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Optical Characterization of Calcium Sulphide (CaS) Thin Films by Chemical Bath Deposition

E. Shobhana

Assistant professor in physics, Kumaraguru College of Technology, Coimbatore, India

Abstract: ***Thin films of Calcium sulphide were deposited on glass microslides using chemical Bath Deposition technique. The films were deposited at room temperature. The optical characterization was carried out which shows low absorbance, high transmittance in the uv-visible region. The photon energy and band gap is determined. These films because of their high transmittance in the UV-Visible region are suitable for various optical applications as photosynthetic, window coating and anti reflection coating material.***

Keywords: Calcium sulphide, Thin film ,UV- visible, photon energy, Bandgap

1. Introduction

Thin film technologies are also being developed as a means of substantially reducing the cost of PV systems. The rationale for this is that thin film modules are cheaper to manufacture owing to their reduced material costs, energy costs, handling costs and capital costs. Electronic semiconductor devices and optical coatings are the main applications benefiting from thin film construction. It is useful in the manufacture of optics for reflective, antireflective coatings, electronic layers of insulators, semi conductors and conductors which form integrated circuits etc. Oldhamite is the name for mineralogical form of Calcium Sulphide (CaS). It is a rare component of some meteorites and has scientific importance in solar nebula research. This white material crystallizes in cubes like rock salt. CaS has been studied as a component in a process that would recycle gypsum, a product of flue gas desulfurization. It has an odour of H_2S, which results from small amount of this gas, formed by hydrolysis of the salt. Calcium Sulphide has a halite structure with molar mass 72.14g / mol and density as 2.600gm^{-1} and it is medically used in Homoeopathy. Calcium Sulphide (CaS) has a low absorbance, high transmittance and low reflectance range throughout the ultraviolet, visible and infrared regions. CaS is suitable for use as a photosynthetic material and window coating [1]**.** Calcium Sulphide thin films were prepared with different thickness doped with Europium and Samarium by pulsed layer deposition technique. The films grown had an amorphous or polycrystalline structure depending on growth temperature and the number of pulses used, and the film characteristics are controlled by the growth conditions [2]. The study was made with the deposition of CaS thin films by atomic layer epitaxy with the use of precursors such as H_2S and $Ca(thd)_2$ and it was found to be crystalline and smooth under optimized condition [3]. The nature phosphorescence decay of CaS phosphors activated by Ce^{3+}, Na^+, Cu^+. The variation in the value of trap depth has been studied by UV excitation in phosphorescence decay by peeling off procedure [4]. The thermally stimulated conductivity of CaS :Pr phosphors is observed in the temperature range of 300-330k..Trap depths relaxation times and filled traps are evaluated using Bucci-Fischi, Cowell-Woods and Ozawa models [5]. Doped CaS phosphors with different concentration of Erbium and Copper were studied by solid phase reaction. From the results he showed that the trap group corresponds to 0.69eV and this has been explained on the basis of superposition theory [6]. In this present work, CaS is chosen as the material to be deposited on a glass substrate by Chemical vapour deposition and to study the optical characteristics.

2. Experimental Details

CaS thin films were deposited onto glass substrates using chemical Bath Deposition technique. The chemicals used for the preparation technique are Concentrated hydrochloric acid, concentrated nitric acid, Calcium Sulphate, EDTA Sodium thiosulphate , Extran Solution and De-ionized water. The steps for the experimental procedure of the formation of CaS thin film are as follows:

2.1 Substrate Cleaning

Initially all the glasswares are washed with ordinary water. Next they are rinsed using Extran and washed thoroughly with distilled water followed by de-ionized water and allowed to get dried. Now, glass slides with dimension *(25.4mm x 76.2mm x 1mm)* are taken, washed with distilled water and soaked in a beaker containing nitric acid for ½ an hour and washed with de-ionized water and again soaked in hydrochloric acid for the same period. Then the glass slides are put in a soap solution and rinsed thoroughly. Again, the slides are washed with de-ionized water and are placed inside the dessicator which consists of silica gel for the absorption of water and are dried. Thus, the substrate for the film deposition has been prepared. After the glass slides are fully dried, label the particular slide and the weight of the glass substrate has been determined using Mass Balance. Care must be taken so that there should not be any traces of water in the slide before deposition.

2.2 Preparation of the Chemical Bath

0.5M of $CaSO_4$, 0.10M of EDTA and 1.0M of $Na_2S_20_3.5H_20$ solutions are prepared using de-ionized water. From these prepared fresh solution 3.5ml of Calcium Sulphate, 3.5ml of EDTA and 7.0ml of Sodium thiosulphate are taken in a separate beaker which is finally added with 34 ml of water. Now, the cleaned substrate is immersed inside the chemical bath and kept undisturbed for 48 hrs to get deposited. After the prescribed time, the deposited substrate is washed with de- ionized water to remove the granules and is allowed to get dried in a dessicator. The experimental setup is as shown in Figure 1. The experimental procedure is repeated for different reaction bath BI, BII and BIII with molarities of $CaSO_4$ as 0.5M, 1.0M… and of EDTA with 1.0M, 0.10M and of Sodium thiosulphate with 1.0M .The deposition time is also varied and different CaS films are prepared for deposition hours of 48 hrs, 17hrs and 18 hrs as shown in Table 1.

Table 1: Chemical Bath Conditions

Reaction Bath	Deposition Time (hours)	Temperature (°C)	$CaSO_4$		EDTA		$Na_2S_2O_3.5H_2O$		H_2O Vol (ml)
			Mol (M)	Vol (ml)	Mol (M)	Vol (ml)	Mol (M)	Vol (ml)	
B I	48	Room	0.5	3.5	0.10	3.5	1.0	7.0	34
B II	17	Room	1.0	3.0	1.0	3.0	1.0	3.0	34
B III	18	Room	0.5	3.0	0.10	3.0	1.0	3.0	28

Figure 1: Chemical Bath Setup of a Cas thin film

2.3 Mechanism of the Reaction

The reaction that occurs due to $CaSO_4$, $Na_2S_2O_3.5H_2O$ and water are as follows:

When $CaSO_4$ and EDTA are added up, the Sulphate ions get separated and it occurs as:

$$CaSO_4 + EDTA \Leftrightarrow [Ca\,(EDTA)^{2+}] + SO_4^{2-}$$

There occurs a reversible reaction and hence $[Ca\,(EDTA)^{2+}]$ becomes,

$$[Ca\,(EDTA)^{2+}] \Leftrightarrow Ca^{2+} + EDTA$$

Thus, EDTA get separated giving Ca^{2+} ion.

The next reaction goes on with sodium thiosulphate and it produces a sulphide ion

$$Na_2S_2O_3.5H_2O \Leftrightarrow Na_2O_3 + 5H_2O + S^{2-}$$

From this two process Ca^{2+} and S^{2-} combine to from the precipitate of CaS.

$$Ca^{2+} + S^{2-} \Leftrightarrow CaS \downarrow$$

2.4 Measurement of thickness of the thin film

After the deposited film has been dried, the film is etched with Hcl on one side. Now, the dried deposited substrate is weighed using Mass Balance and the weight of the film after deposition is noted.

$$\text{Weight of the thin film on the Glass substrate (W)} = \text{Weight after deposition} - \text{Weight before deposition}$$

Now, the thickness of the thin film is determined from the mass difference before and after deposition.

$$t = \frac{W}{\rho A}$$

Where, ρ is density of the material chosen for deposition ($2600 Kg/m^3$) and A is area of deposition.

The thickness of the three samples is found to be in micrometer range (0.96154µm, 0.58719µm and 0.89969µm) as shown in Table 2.

Table 2: Thickness of the film samples

Samples	Weight Before Deposition (gm)	Weight After Deposition (gm)	Thickness (µm)	Area m^2
Sample	4.389	4.391	0.96154	0.0800

3. Result and Discussion

3.1. Optical characterization for the thin film

The optical Characterization was carried out using ***Jasco V-570 spectrophotometer*** and the investigation includes absorbance, transmittance, extinction coefficient, band gap energy etc. The optical properties of the thin films were studied in the UV – VIS – NIR region using bare glass slide as reference.

3.1.1 Transmittance T (%)

The ratio of flux transmitted by a medium to the incident flux.The transmittance percentage of the thin film is measured using the above spectrophotometer and they are obtained as, $T = I/ I_0$ where I – transmitted flux and Io – incident flux is shown in figure 2.

3.1.2 Absorbance (A)

$$\text{Absorbance} = \log \frac{1}{\text{Transmittance}}$$

The absorbance value of the film in the IR region is the logarithmic reciprocal of the transmittance and the curve is obtained by taking the absorbance value along Y –axis and λ along X axis is shown in figure.3.

3.1.3 Extinction Coefficient (K_f)

The extinction coefficient is calculated as follows:

$$K_f = \frac{2.303 \ x \ \log \left(\frac{1}{T}\right) x \ \lambda}{4\Pi t}$$

Where T is the Transmittance (%), λ is the Wavelength (m) and t is the Thickness (μm).

3.1.4 Absorption coefficient (α)

With the help of extinction coefficient (K_f) and wavelength (λ), α is calculated as $\alpha = \frac{4\Pi Kf}{\lambda}$ m^{-1}

From α , Eg is determined.

3.1.5 Energy Band Gap (Eg)

The photon energy is

$$h\nu = \frac{hc}{\lambda} = \frac{6.626 x 10^{-34} x 3 x 10^{8}}{\lambda} \text{ eV}$$

Where h – Planck's constant, ν – Frequency and c – Velocity of light . From the value of α and hν , $(\alpha h \nu)^2$ is calculated.Taking hν along X-axis and $(\alpha h \nu)^2$ along Y – axis, graph is plotted and the intercept on X axis gives the value of Eg and it is given by the relation . Eg = hν - α With the value of Eg and thickness, a graph is plotted for all the samples as shown in figure 4.

3.1.6. Reflectance (R)

The percentage of light reflected back from a surface, the difference having been absorbed or transmitted from a surface. Reflectance is given by, R= 1- A- T , where A is the absorbance , T is the transmittance. Reflectance graph are shown in figure 5. The spectral absorbance of the CaS thin films are displayed and the absorbance value are found to be low in the range of 0-0.17% with varying bath conditions. The film exhibits high transmittance, ranges from 70-85% in the UV-VIS region and the band gap was found to be in the range of 3.9eV, The plot against photon energy and extinction coefficient for the Sample is shown in figure 6 and maximum extinction coefficient value ranges from 0.12-0.2 in the UV region.

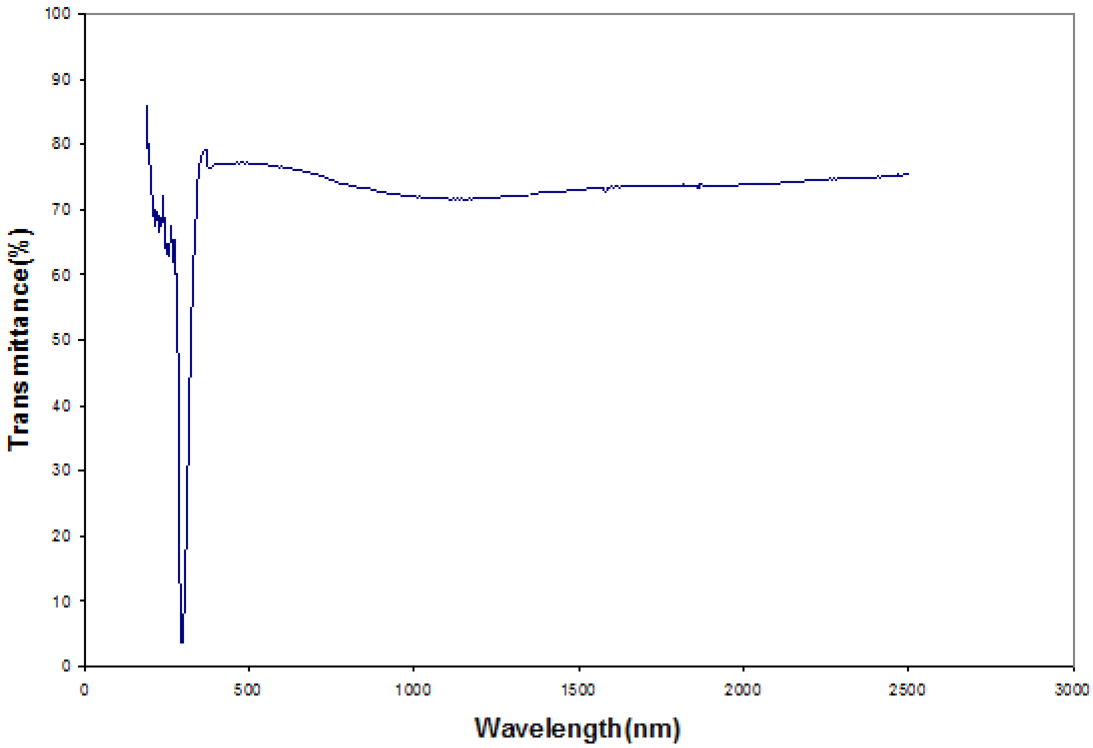

Figure 2: Transmittance Spectrum for the Sample

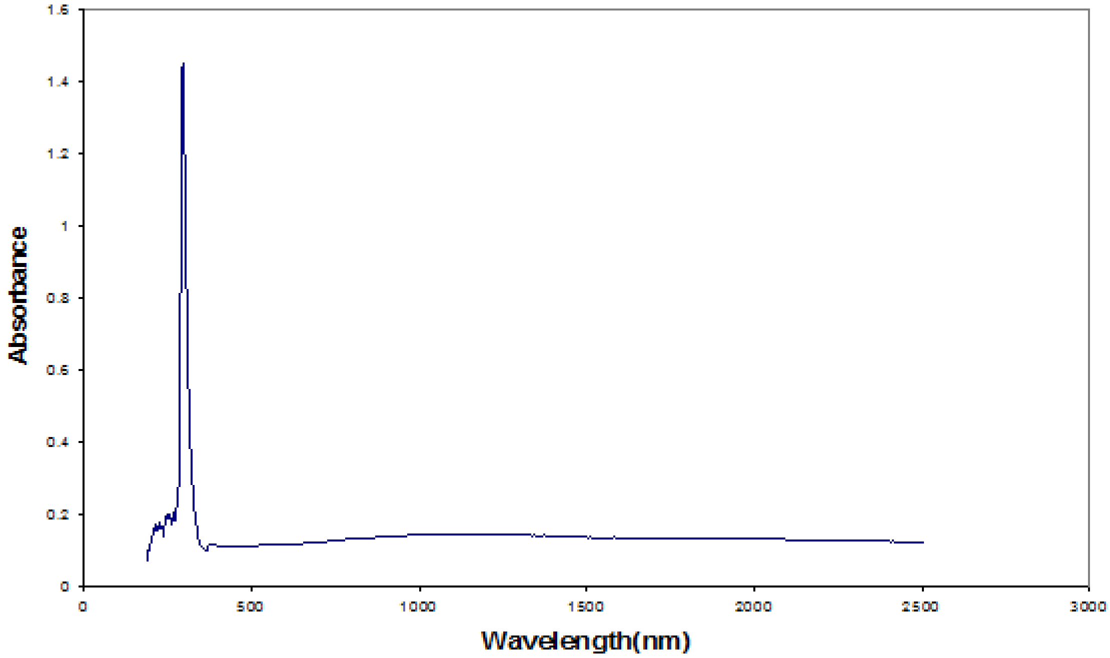

Figure 3: Absorbance Spectrum for the Sample

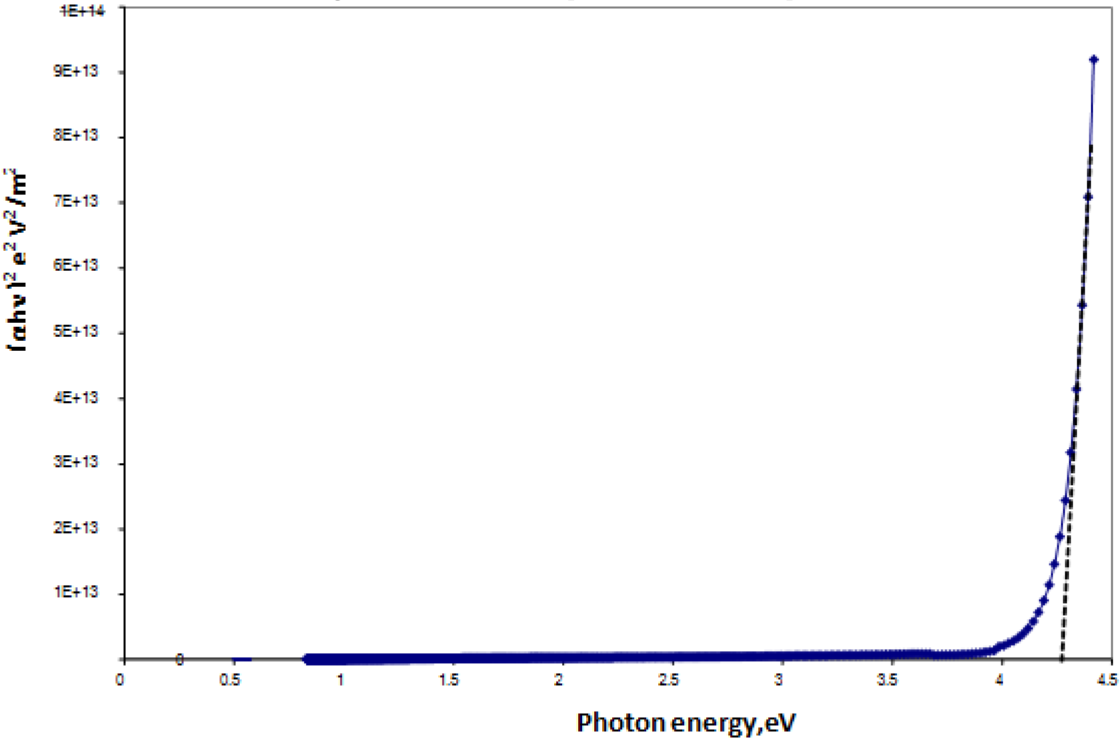

Figure 4: Band gap Energy for the Sample

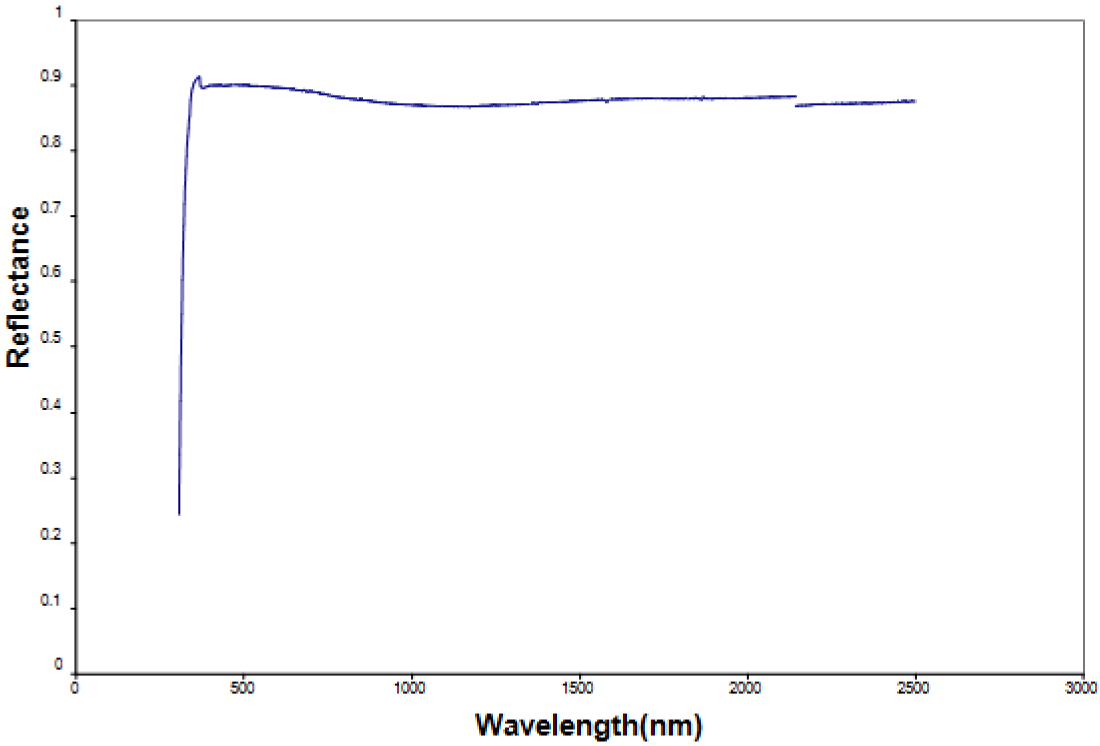

Figure 5: Reflectance for the Sample

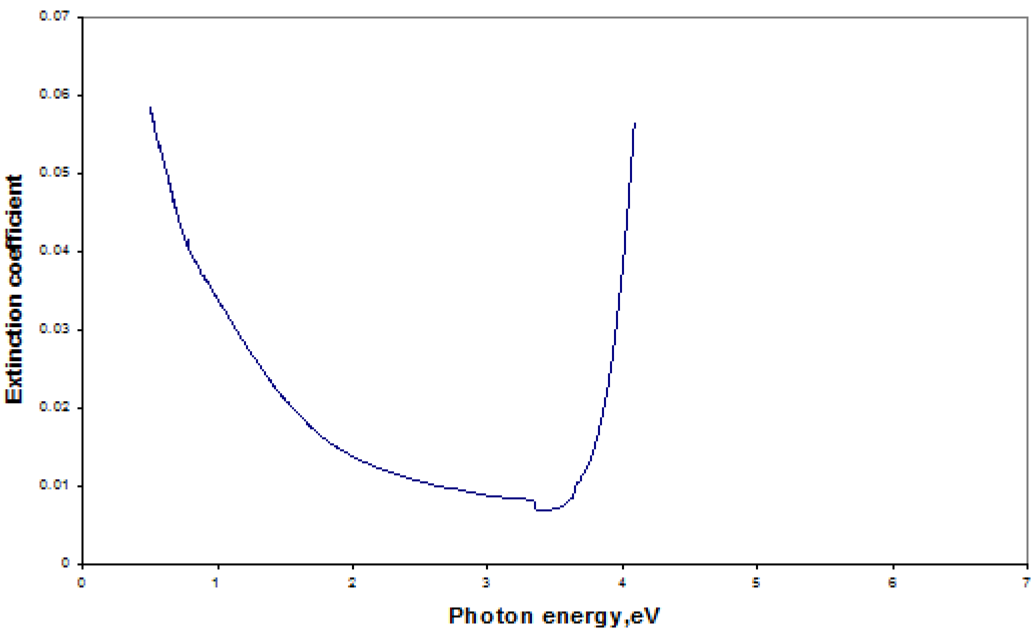

Figure 6: Photon Energy Vs Extinction Coefficient for the Sample

4. Conclusion

In the present work, Calcium Sulphide is chosen as the depositing material since it involves wide range of applications in the field of semiconductor devices and optical coatings.It is suitable for use as a photosynthetic and window coating material. Of all the deposition technique CBD is the least cost by technique. Chemical Bath Deposition technique is chosen to deposit thin films of CaS on glass substrate at varying bath parameters as the technique involves the precipitation from solution of a compound on suitable substrate. Thin films with less than one micron in thickness can be conductive or dielectric and are used to make solar panels and solar roof shingles. The optical Characterization was carried out and the samples exhibit a low absorbance of 0-0.17% and high transmittance which ranges from 70-85% in the UV-Visible region. The range of extinction coefficient is 0.12 – 0.2 for photon energy of 4.2eV. The band gap determined from $(\alpha h\nu)^2$ Vs hν graph is found to be ~ 3.9eV. Since the material exhibits high transmittance in the UV-Visible region it is suitable for window coating. The deposited film is also used in solar energy collector and anti reflection coatings

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