemical bath deposited stack films of CdS/PbS have been presented. As-deposited stack films were only amorphous or non crystalline while those thermally annealed at 150 ℃ exhibited impressive crystalline features with band gap of 2.3 eV. Optical transmittance was as high as 80 %. These results provide good basis for specific applications of the stack thin films in solar cells, protective coatings and photodetectors.

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