Heat Treatment Effects on Properties of CdS/PbS Heterojunction Thin Nanofilms

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Abstract-At different temperatures, CdS/PbS heterojunction thin nanofilms grown in polymer matrix have been annealed and the effects of the heat treatments on the solid state and electrical properties of the films studied. The films were fabricated from direct condensation of ionic species that derived from $CdCl_2$, $PbNO_3$ and NH_2CNH_2 in a chemical deposition technique. Suitable capping pores presented by polyvinyl alcohol growth medium enabled early and rapid crystallization onto the surface of plane glass substrate. A two-step approach was used to first grow PbS crystals on top of the substrate and then grow CdS crystals on top of the PbS. The CdS/PbS composite was quickly annealed for an hour at a time at various temperatures between 300K and 673K which resulted in a re-crystallization into a pure $Cd_{1-x}P_xS$ of various stoichiometry where $0 < x < 1$. The fabricated thin films were tested for their surface microstructure, crystallinity, elemental compositions, grain sizes, thickness, electrical resistivity and sheet resistance. Whereas resistivity of the samples decreased sharply, from $200\Omega m$ to $100\Omega m$, with rise in annealing temperature, the grain size increased, from 15.5nm to 44.0nm, enabling marked decrease in the thickness of thin films, from 365nm to 320nm.

Keywords- Annealing, Grain Size, Heterojunction, Nano Films, Recrystallization

I. INTRODUCTION

The science of condensation of atomic, molecular or ionic species by either physical processes or chemical reactions to form ordered thin film (TF) semiconductor crystal is now well understood [1,2,3,4,5]. The orderliness of the crystal is usually enhanced through high temperature annealing. Annealing is of special importance in the development of good grade ternary, quaternary and multinary semiconductors especially when useful heterojunction formation is required [6]. This researcher and his team have been previously involved in developing ternary semiconductors in a two-step chemical bath deposition (CBD) technique in which binary components of the films are fabricated, one on top of the other, in a stack [7,8]. Ternary thin films always derive good characteristics from the separate properties of the two binary components that they consist of. For example, zinc antimony sulphide thin film has band gap of $2.20 \text{ 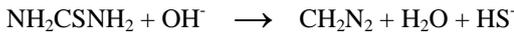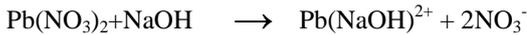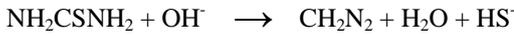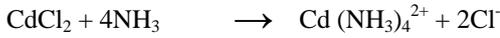eV} - 3.10 \text{ eV}$ [9], different from $1.50 \text{ eV} - 1.80 \text{ eV}$ obtained for antimony sulphide (Sb_2S_3) [10] and 3.60 eV obtained for zinc sulphide (ZnS) in their bulks [11] but closer to the 2.20 eV obtained for thin film Sb_2S_3 [12,13]. In the cadmium lead sulphide TF recently developed using the two-step chemical bath deposition technique [7], the poor crystallinity achieved in as-grown TF improved significantly after annealing even at fairly high temperature such as 120℃. The same experience has variously been reported by other researchers [14,15]. This research seeks to understudy the specific effects of heat treatment on the morphology and properties of cadmium lead sulphide TFs using our already reported two step CBD technique.

II. EXPERIMENTAL DETAILS

Two-step method was used which involved two chemical baths, A and B. This involved fabricating two metal-sulphides: PbS and CdS which are binary thin film components of the cadmium lead sulphide ternary film, one on top of the other, but both on a single substrate. The two chemical baths A and B, containing solutions that could precipitate and grow both corresponding binary thin films were made and the substrate dipped in one bath A to grow first binary film at room temperature. After this, the newly grown binary film in glass substrate was transferred onto the fresh bath B to enable a growth, also at room temperature, of the second binary film on top of the first. A bilayer stack thin film was thus formed on the glass substrate and a heterojunction developed. Even after removal of this composite film from the second bath B, a heterojunction ternary metal-metal sulphide compound continued to develop across the junction for about two hours [7]. This development was enhanced through post-deposition annealing at various temperatures. Such annealing facilitated crossover of charges across the junction. Bath A was used to deposit CdS while bath B was used to deposit PbS binary thin films. Bath A was prepared by mixing 4 ml of 0.8 M $CdCl_2$, 5 ml of NH_3(aq) solution, 5 ml of 1 M $(NH_2)_2CS$ and 30 ml polyvinyl alcohol in a 50 ml beaker, these contents of pH = 8.3 being vigorously stirred for 20 seconds. The loaded slide, 18A was removed after 2 hrs at room temperature with yellowish CdS deposits on it. Bath B was prepared by measuring into it 10 ml of 0.1 M $Pb(NO_3)_2$, 5 ml of 1 M NaOH, 6 ml of 0.6 M $(NH_2)_2CS$ with vigorous stirring. Polyvinyl alcohol was added to make up the solution up to 40 ml that was still stirred into a

homogenous solution of pH = 9.0. Prepared microslide which was loaded and left for 20 minutes at also room temperature was covered by dark PbS deposits and labeled 18B.

Both TFs were deposited basically by the hydrolysis of thiourea in an alkaline solution containing cadmium (Bath A) and lead (Bath B) salt solution. Ammonia acted as a complexing agent in bath A while NaOH did same in bath B.

$$CdCl_2 + 4NH_3 \longrightarrow Cd(NH_3)_4^{2+} + 2Cl^-$$

$$Cd(NH_3)_4^{2+} \longrightarrow Cd^{2+} + 4NH_3$$

$$NH_2CSNH_2 + OH^- \longrightarrow CH_2N_2 + H_2O + HS^-$$

$$HS^- + OH^- \longrightarrow H_2O + S^{2-}$$

$$Pb(NO_3)_2 + NaOH \longrightarrow Pb(NaOH)^{2+} + 2NO_3^-$$

$$Pb(NaOH)^{2+} \longrightarrow Pb^{2+} + NaOH$$

$$NH_2CSNH_2 + OH^- \longrightarrow CH_2N_2 + H_2O + HS^-$$

$$HS^- + OH^- \longrightarrow H_2O + S^{2-}$$

$$Pb^{2+} + S^{2-} \longrightarrow PbS$$

The deposition of CdS thin film on top of PbS to form the CdS-PbS stack was achieved by dipping substrate (glass), with PbS deposit on it, on fresh bath of A to form CdS/PbS stack labelled 18D.

Similar growth processes as in 18D were repeated five more times except that each was similarly annealed except at different temperatures 423K, 473K, 523K, 573K 623K and 673K and labeled 18E, 18F, 18G, 18H, 18I and 18J respectively. The TFs were subsequently tested for any temperature induced changes in crystal morphology, solid state and electrical properties.

It has been shown [7] that the band gap of the ternary heterojunction thin film thus formed from the binary components will take values somewhere between those of both binary thin films but with the band gap of the binary TF away from the substrate having predominant influence. This informed the order of growth arrangement in this work in which CdS TF was stacked upon PbS already grown on the glass substrate. This order favoured higher sticking coefficient as the TF of PbS is more strongly bonded on Boroscillicate glsss than CdS does.

A QUADPRO model 301 auto-calculating four point probe was used to profile TF surface for sheet resistivity and electrical resistivity. For very accurate measurements, the technique requires separate pairs of current-carrying and voltage-carrying electrodes which when simultaneously contacted to the thin semiconductor with probe separation s, the resistivity could be given as [16]:

$$\rho_m = 2\pi s \frac{V}{I} \qquad (1)$$

where the subscript m indicated a measured resistivity, V is potential difference and I the current. The measured value ρ_m becomes equal to the actual value ρ only if the semiconductor sample is of infinite size. For the finite semiconductor TF

fabricated therefore a correction factor, a is introduced whenever the distance from any probe to the nearest boundary is less than or equal to 5s or whenever t/s < 5 where t is the TF thickness. Thus:

$$\rho_m = 2\pi a s \frac{V}{I} \qquad (2)$$

Since film thickness, t << s in this work, current would ring out from probe points, instead of spheres as in the bulk three dimensional semiconductors. The differential resistance is therefore given as:

$$\Delta R = \rho \frac{ds}{dA} \qquad (3)$$

Therefore,

$$R = \int_{x1}^{x2} \rho \frac{dx}{2\pi xt} \qquad (4)$$

where $2\pi xt$ is the cross-section area of thin film of thickness t. Therefore,

$$R = \int_{x1}^{x2} \rho \frac{dx}{2\pi xt} \qquad (5)$$

$$= \int_{s}^{2s} \rho \frac{dx}{2\pi tx}$$

$$R = \frac{\rho}{2\pi xt} Ln\ 2 \qquad (6)$$

Therefore,

$$\rho = 2\pi Rt/Ln\ 2$$

$$= \frac{2\pi t}{Ln\ 2} \left(\frac{V}{I} \right) \qquad (7)$$

Sheet resistivity can generally be expressed as $\rho/t = R_s$, where:

$$R_s = k \left(\frac{V}{I} \right) \qquad (8)$$

and k is a geometric factor which does not depend on the probe spacing. In fact [16]:

$$k = \frac{2\pi}{Ln\ 2} = 9.0 \qquad (9)$$

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 radiator as choice X-rays of λ = 0.15406nm to scan films continuously from 2θ = 10 – 99° in step size of 0.2° at room temperature of 288K. These characterizations enabled the effect of heat treatment on the crystallinity of samples to be deciphered. 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 in dust free environment.

III.   RESULTS AND DISCUSSIONS

A. Morphology results of TF surfaces

The results of surface magnified transmission electron microscope pictures are as given in Figs. 1, 2, 3 and 4 for as-deposited TF grown at room temperature of 300K and those

grown at 423K, 523K and 623K respectively. It is easily discernible that the as-grown film could not form well-ordered crystal. The film could be completely amorphous. There were clear localized surface potholes which were likely to be voids, interstitial vacancies and impurity sites. Figs. 2 could show that annealing clearly improved the crystallinity of TFs as local islands or crystallites began to form which homogeneity increased as the temperature of annealing increased as in Figs. 3 and 4. These findings were also evidenced in the RBS results where the micrograph for as grown film, unlike that of annealed film, did not show discernible patterns and peaks.
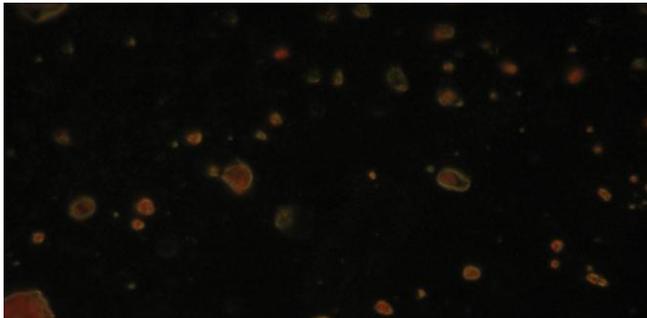

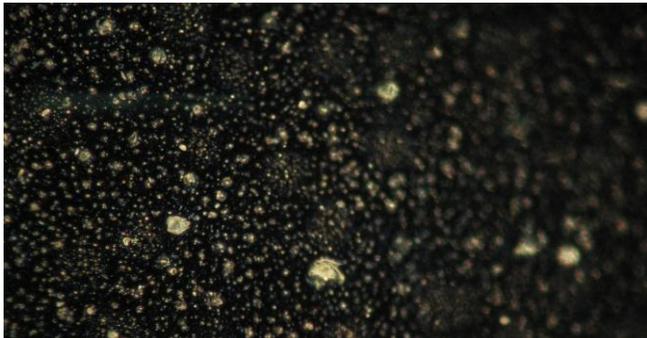Figure 1. Micrograph of as-deposited cadmium lead sulphide TF unannealed (1000X)

Figure 2. Micrograph of cadmium lead sulphide TF annealed at 423K (1000X)
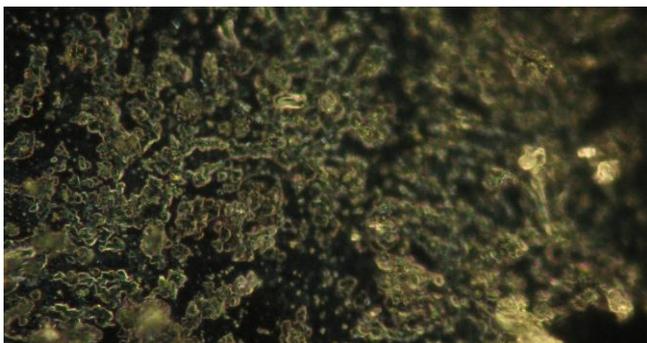

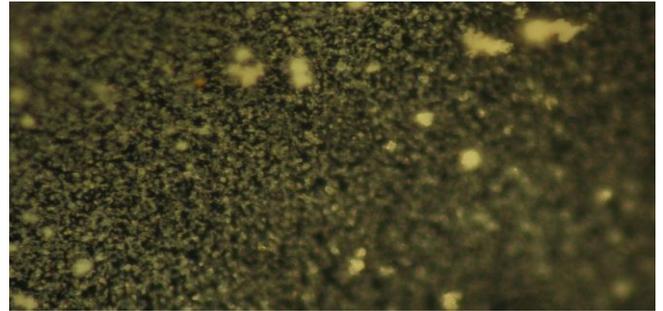Figure 3. Micrograph of cadmium lead sulphide TF annealed at 523K (1000X)

Figure 4. Micrograph of cadmium lead sulphide TF annealed at 623K (1000X)

Annealing enables atoms and electrons, at increased energy, migrate easily in the structure and also cross over the interface between the binary TFs to the ternary heterostructure. It also deoxygenates the thin films and removes dislocations and vacancies. This induces recrystallization into larger grain size structures, as the composite film undergoes controlled cooling, to enable finer and more ordered structure that is also more conductive [17].

B. X-Ray Diffraction (XRD) Result

The XRD pattern of as-grown film (18D) that is not annealed is as shown in Fig. 5. Its pattern a peaks were not definite and prominent thus indicating poor crystalline or amorphous crystals. However after annealing, the diffraction pattern (18E) showed clear pattern and peaks and so also the reflection planes and crystal phase that were identified in JCPDS card number 03-065-61623 to be those of cadmium lead sulphide crystals. Similar X-ray diffraction done on other samples revealed good crystal formation of cadmium lead sulphide, $Cd_{1-x}Pb_xS$, $0<x<1$, of varying stoichiometry.

Debye Scherrer's relation:

$$D = \frac{0.89\lambda}{\beta\cos\theta} \tag{10}$$

was used to calculate the average size, D of crystal grain, where λ is the wavelength of X-ray used, θ the diffraction angle and β the full width at half maximum (FWHM) of peaks.
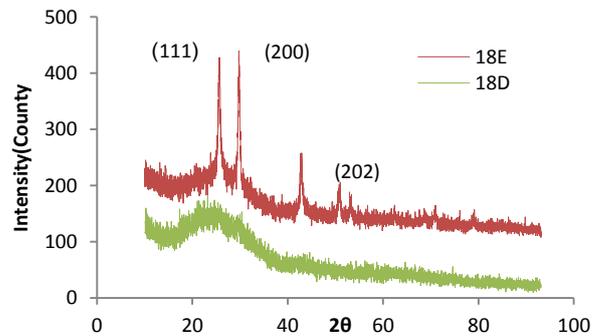

Figure 5. XRD Pattern of as-deposited (18D) and annealed (18E) cadmium lead sulphide Thin Films

The calculated grain size was as shown in Tab. 1 for film annealed at a temperature of 423K.

TABLE I.   XRD RESULT OF SAMPLE 18E (CARD NO. 065-61623)

(h k l)	D(nm)	2θ (°)	FWHM	D(nm)
(1 1 1)	647.43	26.10	0.7232	21.47
(2 0 0)	600.00	29.13	0.8130	17.45
(2 0 2)	511.11	43.00	0.7931	18.79
(3 1 1)	498.75	40.20	0.7773	18.99

Average D: 19.23nm

Similarly grain size D of each thin film annealed at different temperatures was obtained and presented in the plot of annealing temperature against size of grains (Fig. 6). Thus size of grains increased as annealing temperature increased.
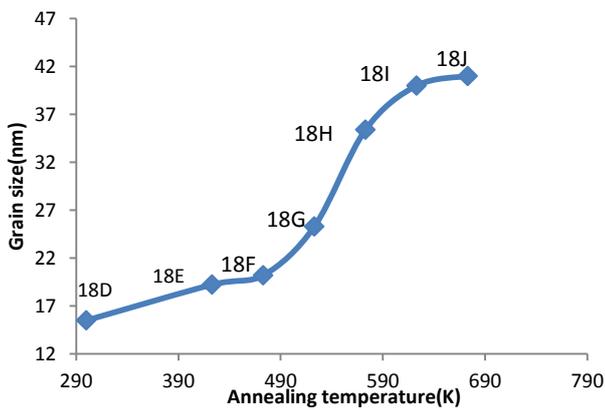

Figure 6.   Plot of grain size against annealing temperature

C. Compositional Results

The Rutherford backscattering analysis result deciphered the elements contained in the TF sample annealed at temperatures of 423K as well as in the glass substrate. The results also showed the thicknesses of cadmium lead sulphide deposits. Figure 7 shows the RBS micrograph for sample 18E which has a thickness of 365 nm. Here layer 1 refers to the thin film while layer 2 refers to the substrate. Here also, the presence of elements C, Pb and S is revealed and so also their percentage composition. The RBS result for as-deposited TF (not shown) contains low percentage oxygen which the well annealed films do not. Similar RBS exercises on other TFs were completed (not shown) and results showed that annealing affected the thickness of TF deposits as can be seen in Fig. 8. X-ray diffraction results have earlier shown in Fig. 6 that high temperature annealing also affected grain sizes. It increases the size rather geometrically except for sample 18J annealed at 673K at which excess heat would have initiated uncontrollable oxidation that vitiated orderly crystal growth. Whilst grain size grew geometrically with annealing temperature, TF thickness decreased sharply until temperature of 523K when it leveled down to a constant value of 320nm (Fig. 8). This trend was not

same between room temperature (300K) and 400K when annealing effect had not started. Other researchers [18,19] got similar trend and described that under annealing at relatively high temperature, the material quality is improved in terms of micro and macro-structural features such as density, grain size, porosity, intra- and inter-granular pore distribution, phases, crystalline morphology, *et cetera*, in order to make homogeneous and compact materials. Annealing of the sample resulted in decrease of dislocation density and strain value. The decrease in dislocation density suggests an increase in crystallinity of the film. Furthermore, under annealing, materials transform into more ordered phase and reduce defects and then dimensional changes due to shrinkage. Due to shrinkage, the thickness decreases.
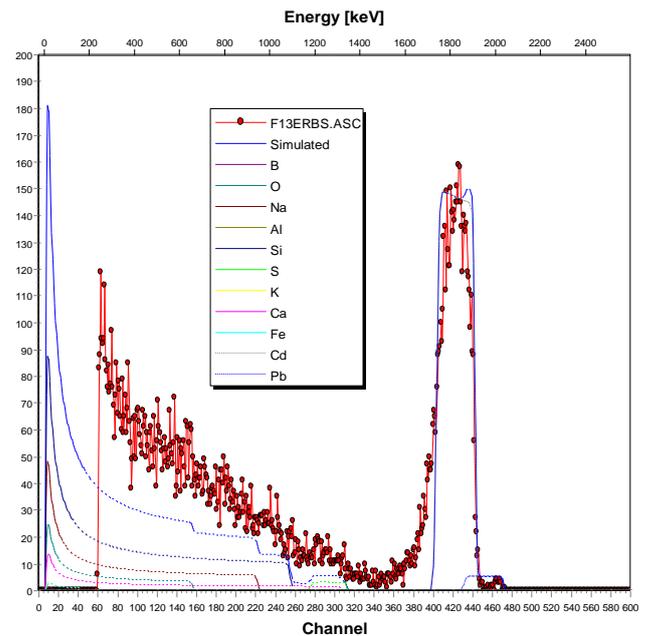

Figure 7.   RBS micrographs for cadmium lead sulphide thin film annealed at 150 ℃. Layer 1: Thickness: 365 nm. Compo: Cd 54.27 %. Pb 2.19 %. S 43.54 %. Layer 2: Thickness: 677894 nm Compo: Si 31.97 % . O 32.89 %. Na 25.85 %. Ca 1.64 %. Al 0.25 %. K 1.05 %. Fe 0.38 %. B 5.89 %. Layer 1 refers to thin film
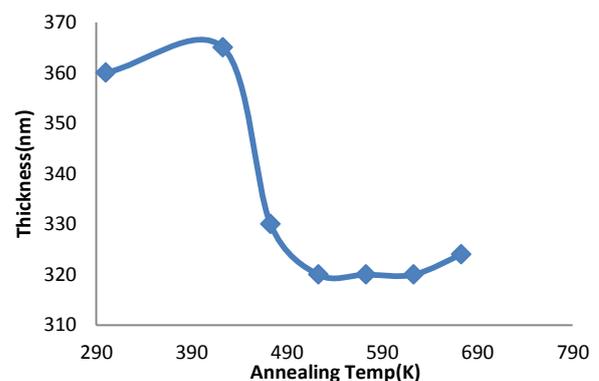

Figure 8.   TF thickness against annealing temperature

D. Resistivity Analysis Result

The four point probe survey profiled across various positions of the TF surface revealed that annealing treatments also affected the resistivity and the sheet resistance of the thin films. Table 4 shows the results of such survey and Fig. 9 shows that at higher annealing temperatures, the resistivity decreased from 200 Ωm to 100 Ωm and sheet resistance also decreased from 5.56 $\times 10^8$ Ωsq to 3.13 $\times 10^8$ Ωsq. Again at sufficiently high temperature (600K) the resistivity instead increases as oxidation sets in. The observation is consistent with [6] that reported similar higher conductivity for annealed heterogeneous $SiO_2/Pt/SiO_x$ thin films.

TABLE II. RESISTIVITY AND SHEET RESISTANCE OF FILMS ANNEALED AT DIFFERENT TEMPERATURES

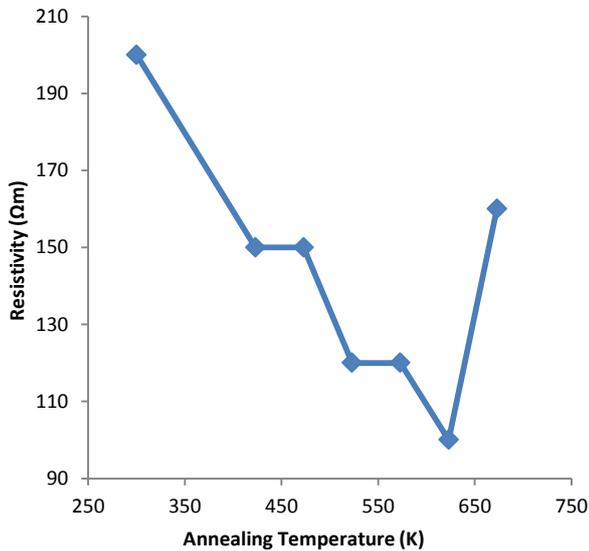| Sample	Anneal. Temp.	Resistivity (Ωm)	Sheet resistance $\times 10^8$ (Ωsq)
18D	300	200	5.56
18E	423	150	4.11
18F	473	150	3.17
18G	523	120	3.75
18H	573	120	3.75
18I	623	100	3.13
18J	673	160	4.94

Figure 9. Resistivity of TF versus annealing temperature

IV. CONCLUSION

Stack thin films of CdS/PbS similarly fabricated using two-step process were heat treated (annealed) at different temperatures for an hour each time and the effects of such heat treatments on the TF was dramatic. There was re-crystallization of the stack TF into a composite heterostructure. The crystallinity improved as the temperature of annealing increased up to 623K. Grain size increased as the temperature

in that order. Annealing at higher temperature also decreased both the resistivity and sheet resistance of the thin films. Heat was thought to have enabled crossover of carriers across the heterostructure enabling formation of composite cadmium lead sulphiode, $Cd_{1-x}Pb_xS$, $0<x<1$, of varying stoichiometry

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