Photovoltaic Potential of *Hawleyite* Cadmium Sulphide (CdS) Nanofilms

ABSTRACT

Thin films of Cadmium Sulphide were deposited on degreased glass substrate, from a bath containing the precursors via Chemical Bath Deposition (CBD) technique. The Physical, Structural, and optical properties were investigated by X-Ray diffractometer, Scanning Electron microscopy (SEM), surface profilometer, Energy dispersive X-ray spectroscopy (EDX) and spectrophotometer. The 9hours CdS sample showed peak intensities at 30.95^{o} and 51.77^{o} with *hkl* values of (1 1 1) and (2 2 0). The 12hours sample showed peak intensities at 30.95^{o} and 51.55^{o} with *hkl* values of (1 1 1) and (2 2 0. The planes of cubic phase correspond to the mineral Hawleyites for both samples. The average Crystallite grain size for the 9hours sample is 27.72nm and 38.99nm for the 12hours samples. The Scanning Electron microscopy analyses illustrate the morphology and the level of uniformity of the CdS coating across the surface of the 9hours sample and 12 hours samples. The micrographs although slightly similar, the 12hours sample appeared to be more uniformly coated when compared to the 9hours sample. Electron-Dispersive X-ray Spectroscopy (EDX) indicated the percentage composition of Cadmium and Sulphide present in the both 9hours and 12hours samples, with Cadmium having an average composition of 26.45% and sulphide 8.65% for the 9hours sample, and 61.95% for Cadmium and 16.43% for Sulphide in the 12 hours CdS sample. The Spectrophotometer was used to investigate the behavior of both samples in the UV (≤ 400nm), Visible and part of the Infrared region. The bandgap energies of both 9hours and 12hours sample were 2.36eV and 2.257eV respectively. The average value for the optical conductivity for 9hours sample is 5.099×10^{13} and 7.75×10^{13} for 12hours sample. The average values of the extinction coefficients, k for 9hours sample is 1.07×10^{9} and 2.02×10^{9} for 12hours sample. The average thickness value of CdS Sample deposited for 9hours is 14.10×10^{-9}m while that of the CdS sample deposited for 12hours is 14.5×10^{-9}m. The results affirm the choice of CdS film as buffer layer of the photovoltaic cells.

Keywords*:* *Cadmium Sulphide, Chemical Bath Deposition, Glass Substrate, X-ray Diffractometer, Bandgap Energies.*

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INTRODUCTION

Nanostructured materials are now being studied for their possible uses and across many disciplines, plus photovoltaics, electro-optics, micromechanics, and sensor systems [1]. Nanoparticles are extremely tiny particles (often between 1 and 100 nm in size) [2]. In order to

commercially create low-cost solar cells with great efficiency, it is now necessary to make use of nanotechnology.

Nanostructures may take many forms, such as atomic groups, multilayer (lamellae) layers, filament patterns, and particles. They all have one thing in common: they have dimensions on the nanoscale, which is defined as having at least one dimension of less than 100 nm and typically less than 50 nm. Nanoscale materials picked scientists' attention since their physics may be drastically different from that of the same substance at a larger scale, resulting in frequently better qualities [3].

Nanoscale semi-conductors have the potential to revolutionize a variety of industries due to their unique electrical, optical, and magnetic capabilities compared to bulk partial conductors. Among them are the areas of electronics, optoelectronics, energy and medicine [4].

Due to the fact that semi-conductor nanoparticles differ in electrical and optical characteristics from bulk partial conductors, a great deal of attention has been paid to them. Sensing, catalysis, and optoelectronics are just a few of the fields that may benefit from their high surface-to-volume ratio [5].

Many modern applications make use of semi-conductors because of their exceptional electrical characteristics. Band symmetry, or the symmetry of the energy levels in the partial conductor's electrical band structure, is a characteristic used to categorize partial conductors.

Most sunlight cell partial conductors are inorganic, crystalline solids from atomic groups I through VI [6]. Partial conductor materials may be broken down into four categories based on their chemical make-up: elemental, binary, ternary and quaternary. Some examples of these partial conductors are shown in Table 1.

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Table 1: A list of the materials and components that are appropriate for solar cell applications in the semiconductor industry [7].

Partial conductor Family	**Example of Partial conductors**
Elemental partial conductors	C, Si, Ge
III-V Partial conductors	AIN, AIP, AIAs, AISb, GaN, GaP, GaAs, GaSb, InN, InP, InAs, InSb
II-VI Partial conductors	ZnS, ZnSe, ZnTe, ZnTe, ZnO, CdS, CdTe, CdO
Ternary compound partial conductors	$CuInSe_2$ (CIS), $Cd_xMn_{(1-x)}Te$ (CMT), $Cd_xHg_{(1-x)}Te$, $Al_xGa_{(1-x)}As$
Quaternary Compound	$CuInGaSe_2$ (CIGS), $AgInGaSSe_2$, $Cu_2ZnSnSSe_4$(CZTS)

Semi-conductors may be further classified as either intrinsic or extrinsic, depending on the kind of impurities they allow to enter the material. Intrinsic or i-type partial conductors are those that are undoped or minimally doped with no external dopant species present [8].

CdS belongs to the II-VI group. It has a lot of potential applications in electrical and optoelectronic gadgets. Due to its high light sensitivity and acceptable bandgap, it is an attractive source for the sensing of visible light.

There are a number of ways to synthesize CdS nanoparticles, including chemical precipitation, hydrothermal synthesis, and chemical bath deposition (CBD). Thin film synthesis involves putting materials onto a substrate in the form of extremely thin layers (ranging in thickness from a few nanometers to a few micrometers). Because of its many benefits over conventional bulk solar cells, including reduced manufacturing costs, higher efficiency, thin films are a potentially game-changer. The most common and time-tested technique is CBD. For

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certain applications, the ability to deposit thin films of different nanomaterials/nanoparticles is crucial since the characteristics in terms of both chemistry and physics of the resulting film are determined by the method of deposition and development of the nanoparticles used [6].

Some other techniques of depositing thin films are magnetron sputtering, radio-frequency sputtering, molecular beam epitaxy (MBE), and closed-space sublimation (CSS). Chemical deposition method may be used to chemically manufacture slim-film coatings by using liquid or gaseous precursors to induce a chemical reaction at the surface of the substrate. Electrodeposition (ED), chemical bath deposition (CBD), chemical reduction plating (CRP), spin coating (SC), and chemical vapour deposition (CVD) are just a few examples of deposition processes. Chemical vapour deposition (CVD) encompasses a wide variety of processes, among of which include metal organic chemical vapour deposition (MOCVD) and atmospheric pressure chemical vapour deposition (APCVD) [9].

In this work, Chemical Bath Deposition (CBD) method was employed to deposit Cadmium Sulphide Nanofilms and the results are thus, reported.

MATERIALS AND METHODS

Distilled water, chemicals (AR grade), glass slides, a retort stand, reagent bottles, cork,100 ml beakers, a pipette, washing bottles and measuring cylinder were utilized for depositing CdS thin films.

The bath was prepared by mixing different volumes, concentrations (0.5M, 1M) of each reagents/chemicals (cation, anion compounds and complexing agents compounds), and distilled water was then added to make up the volume for the deposition that will cover at least ¾ of the glass slide length when placed in the bath. All chemicals used were AR grade laboratory

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reagents. A 100ml beaker was used as the bath, which contained the precursors. The glass slides were then weighed with sensitive electronic balance and dipped into the solution as the reaction starts. The slide was held in a steady position by means of a cork strip placed across the open end of the beaker, with an opening to hold the slide in the vertical position.

CdS film was deposited as a result of the slow release of Cd^{2+} and S^{2-} ions in aqueous basic baths (pH 10), and the subsequent condensation of these ions on the substrates which were vertically placed in the solution.

Dissociation of thiourea $(SCNH_2)_2$ in alkaline ammonia solution provided the S^{2-} ions. The slides were removed periodically from each of the baths (beakers containing the precursors) after 3, 6, 9, 12 and 15 hours. The deposited CdS films were rinsed with distilled water and allowed to dry. Table 2 shows the deposition parameters for the deposited Cadmium Sulphide thin film.

The dissociation Cadmium from Cd^{2+} from the reaction;

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

Dissociation of thiourea $(SCNH_2)_2$ in alkaline ammonia solution provided the S^{2-} ions;

$$SC(NH_2)_2 + OH^- \longrightarrow CH_2 + H_20 + SH^-$$

$$SH^- + OH^- \longrightarrow S^{2-} + H_20$$

The Cd^{2+} and S^{2-} ions then condense to give CdS (Solid) coating.

Table 2: Deposition parameters of Cadmium Sulphide thin- film.

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Reaction Bath (100ml Beaker)	Deposition Time (Hours)	Cation Compound (X)		Ammonia solution		Na_2SO_3/Na_2SO_4		Distilled Water
		Mol.(M)	Volume (ml)	Mol.(M)	Vol.(ml)	Mol.(M)	Vol.(ml)	Vol.(ml)
A_1	3	0.5	10	1	5	0.5	10	65
A_2	6	0.5	10	1	5	0.5	10	65
A_3	9	0.5	10	1	5	0.5	10	65
A_4	12	0.5	10	1	5	0.5	10	65
A_5	15	0.5	10	1	5	0.5	10	65

Films, A_3 and A_4 were used to study the structure of as-deposited films, because they appeared to be more uniformly coated than other glass slides from other baths.

The structural properties of the deposited CdS nanofilm were determined through the use of the X-Ray Diffractometer (XRD), Scanning Electron Microscope (SEM), and Energy Dispersive Spectrometer (EDS).

The optical properties of the deposited CdS thin films such as Transmittance, Absorbance, Reflectance, Energy Bandgap, Optical conductivity, Refractive Index and Extinction Coefficient were determined through the use of the UV - Vis Spectrophotometer.

Debye - Scherer equation (eqn. 1) was used for achieving the thickness value of the deposited CdS Nano film.

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$$D = \frac{K\lambda}{\beta COS\theta} \quad (1)$$

Where K is the Scherrer Constant,

λ Wavelength of the Xray beam,

β Full Width at Half Maximum (FWHM),

θ is Bragg angle

The bandgap energy for both the 9hours and 12hours CdS samples were calculated using the Tauc and Davis-Mott relation;

$$(\alpha hv)^n = K(hv - Eg) \quad (2)$$

Where, α = absorption coefficient

h = plank's constant (6.62607004 x 10^{-34} m^2kg/s)

v = frequency (Hz)

k = Energy dependent constant

Eg= Energy of photon

n = Nature of transmission

For calculation of direct bandgap, a graph of $(\alpha hv)^2$ against wavelegnth is plotted and the direct bandgap is evaluated.

The optical conductivity of both 9hours and 12hours sample was computed using;

$$\sigma_{opt.} = \frac{\alpha nc}{4\pi} \quad (3)$$

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Where, σ_{opt} = optical conductivity

α = absorption coefficient

n = refractive index

c = Speed of light in vacuum

This is defined as the property of a material which gives the relationship between the induced current density in the material and the magnitude of the inducing electric field for arbitrary frequencies

The refractive indices of both 9hours and 12hours samples were determined using;

$$n = \frac{1}{Ts} + \sqrt{\frac{1}{Ts-1}} \quad (4)$$

Where, n = refractive index

Ts = Percent transmittance

Refractive index of a material is a dimensionless number that describes how fast light travels through the material. Higher the refractive index, the slower will light travel through the material.

The Extinction coefficients, k of both 9hours and 12hours sample were determined using;

$$K = \frac{\alpha\lambda}{4\pi} \quad (5)$$

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Where, α= absorption coefficient

λ = wavelength

π =3.142

This is defined as the measure of how strongly a chemical substance absorbs light at a particular wavelength, and it depends upon the structure and chemical composition of the material.

RESULTS AND DISCUSSIONS

Analysis of CdS-coated films at deposition time of 9hours revealed peaks at 2theta of 30.95^{o} and 51.77^{o}, corresponding to (1 1 1) and (2 2 0) of the cubic CdS phase. The spectrum of the peaks and the 2theta values are shown in Figure 1a.

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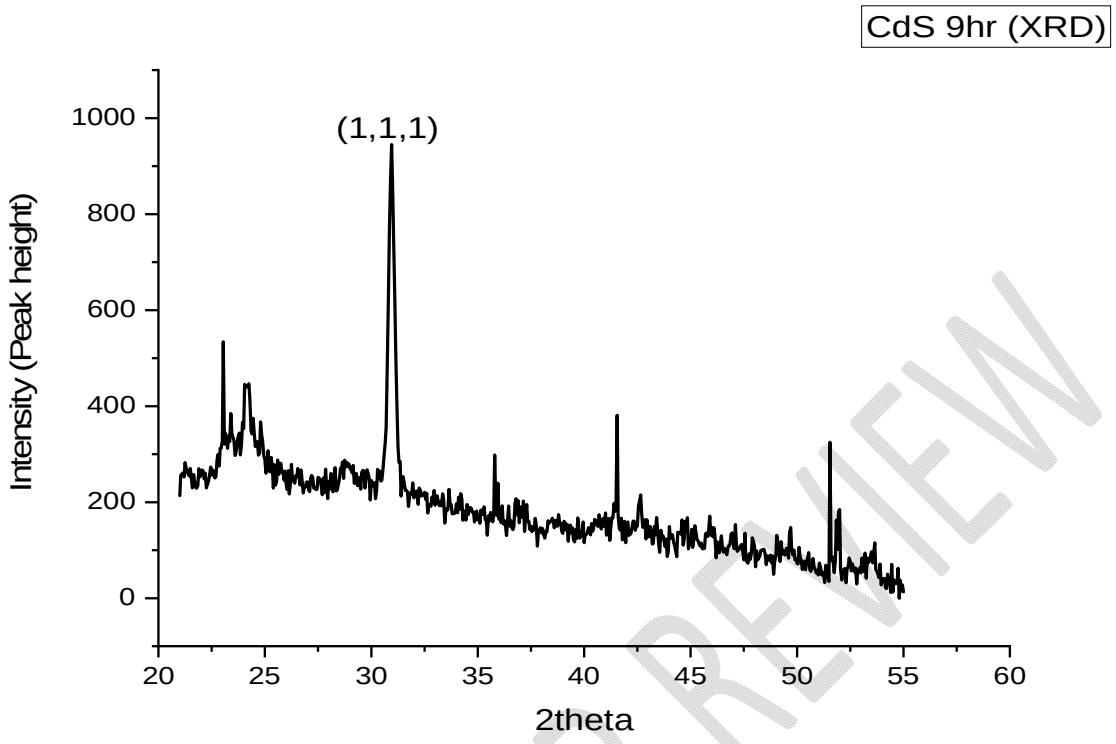

Figure 1a: XRD Intensity against 2theta value of *Hawleyite* CdS film coated for 9hours deposition time.

The 12hours sample showed peaks at 2tetha of 30.95^{o} and 51.55^{o} corresponding to the (1 1 1) and (2 2 0), planes of the cubic CdS phase (Figure 1b), respectively.

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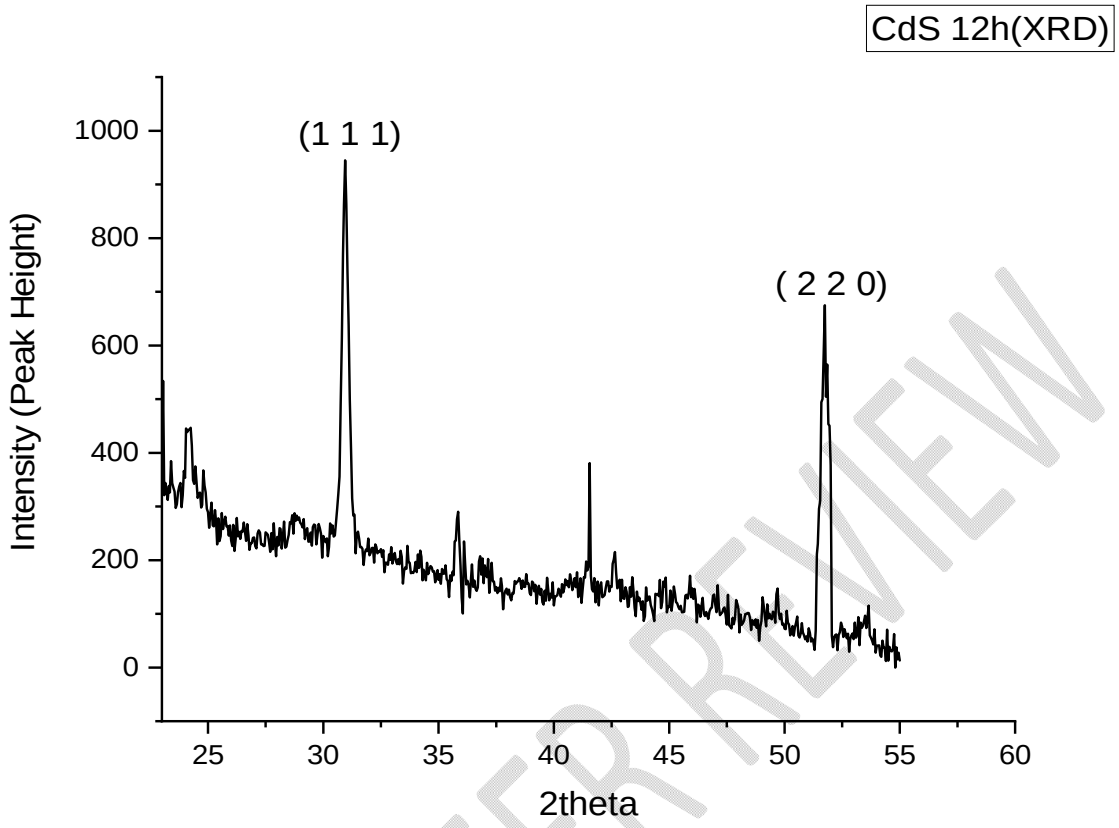

Figure 1b: XRD Intensity against 2theta value for *Hawleyite* CdS nanofilm at 12hours deposition time.

Comparing the XRD intensities from both 9hours and 12 hours samples, the 12 hour CdS samples had more matching peak intensities, (h, k, l) with the mineral name - Hawleyite. The XRD patterns obtained for both the 9hours and 12hours samples matches with the JCPDS data (96-101-1251 Hawleyite) with mineral name CdS Hawleyite. So with these data, it can be inferred that the 12hours CdS sample had a more defined crystal structure compared to the 9hours CdS sample.

Tables 3a and 3b show the crystalline grain sizes of the deposited CdS films at 9hours and 12hours deposition time. The 9hours sample has an average Crystallite grain size of 27.72nm, whereas the 12hours sample has an average grain size of 38.99nm.

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Table 3a: Crystallite grain size of 9hours CdS Sample

2theta (^{o})	FWHM	Crystallite Size (nm)
30.95	0.3500	28.62
51.77	0.400	26.82

Table 3b: Crystallite grain size of 12hours CdS Sample

2theta (^{o})	FWHM	Crystallite Size (nm)
24.15	0.3000	32.90
30.95	0.3500	28.62
35.80	0.1500	67.62
51.77	0.4000	26.82

Figure 2a shows the micrograph of CdS nanofilm deposited for 9hrs and imaging magnified at 5kx. The sample appeared to be uniformly coated when viewed with the naked eyes but it is characterized with pin holes at the nanoscale level.

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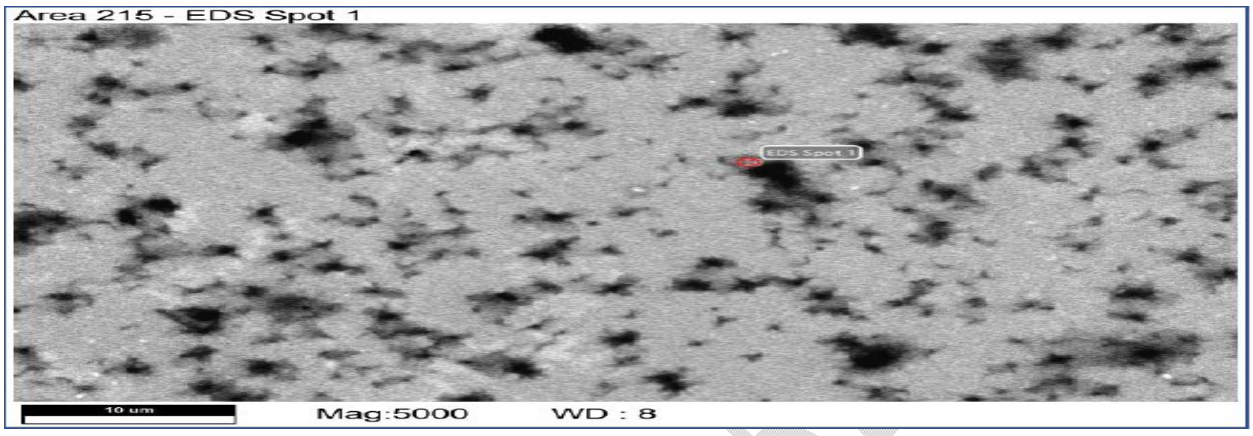

Figure 2a : The micrograph of CdS nanofilm deposited for 9hrs and imaging magnified at 5kx.

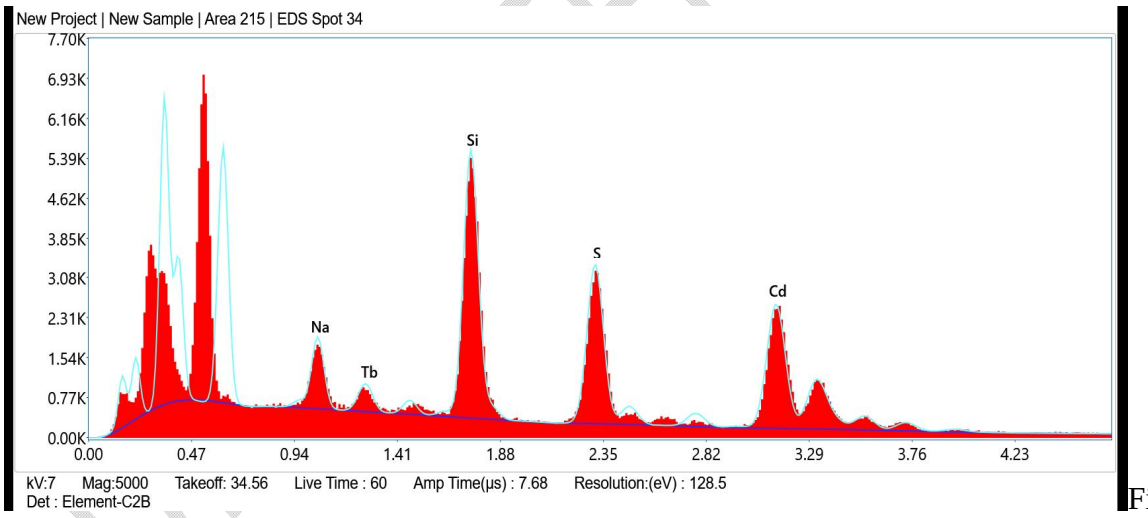

Figure 2b: The micrograph of CdS nanofilm deposited for 12hrs and imaging magnified at 5kx.

Figure 2b shows the micrograph of CdS nanofilm deposited for 12hrs and imaging magnified at 5kx. The sample appeared to be more uniformly coated compared to the 9hours sample.

Figures 3a shows the spectrum of percent compositional elements present in the deposited CdS thin film for 9hours deposition time. Both trace elements and the major elements (Cadmium and Sulphide) are clearly revealed in the Figure.

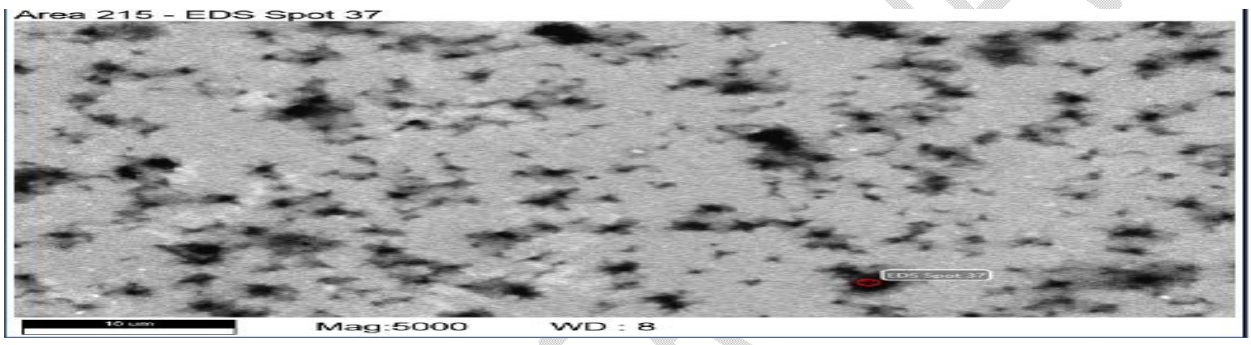

Figure 3a: The graphical representation of compositional elements in the CdS thin film deposited for 9hours.

Figure 3b shows the graphical representation of various elements present in the CdS thin film deposited for 12hours. Both trace elements and the major elements (Cadmium and Sulphide) are revealed in the figure. The figure 3b Indicates that more amount of Cadmium and Sulphide were deposited in 12hours sample than 9hours sample.

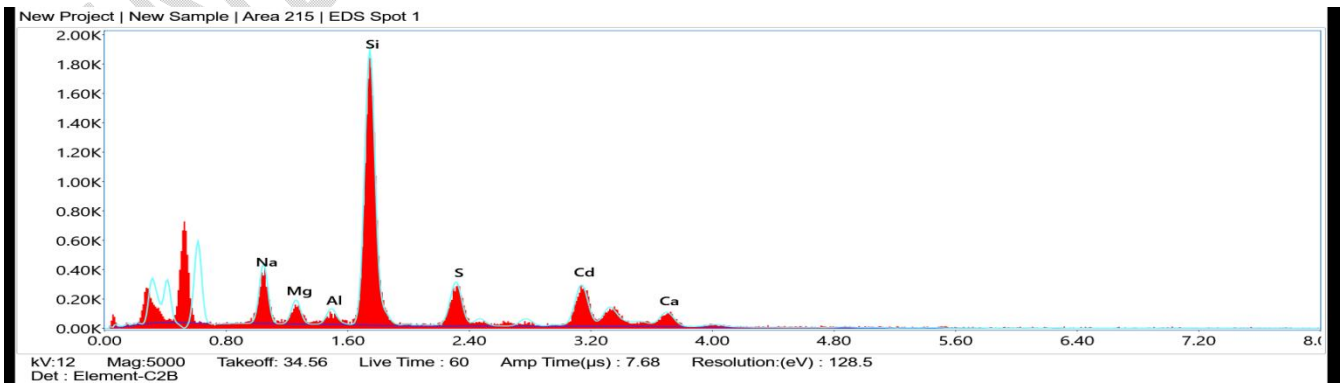

Figure 3b: The graphical representation of compositional elements in the CdS thin film deposited for 12hours.

Tables 4a and 4b illustrate the compositional details of Cadmium, Sulphur and other elements in the deposited films for 9hours and 12hours respectively.

Table 4a: Compositional details of Cadmium, Sulphide and other elements present as illustrated by the spectrum for the 9hours CdS sample.

Element	**Weight %**	**Atomic**	**Error**	**Net Int.**	**R**	**A**	**F**
Na	9.69	15.39	9.21	48.37	0.8630	0.5223	1.0062
Mg	3.13	4.70	10.89	20.63	0.8694	0.5998	1.0103
Al	2.07	2.80	12.73	14.15	0.8756	0.6891	1.0176
Si	38.59	50.17	4.97	271.25	0.8815	0.7660	1.0083
S	9.83	11.20	7.19	46.43	0.8930	0.7643	1.0143
Ca	6.53	5.95	16.20	16.63	0.9156	0.8791	1.0128
Cd	30.16	9.80	7.76	50.50	0.9103	0.8786	1.0042

Table 4b: Compositional details of Cadmium, sulphide and other elements present as illustrated by the graph for the 12hours CdS sample.

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Element	Weight %	Atomic	Error	Net Int.	R	A	F
Na	3.73	9.06	8.41	158.50	0.8208	0.6472	1.0039
Si	15.29	30.43	5.33	710.46	0.8482	0.8646	1.0112
S	16.51	28.79	5.55	468.67	0.8680	0.9106	1.0178
Cd	62.15	30.91	6.78	414.75	0.9063	0.9507	1.0039
Tb	2.32	0.82	12.77	22.06	0.8296	0.7429	1.0146

The thickness values for the deposited CdS thin films are 14.10nm and 14.50nm for 9hours and 12hours sample respectively (Table 5).

Table 5: Thickness and time of deposition for both 9hours and 12 hours CdS sample.

Samples	Time of Deposition(Hours)	Thickness (10^{-9}m)
CdS 1	9	14.10
CdS 2	12	14.50

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Figure 4 is a plot of Thickness against time of deposition for all the CdS film samples. This graph clearly illustrates the linear progression of thickness with time of deposition, i.e. the higher the time of deposition, the thicker the coated samples. In conclusion, thickness of the coating can be said to be directly relative to the period of deposition.

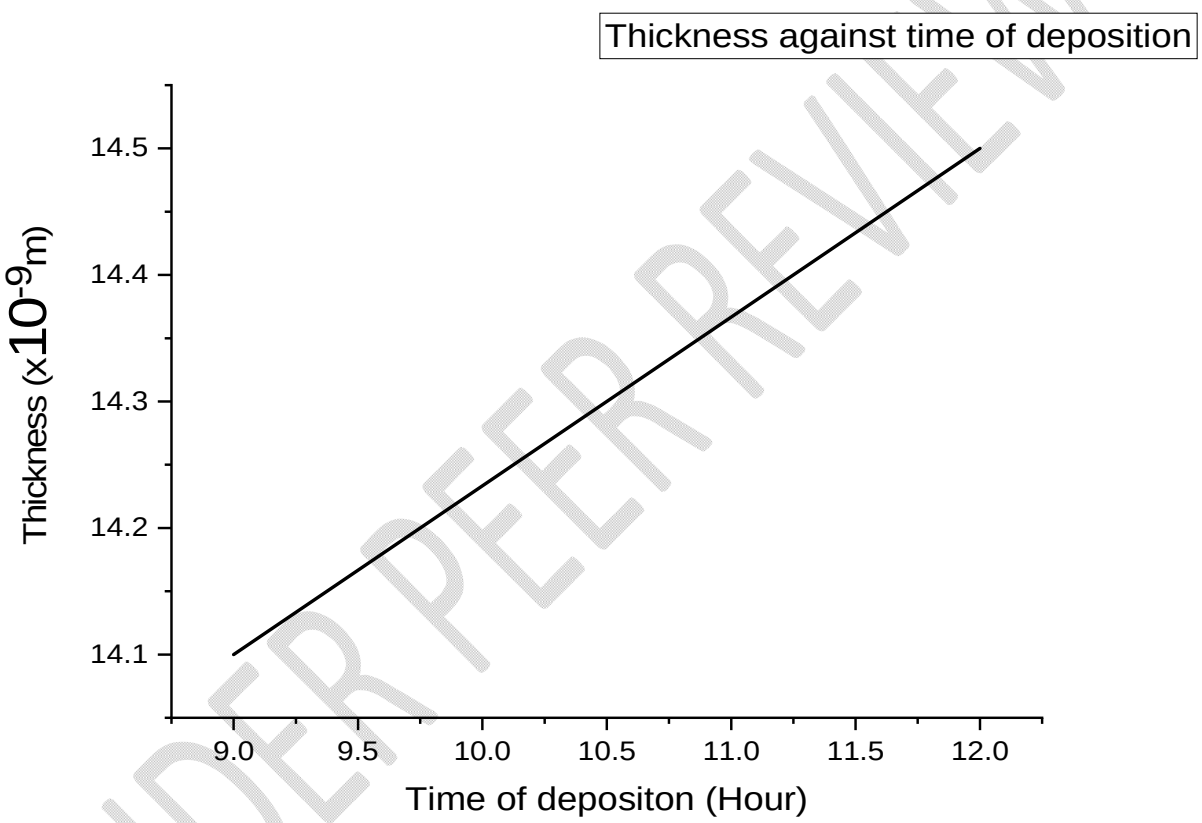

Figure 4 : Plot of Thickness against time of deposition for all the CdS film samples.

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The transmittance vs wavelength curves of 9hours and 12hours CdS thin films are shown in figures 5a and 5b, respectively. The transmittance properties of the 9 and 12hours CdS in various

areas are compared in Figure 5c. The results show that both CdS films have little UV- Visible light transmission.

The transmittance of both samples were defined using the equation;

(6)

Where, T = Transmittance

= Incident Light

= Amount of light that passes through the sample.

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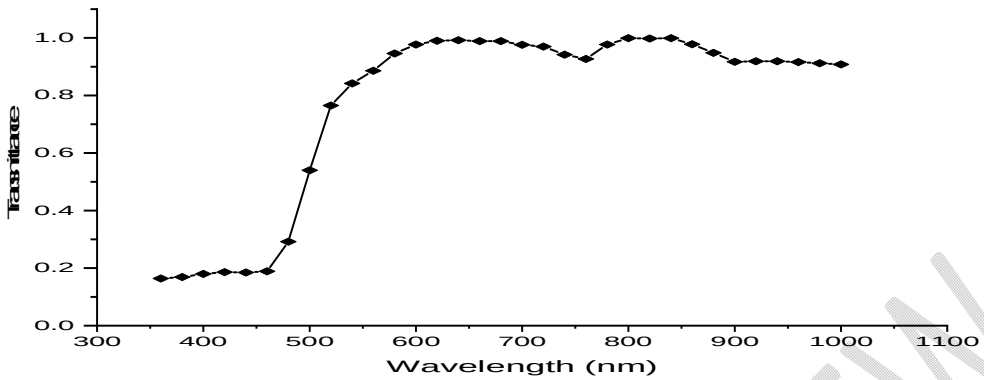

Figure 5a: Transmittance vs. wavelength for a 9-hour CdS film.

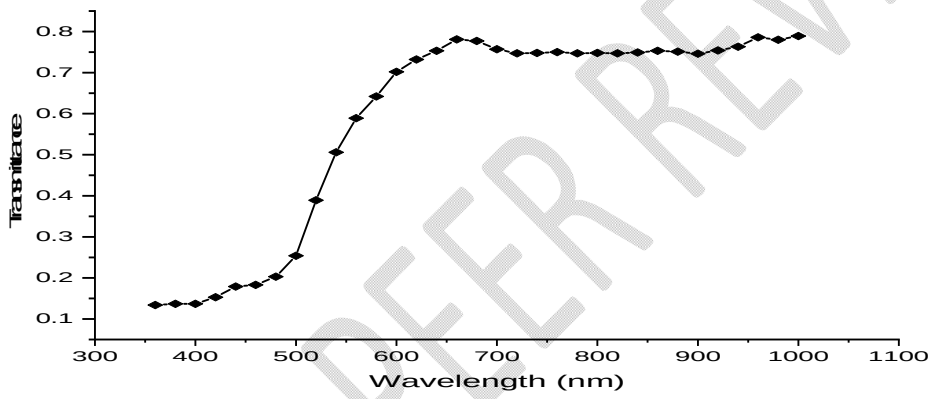

Figure 5b: Transmittance vs. wavelength for a 12-hour CdS film.

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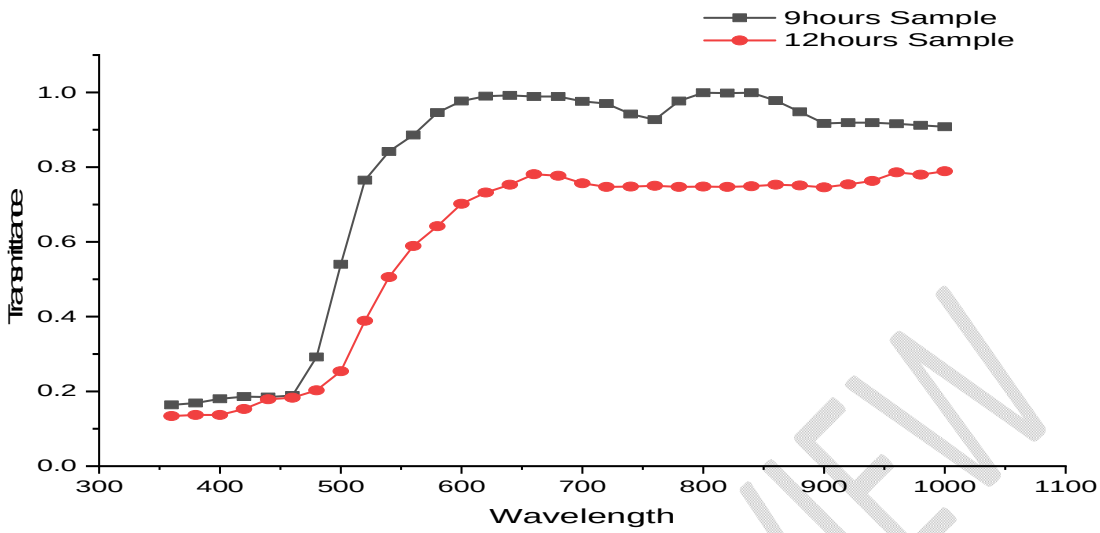

Figure 5c: Transmittance against wavelength of both 9hours and 12 hours sample compared.

Figures 6a and 6b clearly show the absorbance against wavelength plots of 9hours deposition time and 12hours deposition time respectively. As clearly indicated in these figures, both the 9hrs and 12hours samples of the CdS thin films have high spectral absorbance in the UV region, and relatively low in the visible and infrared region (Figure 6c).

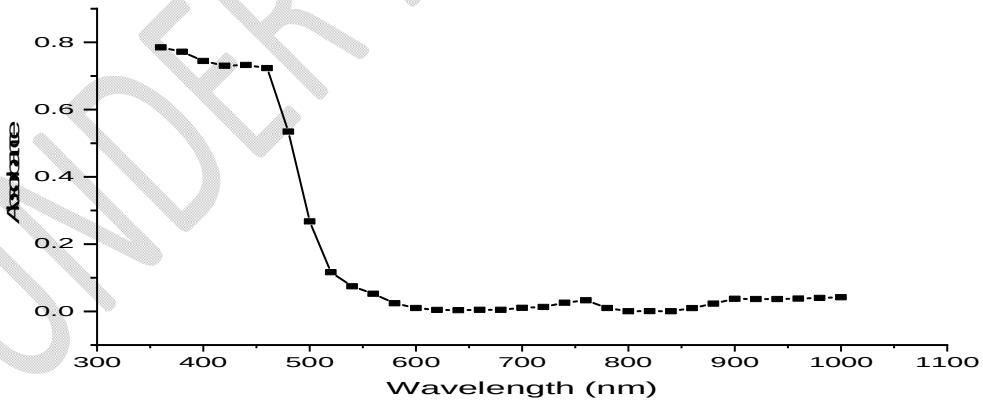

Figure 6a: Absorbance against Wavelength for 9hrs CdS Sample.

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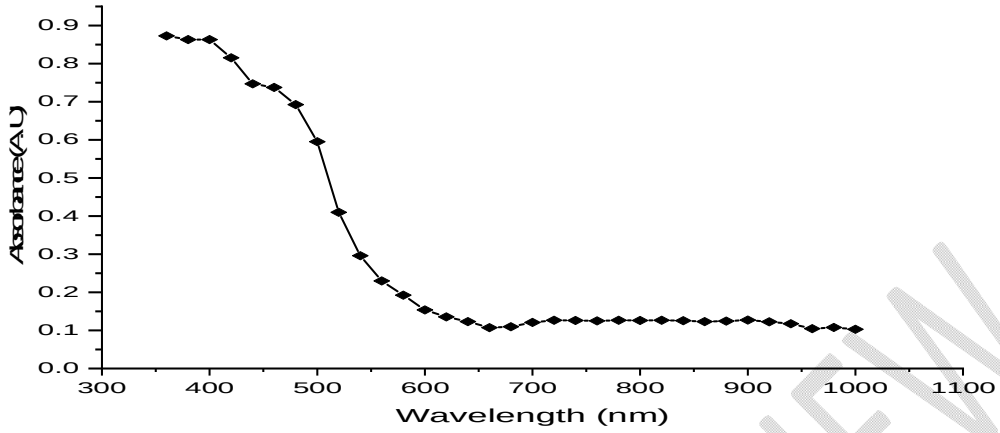

Figure 6b: Absorbance against Wavelength for 12hrs CdS Sample.

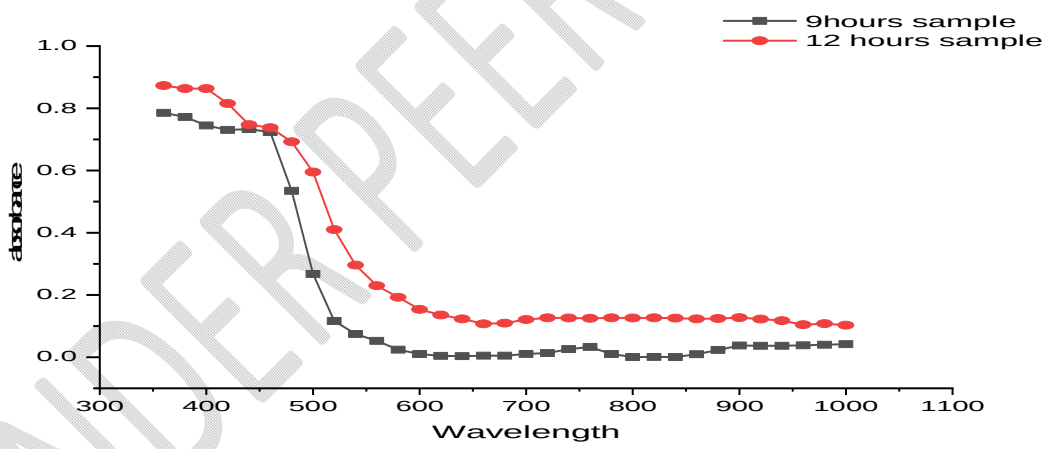

Figure 6c: Absorbance against wavelength of both 9hours and 12 hours sample.

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The optical bandgap for both 9hours and 12hours CdS thin film samples were obtained from figures 7a and 7b by the extrapolation of the best fit line between $(\alpha hv)^2$ against hv(ev) to intercept hv at $(\alpha hv)^2 = 0$.

The bandgap energies of the 9hours and 12 hours CdS film samples are 2.36 eV and 2.257eV respectively. This variation in the bandgap energy of both samples could be as a result of varied deposition time, difference in the crystal structure as indicated by the X-ray Diffraction spectra of both samples, the morphologies and varied percent elemental composition of both films.

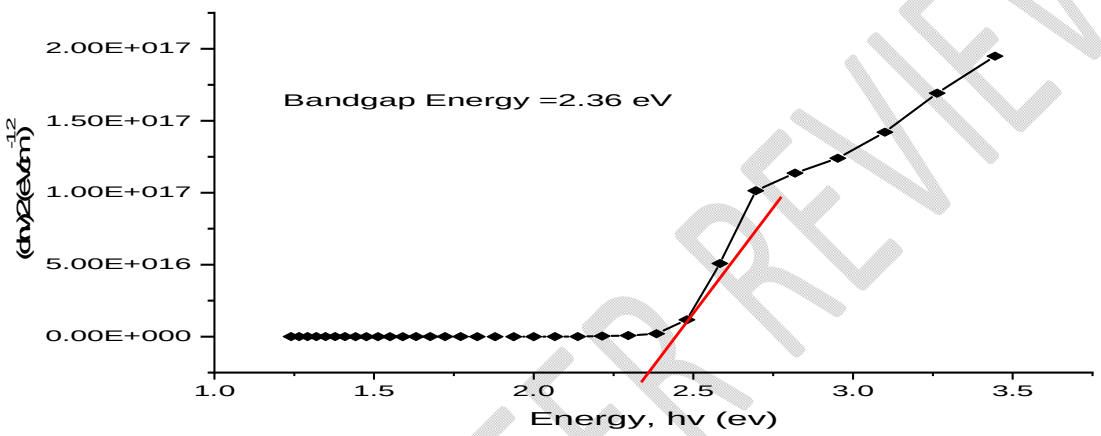

Figure 7a: Bandgap Energy for 9hrs CdS film Sample.

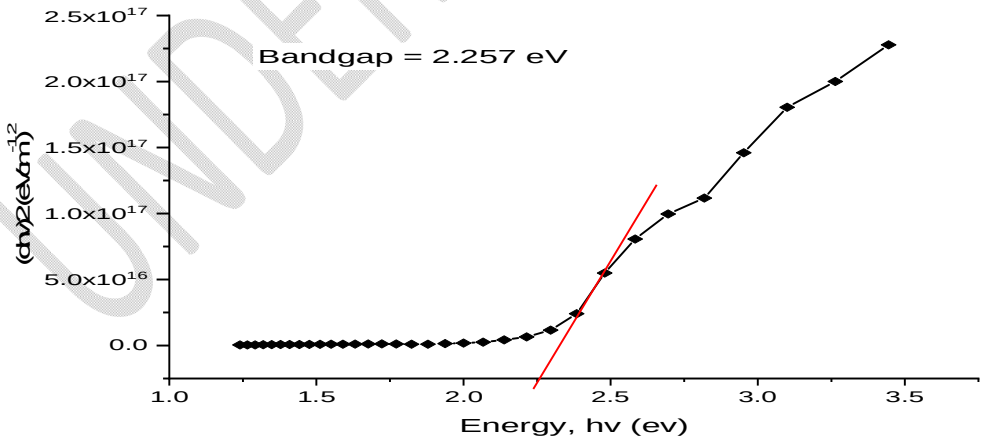

Figure 7b: Bandgap Energy for 12hrs CdS Sample.

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The average value for the optical conductivity (5.099×10^{13} and 7.75×10^{13}), and the average values of the extinction coefficients, *k* (1.07×10^{9} and 2.02×10^{9}) were obtained for both the 9hours and 12 hours samples respectively.

CONCLUSION

CdS Nanofilms were deposited using Chemical Bath Deposition (CBD) method. The X-ray diffraction pattern of the 9hours CdS sample showed peaks at 2theta positions of 30.95^{o} and 51.77^{o} corresponding to (1 1 1) and (2 2 0) of the cubic CdS Phase. The X-ray diffraction pattern of the 12hours CdS sample showed peaks at 2theta positions of 30.95^{o} and 51.55^{o} corresponding to the (1 1 1), (2 2 0) planes of the cubic CdS Phase respectively. The micrographs for the 9hours CdS sample and 12hours CdS although slightly similar, the 12hours sample appeared to be more uniformly coated and more evenly distrubuted across the coated surface. With EDX, the 12hours sample showed a higher percentage composition of both Cadmium and Sulphide compared with 9hours sample, although other trace elements were also present. The bandgap energy of the 9hours and 12 hours CdS samples are 2.36 eV and 2.257eV respectively. The average value for the optical conductivities are 5.099×10^{13} and 7.75×10^{13} for 9hrs and 12hrs CdS film samples respectively. The average values of the extinction coefficients, *k* are 1.07×10^{9} and 2.02×10^{9} for 9hrs and 12hrs films respectively.

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