EFFECT OF DEPOSITION MEDIUM ON THE OPTICAL AND SOLID STATE PROPERTIES OF CHEMICAL BATH DEPOSITED CdSe THIN FILMS

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CdSe thin films were synthesized on the glass substrate by chemical bath deposition technique within the pores of polyvinyl alcohol (PVA) at 60^oC. In order to study the effect of the capping polymer on the properties of these films, similar deposit was carried out using water as the deposition medium. The as-deposited films were annealed in the oven at 200^oC and characterized for the composition and optical properties. These properties were studied by means of Rutherford backscattering (RBS) and optical spectrophotometer. The optical properties revealed the presence of direct band gaps with energies in the range of $0.9 - 1.2eV$ (for the films deposited in water medium) and $1.8 - 2.0eV$ (for the films deposited in PVA medium). The deposition medium has significant influence on other optical and solid-state properties studied.

1. Introduction

Thin film technology occupy a prominent place in basic research and the use of thin film semiconductors have attracted much interest in an expanding variety of applications in various electronic and optoelectronic devices due to their low production costs. The review of literature shows that many research groups have explored thin film technology. This has led to the emergence of several deposition techniques, most of which require steady power supply because they involve high temperature process [1-3].

Nowadays, inorganic thin films with controlled morphology and properties can be fabricated using chemical bath deposition (CBD) technique. A variety of substrates such as insulators, semiconductors or metals can be used, since it is a low temperature process. This technique is relatively less expensive, simple, convenient for large area deposition and ease of application to many compounds such as sulphides and selenides, which include ZnS, CdS, PbS, CdSe, CuS_2, ZnSe and Sb_2S_3 [4-10].

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. Nanocrystalline thin films are also polycrystalline in nature but with sizes of crystallites of the order of a few nanometers. Extensive literature on size reduction effect is available [11-14]. Thin film deposition carried out within the pores of PVA is an effective means of modifying the sizes of the crystallites [11,12,15].

In the present study, we report the synthesis of thin films of CdSe by chemical bath deposition technique in PVA solution and distilled water as the deposition media. The effect of post deposition annealing was also studied by annealing the as-grown films in the oven at a temperature of 200^oC.

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2. Experimental Procedure

The preparation of CdSe thin films on glass slide was carried out using chemical bath deposition technique. First the PVA solution was prepared by adding 450 ml of distilled water to 0.9 g of solid PVA ($-C_2H_4O)_n$ (where n=1700), and stirred by a magnetic stirrer at 90^oC for 1hour. The solution was aged until the temperature drops to room temperature.

The reaction baths for the deposition of CdSe thin films contain 5ml of 1M $CdCl_2$, 10ml of 7.4M TEA, 5ml of 13.5M NH_4OH, 5ml of 1M Na_2SeSO_3 and 40 ml of the solution put in that order into 80ml beaker. A clean micro-slide was then inserted vertically through synthetic foam into the mixture. Two films each were deposited using distilled water and PVA solution. In each case the deposition lasted for 8 hrs, after which the coated substrate was removed from the bath, washed well with distilled water and allowed to dry. The as-grown sample was annealed in the oven at 200^oC for 1 hr. and the films labelled H12 and P17 (for the samples annealed at 200^oC) and H15 and P20 (for as-grown films).

The samples were characterized with RBS and UV-VIS Spectrophotometer. Optical properties of chemical bath deposited CdSe thin films were measured at room temperature from Unico – UV-2102PC spectrophotometer at normal incident of light in the wavelength range of 200-1000nm. Optical band-gaps of the samples were calculated from the absorption spectra. The composition of the films was determined by using Rutherford back scattering.

3. Results and discussion

The UV-VIS-NIR absorption and transmission spectra of the CdSe thin films prepared in two different media are shown in figs. 1- 2. A close observation of fig.1 shows that the films deposited in PVA medium have higher absorbance value when compared with the films deposited in distilled water, in all the wavelength range studied. The figure also shows that the films annealed in the oven at 200^oC have higher absorption of visible portion of the solar light energy when compared with the as-grown films. The pronounced effect of the deposition medium on the films is not limited to absorbance only. We also observe, from fig.2, a wide difference in the transmittance values recorded for the films deposited in the two media. The reason for the observed differences is not far fetched: The crystallites of the films deposited in PVA medium are capped within the pores of the polymer, leading to formation of grains whose sizes are in the nano-meter range. The crystallites are also more dense and compact and so less light gets transmitted, rather, more of the light is absorbed as shown in fig.1. This observation is more obvious in the plot of absorption coefficient against photon energy shown in fig.3.
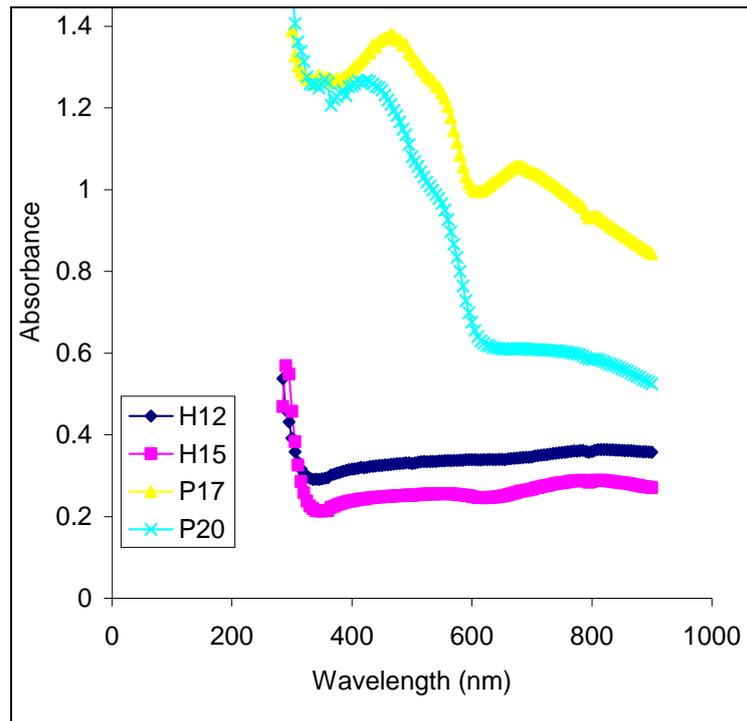
Fig.1: Absorption spectra of CdSe thin films deposited in two different media
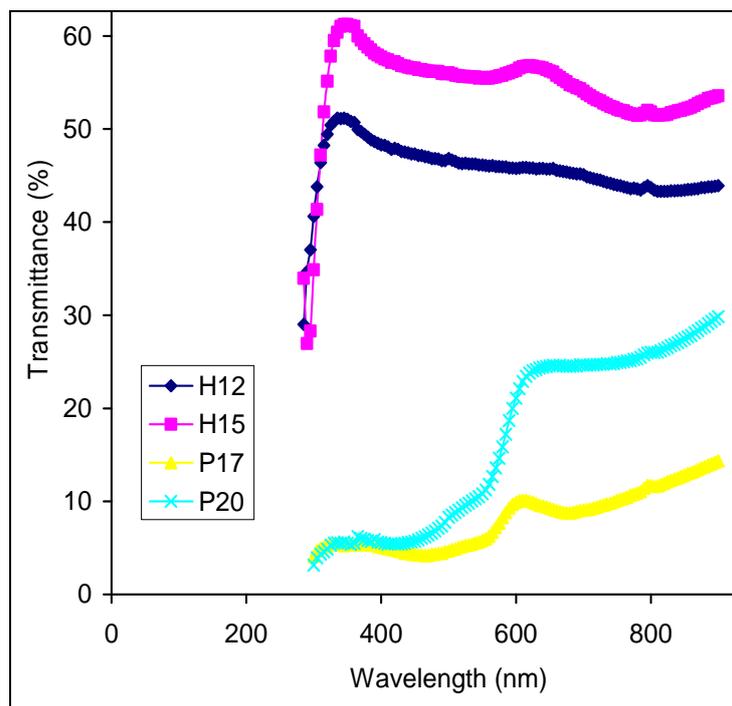
Fig.2: Transmittance spectra of CdSe thin films deposited in two different media
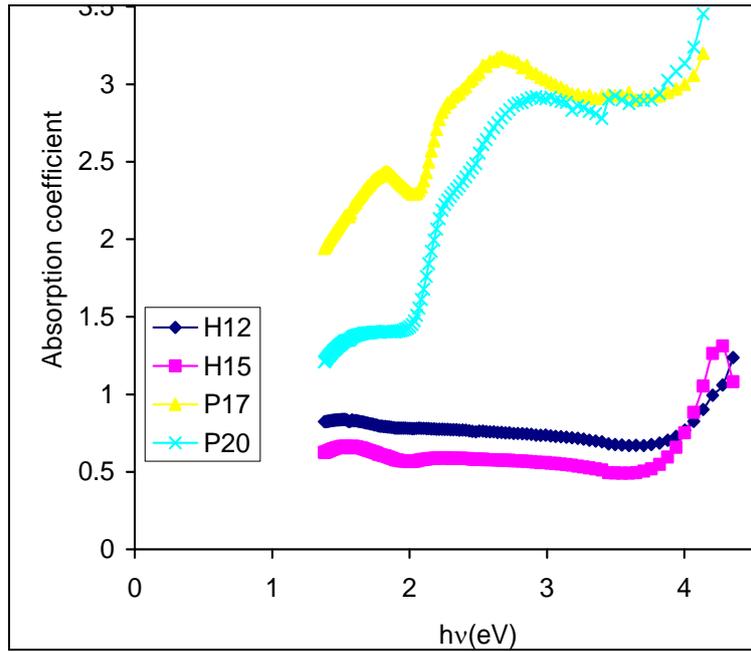
Fig.3: Plot of absorption coefficient vs. photon energy for CdSe thin films deposited in two different media.

The absorption spectra, which are the most direct and perhaps the simplest method for probing the band structure of semiconductors, are employed in the determination of the energy gap, E_g. The E_g was calculated using the following Tauc's relation:

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

where A is a constant, $h\nu$ is the photon energy and α is the absorption coefficient, while n depends on the nature of the transition. For direct transitions n = ½ or ⅔, while for indirect ones n = 2 or 3, depending on whether they are allowed or forbidden, respectively.
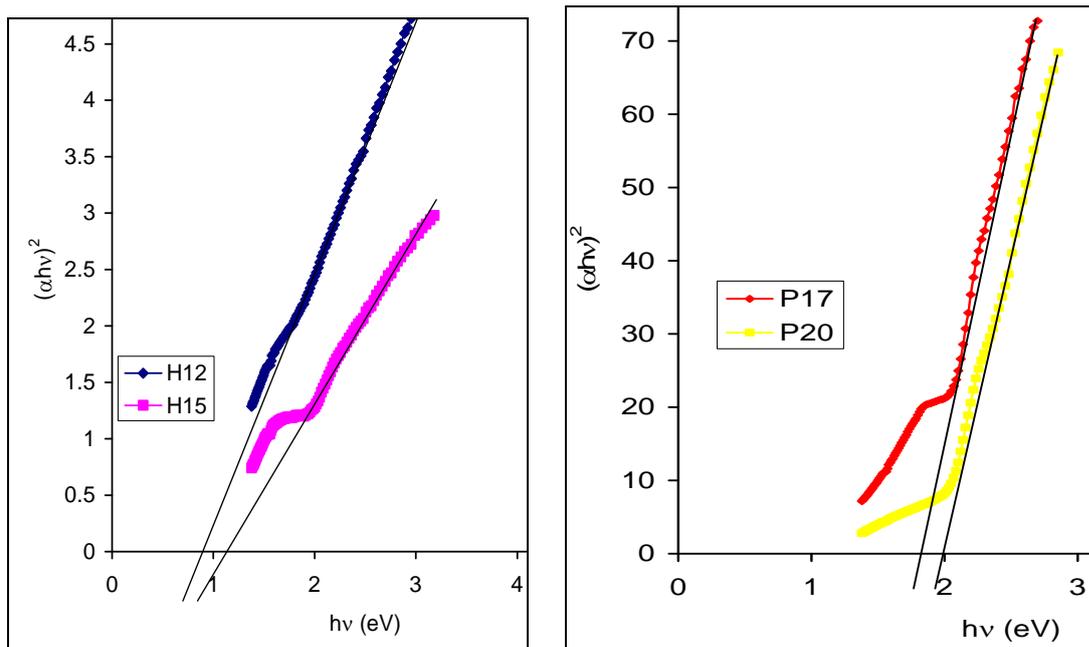
Fig.4: Plot of $(\alpha h\nu)^2$ vs. $(h\nu)$ for CdSe thin films deposited in two different media

The calculated values of the direct energy band gap, from fig.4 are H12 (0.9eV), H15 (1.2 eV), P17 (1.8 eV) and P20 (2.0 eV). This result shows that the as-grown films as well as the films deposited within the pores of a polymer matrix have higher band gap energy. This is a consequence of large crystallite size, which characterizes films annealed at a higher temperature as well as the decrease in the crystallites size expected when films are deposited in a polymer as a matrix. So the band gap decreases at higher annealing temperatures as a result of the increase in crystallite size based on the effective mass approximation [16]. It has been shown from literature that processes which increase the particle size decreases the band gap of most thin films [17 – 19], hence the decrease in the band gap reported here for the annealed films.

The average values of the plots of the refractive index, extinction coefficient, real and imaginary dielectrics constants against photon energy are shown in table 1. The effect of both the deposition medium and annealing temperature are obvious from the table. The plots are shown in figs. 5-8.

Table 1: Average values of some of the parameters studied

	H12	H15	P17	P20
Refractive index	2.27	2.15	0.51	1.19
Extinction coefficient	37.41	29.07	119.52	86.38
Real dielectric constant	5.16	4.65	0.32	1.91
Imaginary dielectric constant	172.24	126.44	129.72	197.97
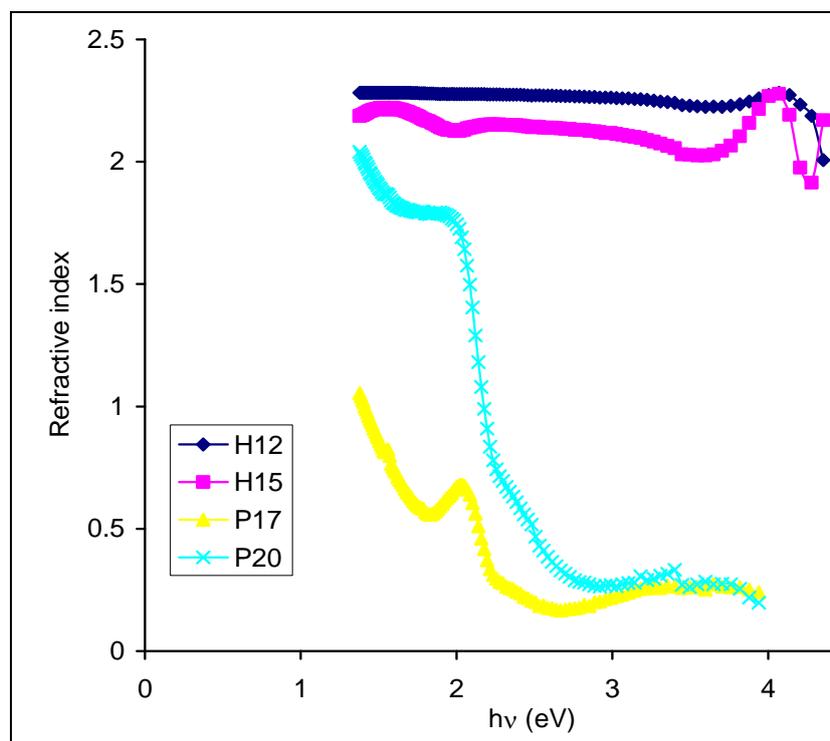
Fig.5: Refractive index vs. photon energy for CdSe thin films deposited in two different media
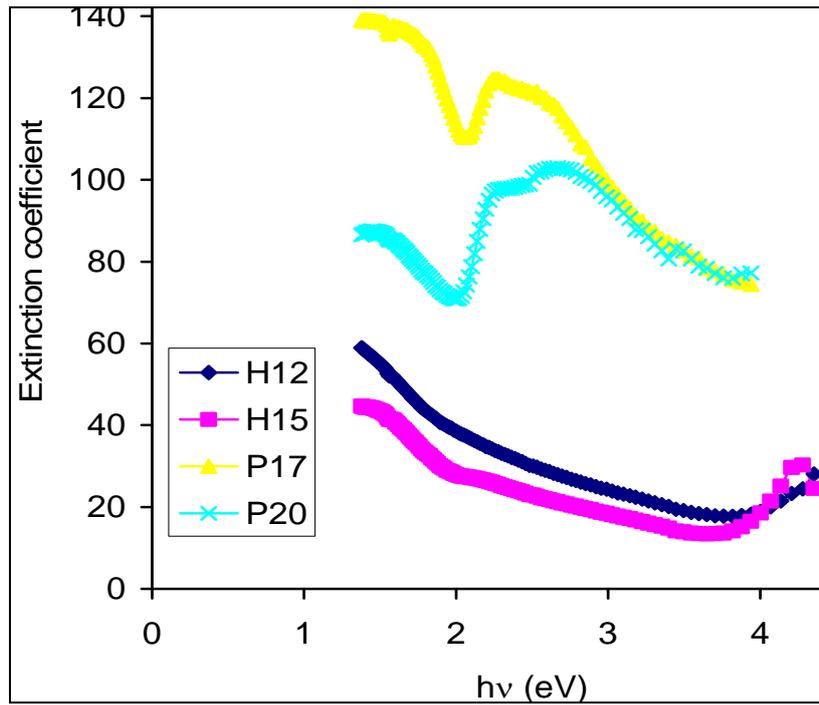
Fig.6: Extinction coefficient vs. photon energy for CdSe thin films deposited in two different media.
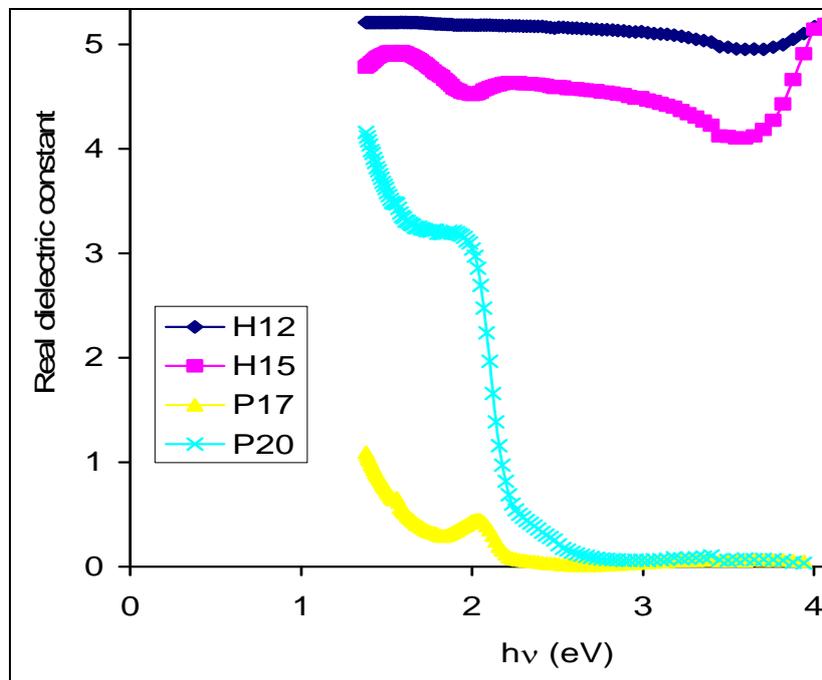
Fig.7: Real dielectric constant vs. photon energy for CdSe thin films deposited in two different media
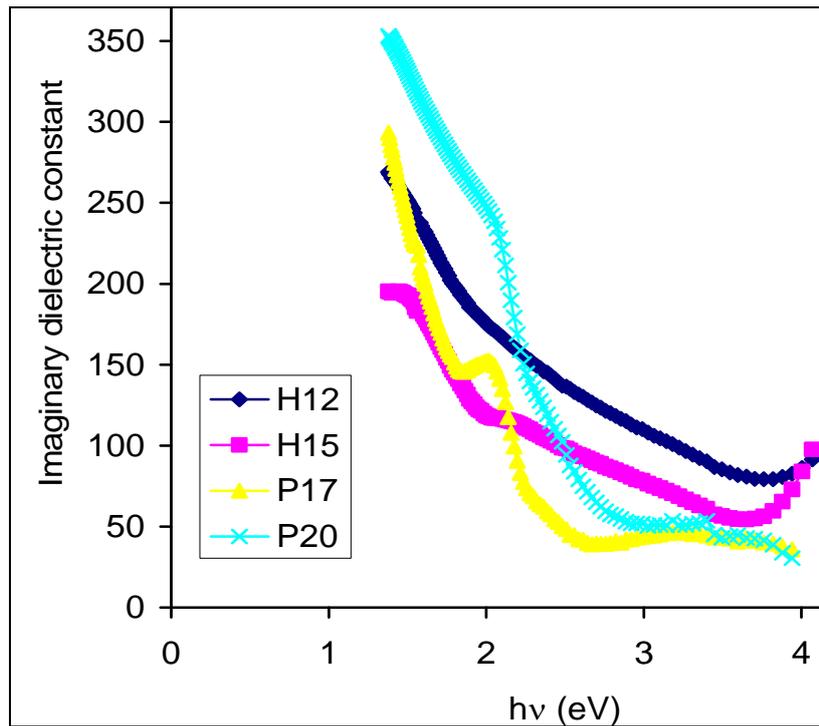
Fig.8: Imaginary dielectric constant vs. photon energy for CdSe thin films deposited in two different media

The elemental composition and chemical states of sample P17 was analysed by Rutherford Backscattering (RSB) at Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife, Nigeria. The results are shown in fig.9. From the film composition presented in table 2, we can deduce that thin film of CdSe deposited in this work has no impurity content.
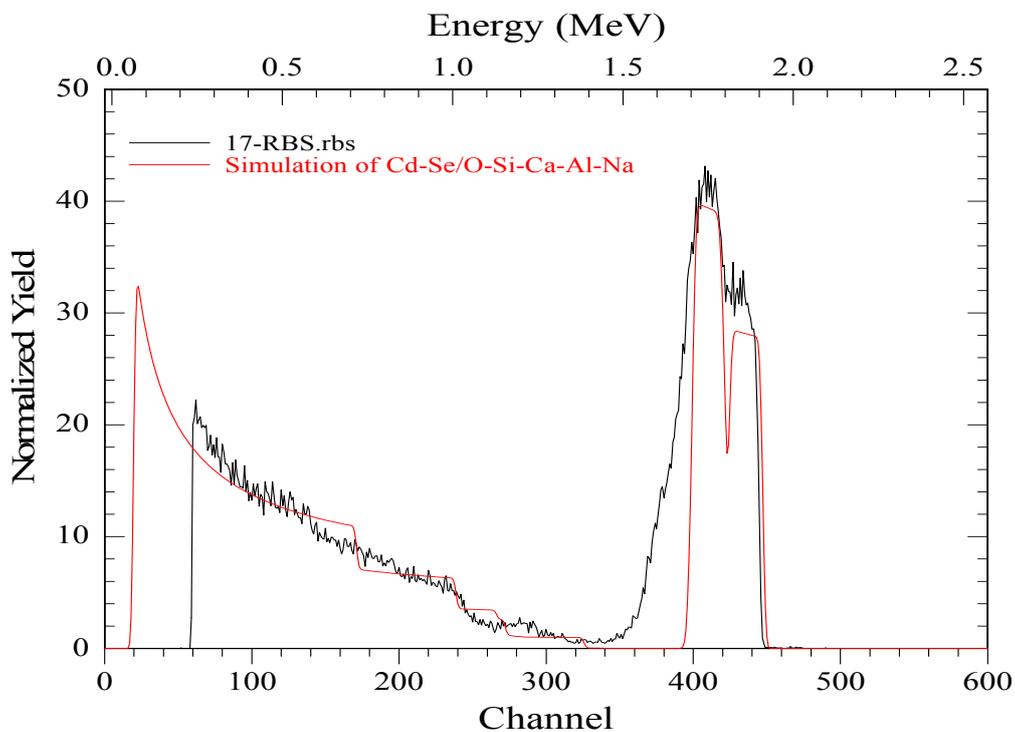
Fig. 9: RBS of CdSe thin film deposited in PVA medium

Table 2: The composition of substrate and CdSe film from RBS analysis

	Cadmium	Chlorine	Oxygen	Silicon	Calcium	Aluminium	Sodium
CdSe thin film	0.267	0.733	-	-	-	-	-
Glass substrate	-	-	0.615	0.080	0.025	0.050	0.230

4. Conclusions

Thin films of CdSe have been successfully deposited on glass substrate by chemical bath deposition technique. The composition, optical and solid-state properties of the film was studied. The optical band gaps of the films lie in the range of 0.9 – 1.2eV and 1.8 – 2.0eV for the films deposited in water medium and PVA medium respectively. Analysis of $(\alpha h\nu)^2$ vs. hν shows that high thermal annealing lowers the value of band gap energy of CdSe thin films irrespective of the deposition medium. The CdSe thin films deposited within the PVA matrix have higher absorption coefficient as well as larger band gap energy. This has potential application in solar cell architecture.

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