

Effects of Deposition Medium on the Solid State Characteristics of Pb-Doped CdS Thin Films Fabricated in Chemical Bath Technique

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Abstract— CdS thin films doped with small quantity lead were synthesized on plane glass substrate using chemical bath deposition technique. The fabrication was within the pores of a polymer (polyvinyl alcohol) medium at 28 °C. In order to study the effect of polymer capping on the growth and properties of films, similar deposition was therefore carried out using water as a deposition medium that could not present any capping pores. The as-deposited films in both media were annealed for an hour in oven at 200 °C and thereafter characterized for their morphology, composition and band gaps. The film grown in PVA medium, by far, showed less crystal imperfection and wider band gap (2.30 eV) than that in water medium (3.23 eV). It also exhibited higher Pb doping (2.26 %) than that grown in water medium (1.10 %).

Index Terms— CdS thin film, PVA medium, Pb-doping, polymer capping.

1. INTRODUCTION

IN recent time, inorganic thin films of semiconductors have been variously fabricated using techniques that controlled film morphology, composition and properties [1], [2], [3], [4], [5]. Such techniques usually involved high temperature and therefore required steady power supply. Thin films of semiconductors are now of much interest because of their ever expanding applications in electronic, surface coating, solar cell and optoelectronic devices. Prominent among thin film fabrication techniques is the chemical bath deposition (CBD), often used because of its simplicity, low cost, low temperature and applicability for large area and irregular surface coverage and has been previously used successfully to deposit binary metal chalcogenides such as PbS [6] and CdS [7], ternary heterojunction nanofilms such as CdS/CuS [9], [10] and other thin films of multinary composition [11].

In CBD deposition, the media of choice are usually polyvinyl alcohol (PVA) and distilled water. PVA has self organized and distinct pores which water does not have. It is thought that the pores of PVA polymer easily present capping mechanism for the growth of crystal monomers and hence enhance early crystallization and size reduction. Size reduction is of interest since material properties could be easily changed by altering the crystallite size of films [12]. Presently nanocrystalline materials have opened new chapter in the field of electronic application since material properties could be changed by changing the crystallite size of films. Thin films are examples of such nanomaterials and can be polycrystalline with crystallite sizes of the order of a few nanometers. Extensive literature on size reduction effect is

available [13], [14], [15], [16]. Thin film deposition carried out within the pores of PVA is an effective means of modifying the sizes of the crystallites [12].

In this work, the effect of using different media: water and PVA, on the crystallite size, band gap and surface characteristics of film is studied. The thin film of interest is Pb-doped CdS. This thin film has been variously synthesized, sometimes using water [17] and other times using polyvinyl alcohol media [18]. In this research, such synthesis was carried out separately in both media and the effects on film composition and properties were studied.

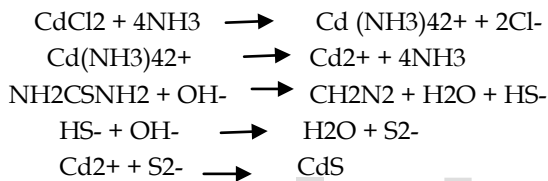
2. EXPERIMENTAL DETAILS

Lead-doped cadmium sulphide thin films were fabricated by measuring onto a 50 ml beaker 7 ml of 0.9 M CdCl₂, 5 ml of NH₃, 5 ml of 0.8 M NH₂CSNH₂ and 5 ml of 0.6 M Pb(NO₃)₂ while stirring vigorously. Also 1.2 ml of 0.1 M of Pb(NO₃)₂ was added to the bath, while still stirring vigorously, in this small quantity that maintained low ionic ratio Pb²⁺: Cd²⁺ of X:100 of 1 < x < 8 since only a small doping level is necessary to alter semiconductor properties without significantly altering film ordered structure. Distilled water (35 ml) was measured onto the beaker while still stirring and a bath pH of 8.4 was recorded. A substrate of plane glass slide of size 75 mm long, 25 mm wide and 0.7 mm thick was dipped into the solution through the synthetic foam cover that thus also became the support for the substrate. The substrate glass slide was previously degreased and pre-cleaned with hydrochloric acid, acetone and ethanol. The bath was kept uninterrupted for 2 hours at room temperature after which the slide, which was now covered with yellowish CdS deposits, was removed,

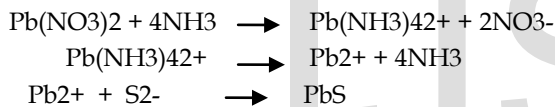
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rinsed in plenty of distilled water and drip dried in dust free environment. In order to enhance film structural characteristics and also deoxygenate the film, which was now labeled 18A, it was annealed for an hour in dust free environment at a temperature of 200 °C. A similar growth was done on another substrate and labeled 18B, except that 35 ml PVA instead of water was used. The PVA solution was prepared by adding 450 ml of distilled water to 0.9 g of solid PVA (C₂H₄O)_n (where n=1700), and stirred by a magnetic stirrer at 90 °C for 1 hour. The temperature of the solution was left to drop to room temperature of 28 °C. Both films were studied for their different characteristics.

Formation of deposits was basically a hydrolysis of thiourea (NH₂CSNH₂) in an alkaline solution containing cadmium. Ammonia acted as a complexing agent that controlled precipitation rate and a pH stabilizer in the bath where reactions were as follows:



Also,



Scanning electron microscopy (SEM) of films grown on both media was taken, and so also their optical absorbance. The latter was accomplished using a Unico-UV-2102PC spectrophotometer at normal incident of light in the wavelength range of 200 – 1100nm. From this absorbance, the absorption coefficient of the film was calculated and film band gaps deciphered using its well known mathematical relationship with the absorbance [19]. The composition of the films was determined using Rutherford backscattering technique and the structure of the film was obtained using X'Pert-Pro diffractometer which applied Cu K α radiator of $\lambda = 0.15406$ nm to scan films continuously as 2θ varied from 0 – 100° at a step size of 0.02° and at a scan step time of 0.2 s.

3. RESULTS AND DISCUSSION

3.1 Surface Morphology Results

The surface structures of the thin films grown were as given in Fig. 1a. for film grown in water medium and Fig. 1b. for thin film grown in PVA medium. In films grown in water medium, there were lots of pin holes, voids and discontinuities while films grown in PVA medium definitely showed better crystal order with fewer crystal imperfections. The crystallites of the

films deposited in PVA medium were capped within the pores of the polymer, leading to early formation of grains whose sizes were in the nanometer range. The crystallites were also more dense and compact and so less light got transmitted, rather more of the light was absorbed as shown in the higher absorbance recorded for PVA-based film in Fig. 2.

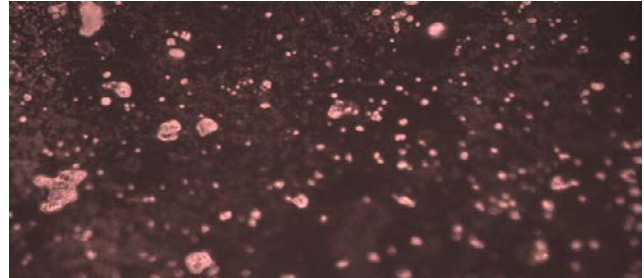


Fig. 1a: SEM micrograph of Pb-doped CdS grown in water medium (1000X)

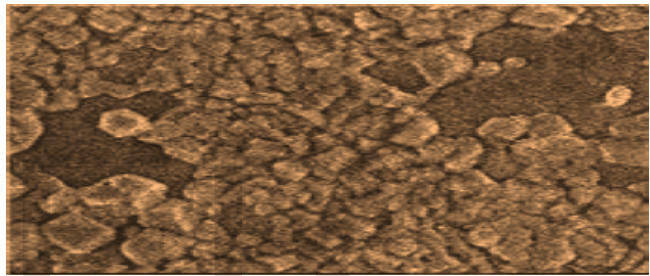


Fig.1b: SEM micrograph of Pb-doped CdS grown in PVA medium (1000X)

3.2 Results of Spectral Measurement

The result of spectral absorbance for films grown in both media were as shown in Fig. 2. It could be clearly seen that absorbance of PVA capped thin film was higher than that grown in water medium from the visible to near infra red ranges while such absorbance was same in the ultra-violet frequencies. In a similar experiment, Chikwenze and Nnabuchi [12] determined that PVA capped CdSe thin film became denser and hence more spectral absorbing than equivalent film grown in in water medium. The absorption coefficient of the films is also shown in Fig. 3. The band gaps, E_g of the films were deduced from a plot of $(\alpha h\nu)^2$ vs photon energy ($h\nu$) where α is the absorption coefficient of the thin film. Such deduction followed from the well known Tauc's relation:

$$\alpha = A(h\nu - E_g)^n / h\nu \quad (1)$$

where A is a constant, $h\nu$ is the photon energy, α is the absorption coefficient, and n depends on the nature of the transition. For direct transitions, $n = \frac{1}{2}$ or $\frac{3}{2}$, while for indirect ones $n = 2$ or 3 , depending on whether such transitions are

allowed or forbidden respectively. Since $n = \frac{1}{2}$ for the doped CdS thin film [20], [21],

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

Hence a plot of $(\alpha h\nu)^2$ versus $h\nu$ is linear provided inter band electron transitions dominate absorption processes. This was actually the case for the thin films grown especially in the visible ranges as can be seen in Fig. 4. The reasons for non-linearity in low photon energy ranges is well established [21], however the extrapolation of the linear portion on the $h\nu$ axis revealed the band Gap.

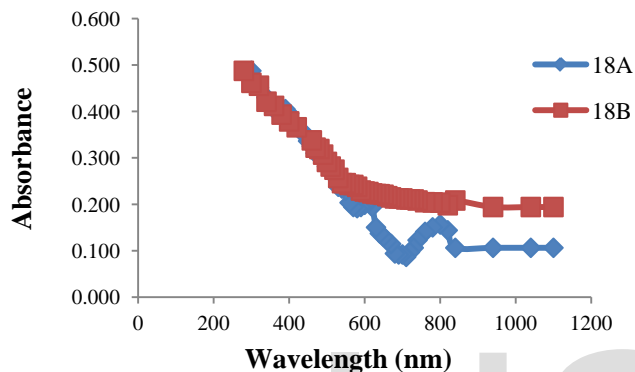


Fig. 2: Spectral Absorbance of Cadmium Lead Sulphide Grown in Two Different Media.

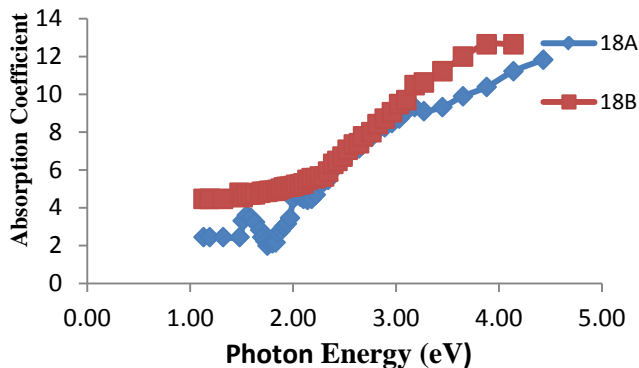


Fig. 3: Absorption Coefficient Vs Photon Energy for Cadmium Lead Sulphide Grown in Two Different Media.

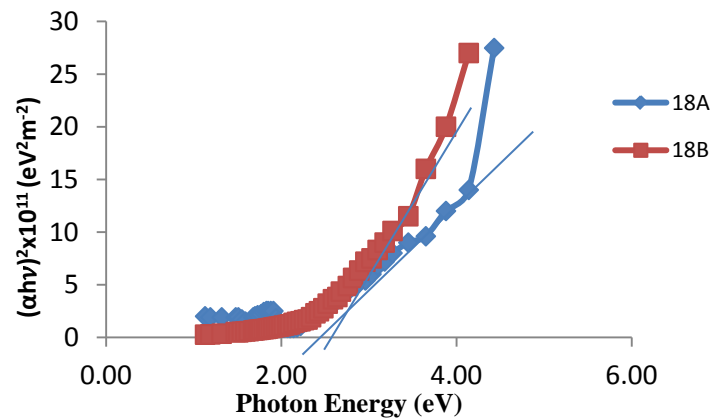


Fig. 4: $(\alpha h\nu)^2$ Vs Photon Energy for Cadmium Lead Sulphide Grown in Two Different Media.

Such band gap for thin film grown in water medium was therefore 2.25 eV while that for thin film grown in PVA matrix was 2.30 eV. Thus whilst Pb-doping has thus red-shifted the band gap of CdS from its typical value of 2.42 eV [22] to these obtained values, the band gap of PVA-capped films had slightly wider band gap than that synthesized in water medium.

3.3 Rutherford Backscattering (RBS) Results

The results of Rutherford backscattering done on both films deciphered the elements they comprised as well as the elements percentage abundances. The analysis also obtained the thickness of thin film deposits as well as those of the substrate glass. The micrograph for films deposited in water medium was as shown in Fig. 5a while that for film grown in PVA medium was as shown in Fig. 5b.

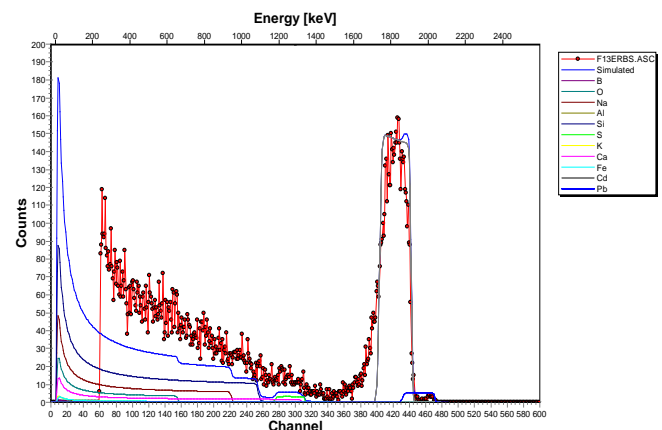


Fig. 5a: RBS micrographs for Pb-doped CdS (18A). Layer 1: Thickness: 400 nm. Compo: Cd 83.35 %. Pb 1.10 %. S 15.62 %. Layer 2: Thickness: 677894 nm, Compo: Si 31.97 % . O 32.89 %. Na 25.85 %. Ca 1.64 %. Al 0.25 %. K 1.05 %. Fe 0.38 %. B 5.89 %. Layer 1 refers to thin film sample while layer 2 refers to substrate.

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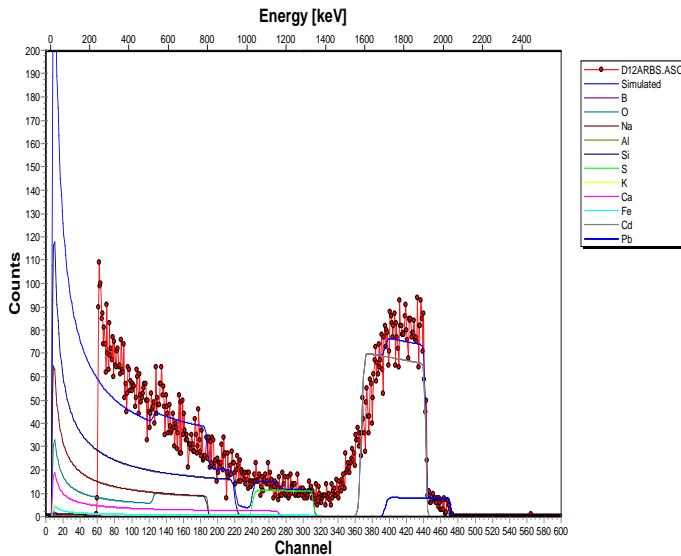


Fig. 5b: RBS micrographs for Pb-doped CdS (18B). Layer 1: Thickness: 552 nm. Compo: Cd 54.20 %. Pb 2.26 %. S 43.54 %. Layer 2: Thickness: 677894 nm: Compo: Si 31.97 % . O 32.89 %. Na 25.85 %. Ca 1.64 %. Al 0.25 %. K 1.05 %. Fe 0.38 %. B 5.89 %. Layer 1 refers to thin film sample while layer 2 refers to substrate.

It can easily be seen that thin films grown in the polymer matrix of polyvinyl alcohol was thicker (552 nm) than that grown in water (400 nm). The doping level of lead ie 1.10 % in the case of water medium increased to 2.26 % for the case of PVA medium. The pores of PVA presented easy development of monomers, diamers and multimers into continuous crystal layers that made overall thickness to be bigger in PVA-based growth. As the film thickness increased the effect of substrate decreased. When thickness of the films increased (irrespective of chemical baths) the crystallite size also increased [23] and the dislocation density and strain decreased. Since the dislocation density and strain are the manifestation of dislocation network in the films, the decrease in the strain and dislocation density indicated the formation of higher quality films. Hence the thicker film in the PVA-based deposit clearly manifested better and more orderly films as could be clearly seen in the SEM micrographs of Figs 1s and 1b.

4. CONCLUSION

Cadmium sulphide thin film grown in water medium has been compared to that similarly grown in polyvinyl alcohol medium. The use of PVA growth medium significantly enhanced crystallization of CdS thin film. It also increases film thickness and grain size, widens CdS film band gap and decreased film crystal imperfection. There was higher doping level in films grown in PVA which suggested an increased electrical conductivity in the CdS thin films.

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