

CHEMICAL BATH DEPOSITION OF CADMIUM BARIUM SULPHIDE (CDBAS) THIN FILM AND ITS THICKNESS EFFECT ON BAND GAP ENERGY

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ABSTRACT

This study was basically centred on the chemical bath deposition technique of CdBaS (Cadmium Barium sulphide), and to determine the effect of thin film thickness on the band gap energy of chemically deposited CdBaS. The thin films of CdBaS were deposited on several samples of glass slides using a chemical bath deposition (CBD) technique. Several precursors were used such as Cadmium Sulphate ($CdSO_4$), Ammonia (NH_3), Thiourea (T.U) CH_4N_2S and Barium Sulphate ($BaSO_4$). The deposition of CdBaS depends on the parameters such as volume of precursors, deposition temperature and dip time to uncover the properties of the thin film using spectrophotometer. Annealing of substrate involves heating of films at high temperatures. Annealing was done at $100^\circ C$, $200^\circ C$, $300^\circ C$, $400^\circ C$ and $500^\circ C$. The concentrations of NH_3 and $BaSO_4$ were varied in different sample of beakers. The result shows that the band gap energy increases as temperature and film thickness increases.

Keywords: Chemical–Bath, Deposition-Technique, Cadmium Barium Sulphide, Spectrophotometer.

INTRODUCTION

The anomalous behaviour of matter if made to exist in the form of thin film is an established phenomenon of modern Physics and is being explored in research into the properties of matter and for industrial application, including microelectronics, optics, magnetic; etc. Progress in each of the area depends on the ability to selectively and controllably deposit this film with thickness ranging from tens of angstroms to micrometres with specific physical properties (Lepek&Dogil, 1983). This in turn, requires control (often at atomic level) of film microstructure and microchemistry. There are vast numbers of

deposit methods available and in use today. However, all methods have their specific limitations and involves compromises with respect to process specifics, substrate material limitations, expected film properties, and cost. This makes it difficult to select the best technique for any specific application.

Thin films are thin material layers ranging from fractions of nanometer (nanolayer) to several micrometers in thickness. Electronic semi-conductor devices and optical coating are the main application benefitting from thin film construction. (Halliday et al., 2001). A familiar application of thin film is the household mirror which typically has a thin metal coating at the

back of a sheet of glass to form a reflective interface. The process of silvering was once commonly used to produce mirrors. A very thin film coating (less than a nanometre) is used to produce two ways mirror. The performance of optical coatings (e.g. anti-reflective, or AR, coatings) are typically enhanced when the thin film coating consists of multiple layers having ranging thickness and refractive indices. Similarly, a periodic structure of alternating thin films of different materials may collectively form a so-called supper lattice which exploits the phenomenon of two dimensions. Thin films are used to produce thin film batteries. Ceramic thin films are in wide use. The relatively high hardness and innerness of ceramic material make these types of thin film coating of interest for protection of substrate materials against corrosion, oxidation and wear. In particular, the use of such coatings on cutting tools can extend the life of these items by several orders of magnitude. Research is being done on a new class of thin film inorganic oxide materials, called amorphous heavy – metal cation multicomponent oxide, which could be used to make transparent transistors that are inexpensive, stable and environmental friendly (Olivia, et al,2001).The band gap generally refers to the energy difference (in electron volts) between the top of the valence band and the bottom of the conduction band which is found in insulators and semiconductors, it is

$$\alpha = \ln(I_0/I)/x$$

Conduction band CB

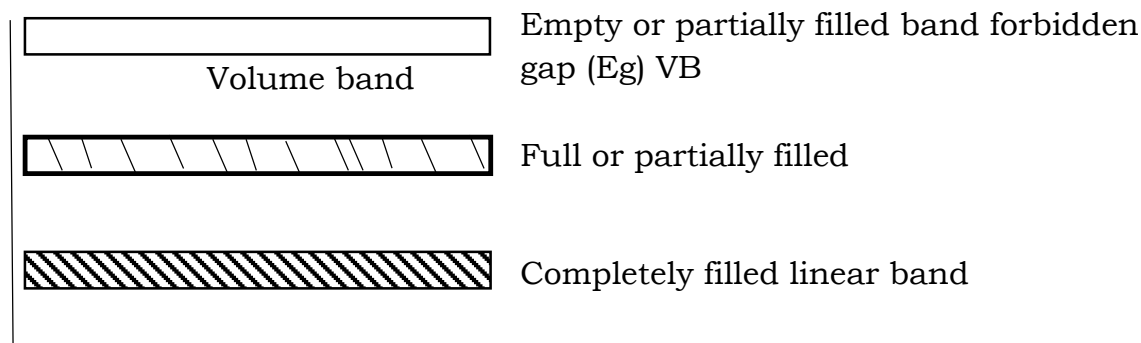


Figure. 1: The band – gap pattern of energy levels

the amount of energy required to free an outer shell electron from its orbit about the nucleus to become mobile charge to move freely within the solid, material (Unlu, 1992). Transmittance is the fraction of incident light at a specified wavelength that passes through a sample. This can be expressed as:

$$T_\lambda = I/I_0 \dots\dots\dots \text{equation (1)}$$

Where I_0 is the intensity of the incident light and I is the intensity of the light coming out of the sample, the transmittance of a sample is sometimes given as a percentage.

Transmittance is related to absorbance A_λ

$$A_\lambda = -\log_{10} T_\lambda = -\log_{10}(I/I_0) \dots\dots \text{equation (2)}$$

Or using the natural logarithm

$$A_\lambda = \ln T_\lambda = \ln (I/I_0) \dots\dots\dots \text{equation (3)}$$

From the equation and the Bear-Lambert law, the transmittance is thus given by

Where α the attenuation coefficient and x is the path length.

The absorption coefficient is a quantity that characterizes how easily a material medium can be penetrated by a beam of light, sound or particle. A large absorption coefficient means that the beam is quickly attenuated (weakened) as it passes through the medium that is relatively transparent to the beam. This can be expressed as:

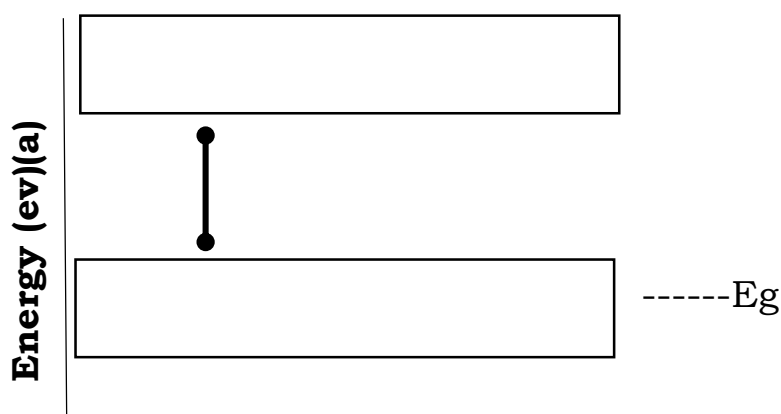


Figure. 2: Energy band diagram showing formation

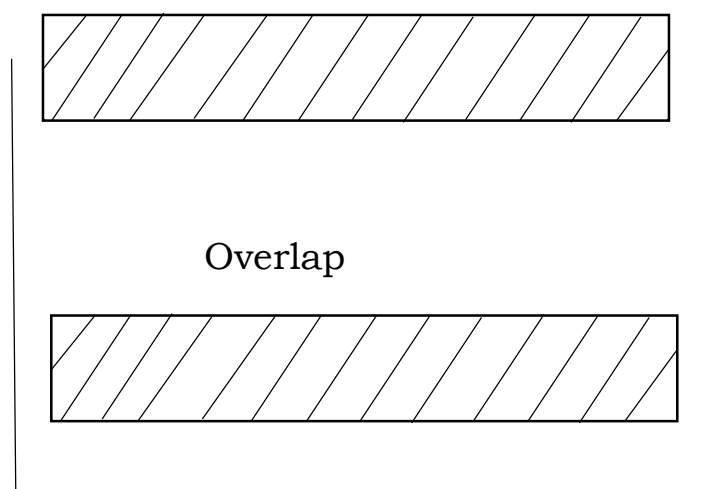


Figure 3: Energy band Conductor

MATERIALS AND METHODS

The apparatus used for the deposition of CdBaS includes

Glass beakers (50mL and 250mL), Stirring rod, and microscopic glass substrate/slide, Electronic weighing balance, Measuring cylinder (100ml), Magnetic stirrer, Temperature regulating oven, Conical flask (250mL), Verniercaliper. Pegs, Syringe (10mL)

The experimental efforts was supported by computational approaches that address complex growth processes, chemical bath

deposition technique (CBD) also known as solution growth technique was used to grow Cadmium Barium Sulphide (CdBaS) heterojunction thin film. The method was used due to numerous advantages which include: low cost and easier fabrication of large area thin film, easier composition control is easier, the technique is associated with low processing temperature even at room temperature, easy coating process of large and complex shaped substrate and possibility of using high purity starting material (Asmaa, et al.,2022).

However, very promising approach to synthesis of inorganic single crystalline thin film is the chemical/solution deposition method (Lange, 1996), these solutions however contain precursors for a variety of elements in film of interest. In other words,

CBD will become one of the key technologies to synthesis of (CdBaS) for different application e.g. Opto-electronic device application. Figure 4 shows the experimental set-up for the deposition of CdBaS thin film.

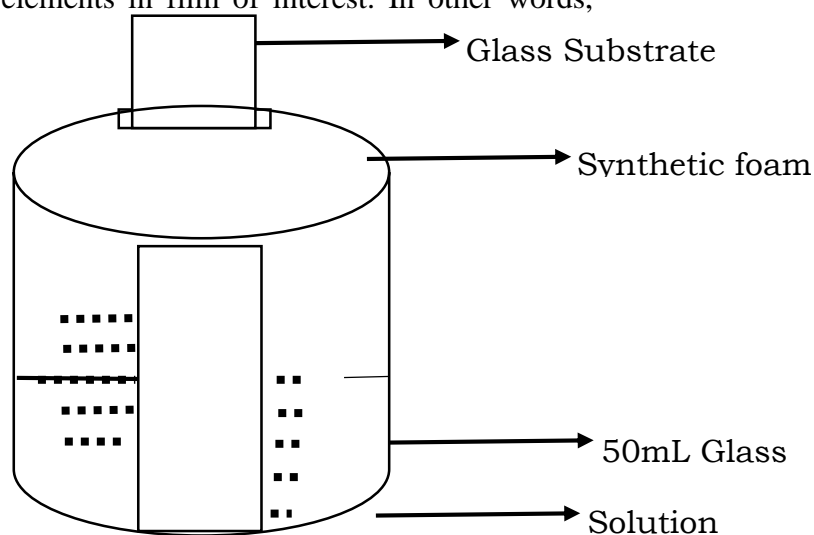


Figure. 4: Experimental set-up for the deposition of CdBaS Thin film

The glass substrates were immersed or dipped in concentrated hydrochloric acid (HCL) or concentrated hydrogen tetraoxosulphate VI acid (H₂SO₄). This is done to degrease the surface or to remove oxides and particles on it. Glass substrates were washed thoroughly in deionized or in distilled water, this was succeeded by hanging slides to dry in air and stored in oven to dry properly and avoid impurities. The synthetic foam protects the reaction bath from intrusion of dust particles and provides a clamp also for substrate through which they make contact with precursors in solution (Roland, et al., 2010). Five (5) beakers of 50mL were employed for film deposition. Precursor's used and their properties are ;Cadmium sulphate (CdSO₄): Molar mass: 769.52g/mol, Ammonia (NH₃) of Molar mass; 17.031g/mol. Thiourea (T.U) CH₄N₂S; Molar mass; 7.612g/mol, Barium sulphate (BaSO₄); molar mass; 233.4g/mol, Distilled water (H₂O).

The precursor CdSO₄ has already been provided or produced by standard in its original molecular weight i.e. 769.52g/mol. In order to obtain the required quantity for solution,

new molar mass was calculated using;

$$\text{Molarity} = 1\text{mol solution} = \frac{\text{mass}}{\text{Molar weight} \times 1000\text{cm}^3} \quad \dots\dots\dots \text{equation (4)}$$

$$100\text{mL} = 100\text{cm}^3$$

To obtain one mole solution

Let x = mass of the compound to be dissolved x (100/1000)

$$10\text{mol} = 1000\text{cm}^3$$

$$\text{Mass} = 1\text{mol} \times \text{molar weight} \times 0.1$$

CdSO₄ molar weight is 769.52g/mol

$$\text{Mass} = 1 \times 769.52\text{g} \times 0.1$$

Required Mass = 769.52g

Theiourea (T.U) has also been provided with molecular weight of 76.12g 1mol, so to obtain its molar mass

$$\begin{aligned} \text{Mass} &= 1 \times \text{m.w} \times 0.1 \\ &= 1 \times 76.12 \times 0.1 \end{aligned}$$

Required Mass = 76.12g 1mol.

Barium Sulphate (BaSO₄) has been provided with molecular weight of 233.4g, so to obtain its molar mass.

$$\begin{aligned} \text{Mass} &= 1 \times \text{m.w} \times 0.1 \\ &= 1 \times 233.4 \times 0.1 \end{aligned}$$

Required Mass = 233.4g 1mol.

Ammonia (NH₃) was already prepared by manufacturers but was collected at different volume (mL). However, H₂O was also used at different volume (mL) for solution preparation.

Deposition of CdBaS thin film experimental steps:

- (i) The glass slides were washed with HCl and rinsed with water to remove impurities.
- (ii) The beakers and syringes were thoroughly washed using soap and sponge, thereafter, rinsed in water then allowed to dry before labelling.
- (iii) The prepared solutions were measured accordingly and sequentially, using syringe and measuring cylinder according to the volumes specified in the tables.
- (iv) The beakers were labelled A_{a1}, B_{b1}, C_{c1}, D_{d1}, E_{e1}, (table 1) and (table 2). Representing each sample of glass slides.
- (v) The mixtures were stirred using a magnetic stirrer.
- (vi) The glass slides were placed vertically in each beaker containing the mixtures for uniform deposition and the beaker were covered with foam at surface to avoid dust, impurities or particles for effective deposition on glass slides.
- (vii) The deposits were grown at room temperature i.e. (38⁰C) it was observed to form a better deposition.
- (viii) The beakers containing the mixture and glass sliders were placed inside the oven..
- (ix) The depositions were then observed, and they were removed from the oven.
- (x) After deposition the glass slide was rinsed in distilled water and hanged in pegs to dry (Munikrishna, et.al; 2013). The deposition time was recorded such that;

A_{a1} dip time was 6 hours.

B_{b1}dip time was 12 hours

C_{c1} dip time was 18 hours

D_{d1} dip time was 24 hours

E_{e1} dip time was 30 hours

RESULTS**Table 1 Deposition of (CdBaS) Thin Film with Varied NH₃**

S/N	CBD/Bath Temp (°C)	Dip time (hrs)	CdSO ₄ (mL)	T.U (mL)	BaSO ₄ mL	NH ₃ (mL)	H ₂ O (mL)
A _{a1}	38 ⁰ C	2hrs	5	5	5	2	33
B _{b1}	38 ⁰ C	2hrs	5	5	5	4	31
C _{c1}	38 ⁰ C	2hrs	5	5	5	6	29
D _{d1}	38 ⁰ C	2hrs	5	5	5	8	27
E _{e1}	38 ⁰ C	2hrs	5	5	5	10	25

The colourless mixture gradually turned into a milky and lemon yellowish colour and there were good deposition on the slides:-

- A_{a1} - has a milky colour
 B_{b1} - has a more milky colour
 C_{c1} - Has a light yellowish colour
 D_{d1} - has a light lemon yellow colour
 E_{e1} - has a lemon yellowish colour.

Table 2 Deposition of (CdBaS) Thin Film with Varied BaSO₄

S/N	CBD/Bath Temp (°C)	Dip time (hrs)	CdSO ₄ (mL)	T.U (mL)	BaSO ₄ (mL)	NH ₃ (mL)	H ₂ O (mL)
A _{a1}	38 ⁰ C	2hrs	4	4	1	4	37
B _{b1}	38 ⁰ C	2hrs	4	4	3	4	35
C _{c1}	38 ⁰ C	2hrs	4	4	5	4	33
D _{d1}	38 ⁰ C	2hrs	4	4	6	4	32
E _{e1}	38 ⁰ C	2hrs	4	4	8	4	30

The colourless mixture gradually turned into deep yellow on slide A_{a1} and B_{b1}.

- A_{a1} - deep yellow colour
 B_{b1} - deep yellow colour
 C_{c1} - yellow colour
 D_{d1} - yellow colour
 E_{e1} - deep yellow colour.

Table 3 shows the parameters of CdBaS film deposited at varied dip time.

S/N	CBD/Bath Temp (°C)	Dip time (hrs)	CdSO ₄ (mL)	T.U (mL)	BaSO ₄ (mL)	NH ₃ (mL)	H ₂ O (mL)
A _{a1}	38 ⁰ C	6hrs	5	5	5	5	30
B _{b1}	38 ⁰ C	12hrs	5	5	5	5	30
C _{c1}	38 ⁰ C	18hrs	5	5	5	5	30
D _{d1}	38 ⁰ C	24hrs	5	5	5	5	30
E _{e1}	38 ⁰ C	30hrs	5	5	5	5	30

Initially, a colourless mixture was observed after deposition.

- A_{a1} - light yellow colour
 B_{b1} - yellow colour
 C_{c1} -yellow colour
 D_{d1} - yellow colour
 E_{e1} -yellow colour:-Remark.

Table 4 shows some deposition parameters of deposited CdBaS thin films.

Slides	M _i (g)	M _f (g)	$\frac{M_f - M_i}{2}$	Length of film dipped (cm)	Width of film dipped	A=L x W	$\frac{T = M}{A \times E}$
1	4.9053	5.4732	0.2840	3.50	2.35	8.23	0.0072
2	4.9053	5.5441	0.3194	3.60	2.35	9.36	0.0071
3	4.9053	5.5245	0.3096	3.60	2.35	9.36	0.0069
4	4.9053	5.4405	0.2676	3.50	2.35	8.23	0.0067
5	4.9053	5.8310	0.4629	2.90	2.35	6.82	0.0014
6	4.9053	5.0648	0.0798	3.20	2.35	7.52	0.0022
7	4.9053	5.3020	0.1984	3.30	2.35	7.76	0.0053
8	4.9053	5.2605	0.1776	3.50	2.35	8.23	0.0045
9	4.9053	5.0602	0.0775	3.20	2.35	7.52	0.0021
10	4.9053	5.2883	0.1915	3.20	2.35	7.52	0.0053

Where

- M_i = mass before dip
 M_f = mass after dip
 A = Area of the Slides
 T = thickness of the film
 E = Density (4.82g)kg/m³

The substrates of CdBaS thin film were annealed at different temperature of 100⁰C, 200⁰C, 300⁰C, 400⁰C, 500⁰C for 1 hour.

Effect of the CdBaS film Thickness on

BANDGAP: -Four samples of chemical bath deposition CdBaS thin films with the thickness of 0.0021, 0.0022, 0.00453 and 0.0053 are shown in figures 5 and 6 below. The value of optical band gap energy for different film thickness is found in the range of 2.35 – 2.45 eV. On the basis of these experimental results band gap of the thin films increases as the thickness of the films increases. The band gap of the films varies with the increase in film thickness in the 0.0021 – 0.0045 range and then increases abruptly for the film thickness of 0.0045 – 0.0053. These measurements included absorbance transmittance, reflectance (Wii, 2002).

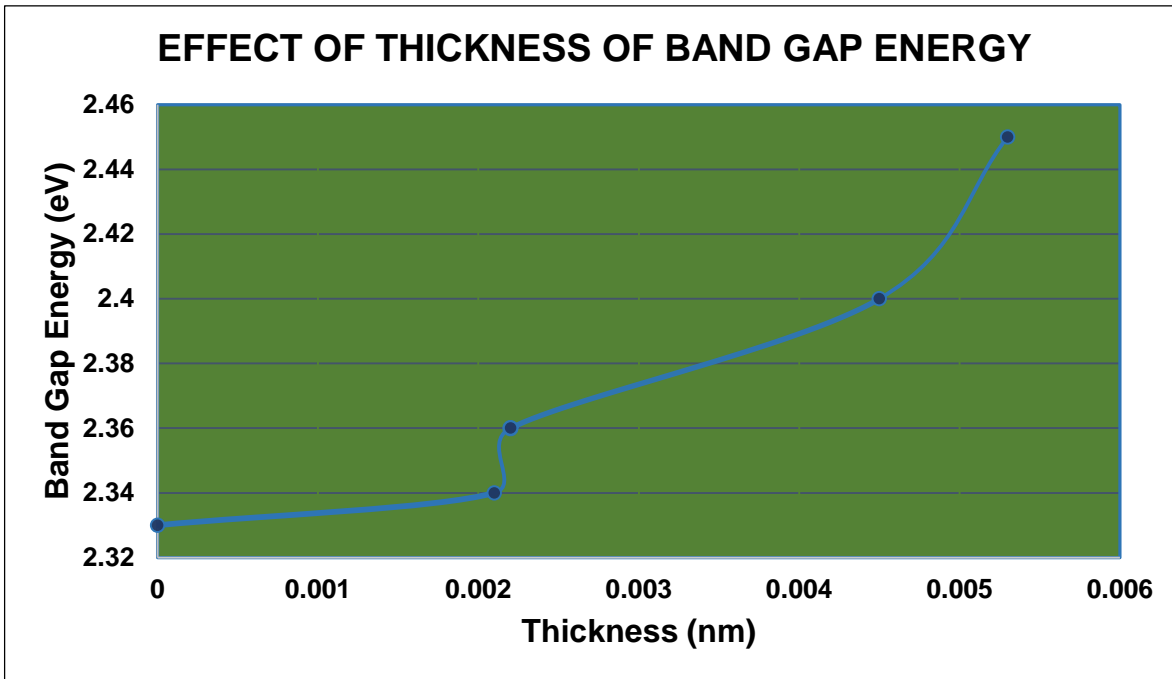


Figure 5: Effect of Thickness of Band Gap Energy

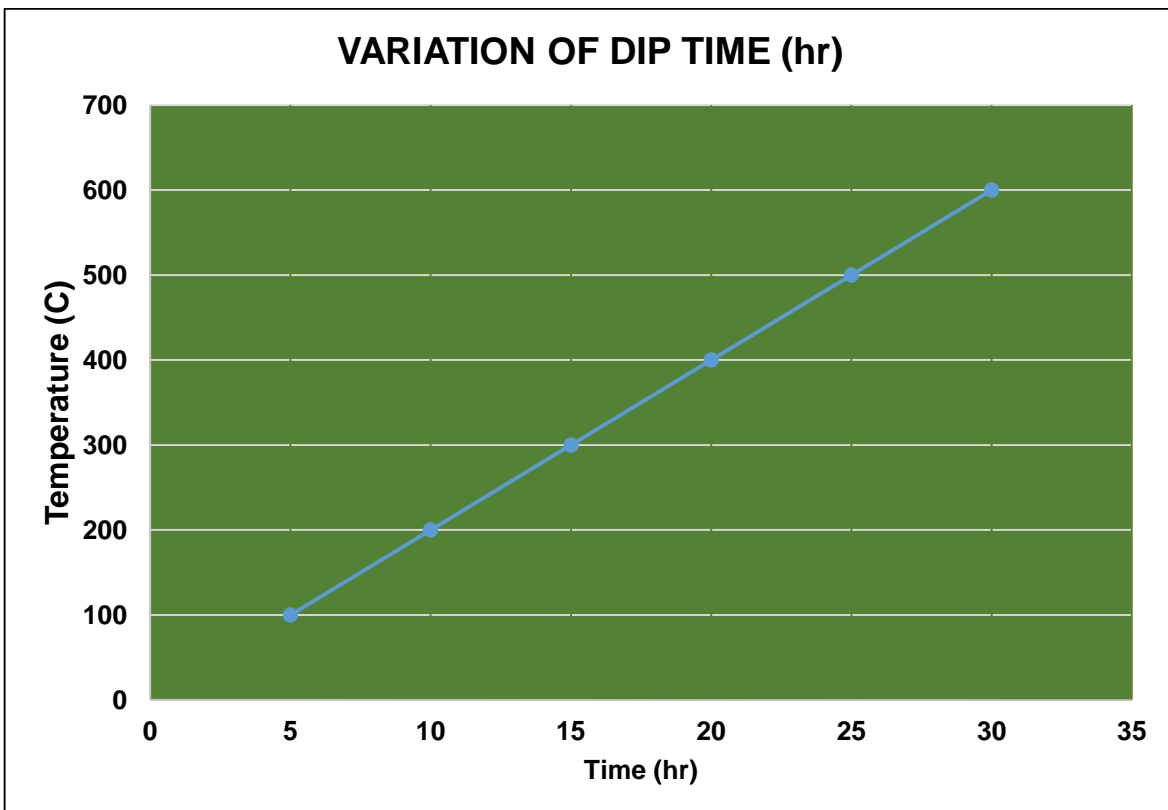


Figure 6: Variation of Dip Time (hr.)

CONCLUSION

CdBaS thin film has been grown or deposited on glass slides at room temperature and at annealing temperature. Deposition temperatures were at 38⁰C and were annealed at different temperature 100⁰C, 300⁰C and 400⁰C. The optical property chemical bath deposited CdBaS thin film showed that it will be a good absorber of photon energy for light for solar energy generator.

From the results of the experiment, it can be concluded that CdBaS is a good absorber of photon energy for light solar energy generator. The relationship between the film thickness temperature and band gap energy is that as the thickness and temperature increases, the band gap energy also increases; this was shown in the chart above. The band gap for each sample used as selected slides and shown in the charts were 0.002thickness (nm), the band gap is 2.3eV-2.35eV, 0.003 thickness (nm) the band gap is 2.40eV and 0.005 thickness (nm) the band gap is 2.45 eV respectively.

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