Potential of *Hawleyite* Cadmium Sulphide (CdS) Nanofilms for PV Cell Applications

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

The search for suitable materials as buffer layer in the development of photovoltaic cell necessitates the study. The objective is thus, to synthesize and characterize CdS nanofilm for photovoltaic cell application. 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 9 hours 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 12 hours 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 9 hours sample is 27.72nm and 38.99nm for the 12 hours samples. The Scanning Electron microscopy analyses illustrate the morphology and the level of uniformity of the CdS coating across the surface of the

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9 hours sample and 12 hours samples. The micrographs although slightly similar, the 12 hours sample appeared to be more uniformly coated when compared to the 9 hours sample. Electron-Dispersive X-ray Spectroscopy (EDX) indicated the percentage composition of Cadmium and Sulphide present in the both 9 hours and 12 hours samples, with Cadmium having an average composition of 26.45% and sulphide 8.65% for the 9 hours 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 ($\leq$ 400nm), Visible and part of the Infrared region. The bandgap energies of both 9 hours and 12 hours 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 12 hours sample. The average values of the extinction coefficients, *k* for 9 hours sample is 1.07×10^{9} and 2.02×10^{9} for 12 hours sample. The average thickness value of CdS Sample deposited for 9 hours is 14.10×10^{-9}m while that of the CdS sample deposited for 12 hours is 14.5×10^{-9}m. The results affirm the choice of CdS film as buffer layer of the photovoltaic cells.

1. 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.

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 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].

CdS film of hexagonal Wurtzite structure having energy bandgaps between 2.3eV – 2.35eV for process one and 2.49eV and 2.65eV for process 2 was reported [10]. Optical constants and the bandgap width for the studies films was 2.39eV [11]. The optical bandgaps when annealed at 300°C for 5minutes and the bandgap was ~ 2.4 eV [12].

Several studies have been performed to optimize factors such as temperature, deposition time, pH, and concentrations of different reagents during the CBD process to produce high-quality CdS thin films [13]. CBD is the simplest, low cost, and is a low temperature deposition technique [14]. The type of deposition technique has great influence on the property of the CdS thin films [15]. The deposition time of CdS thin film also has a great effect on the properties of synthesized CdS thin film [16].

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

2. 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 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;

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

$$SH^- + OH^- \longrightarrow S^{2-} + H_2O$$

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

2.1 Deposition Parameters

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.

2.2 Thickness, and Bandgap Calculation

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

$$D = \frac{K\lambda}{\beta cos\theta} \tag{1}$$

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 9 hours and 12 hours CdS samples were calculated using the Tauc and Davis-Mott relation;

$$(\alpha hv)n = K(hv - Eg) \tag{2}$$

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.

2.3 Optical Conductivity and Refractive Index Calculation

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

$$\sigma_{opt.} = \frac{\alpha nc}{4\pi} \tag{3}$$

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 9 hours and 12 hours samples were determined using;

$$n = \frac{1}{Ts} + \sqrt{\frac{1}{Ts-1}} \tag{4}$$

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.

2.4 Extinction Coefficient Calculation

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

$$K = \frac{\alpha\lambda}{4\pi} \tag{5}$$

Where, α= absorption coefficient
λ = wavelength
π = 3.142

Table 2. Deposition parameters of Cadmium Sulphide thin- film

Reaction bath (100ml Beaker)	Deposition time (Hours)	Cation compound (X)		Ammonia solution		Na_2SO_3/Na_2SO_4		Distilled water Vol.(ml)
		Mol.(M)	Volume (ml)	Mol. (M)	Vol.(ml)	Mol. (M)	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

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.

3. RESULTS AND DISCUSSION

Analysis of CdS-coated films at deposition time of 9 hours 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 Fig. 1a.

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 (Fig. 1b), respectively.

Comparing the XRD intensities from both 9 hours 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 9 hours and 12 hours 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 12 hours CdS sample had a more defined crystal structure compared to the 9 hours CdS sample.

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

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 12 hours 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

Fig. 2a shows the micrograph of CdS nanofilm deposited for 9 hrs 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.

Fig. 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 9 hours sample.

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

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

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

The thickness values for the deposited CdS thin films are 14.10nm and 14.50nm for 9 hours and 12 hours sample respectively (Table 5).
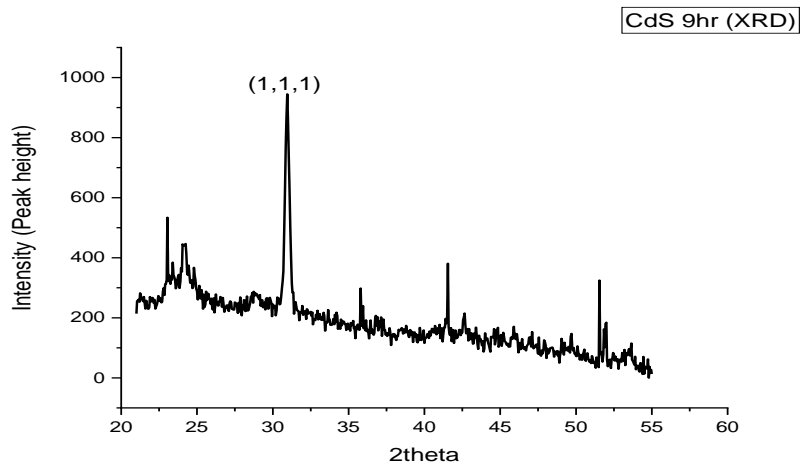
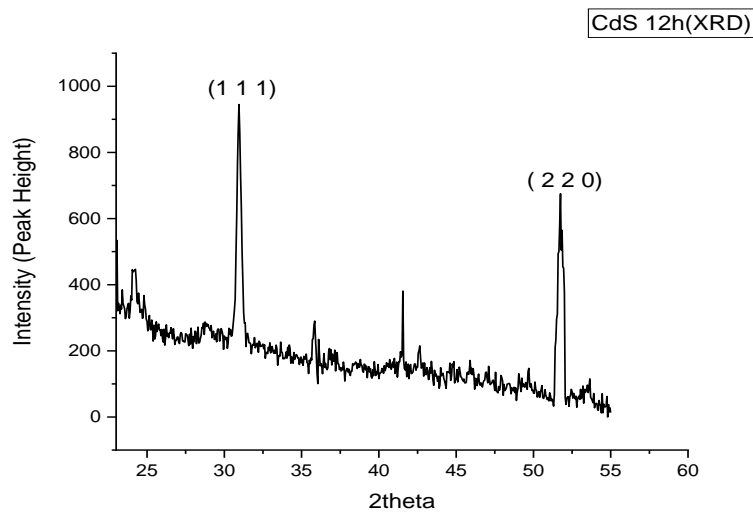**Fig. 1a. XRD Intensity against 2theta value of *Hawleyite* CdS film coated for 9 hours deposition time**

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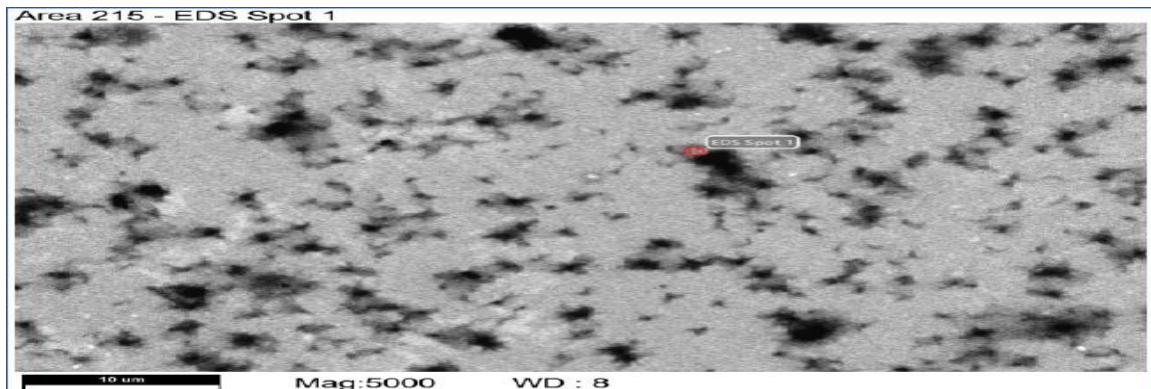

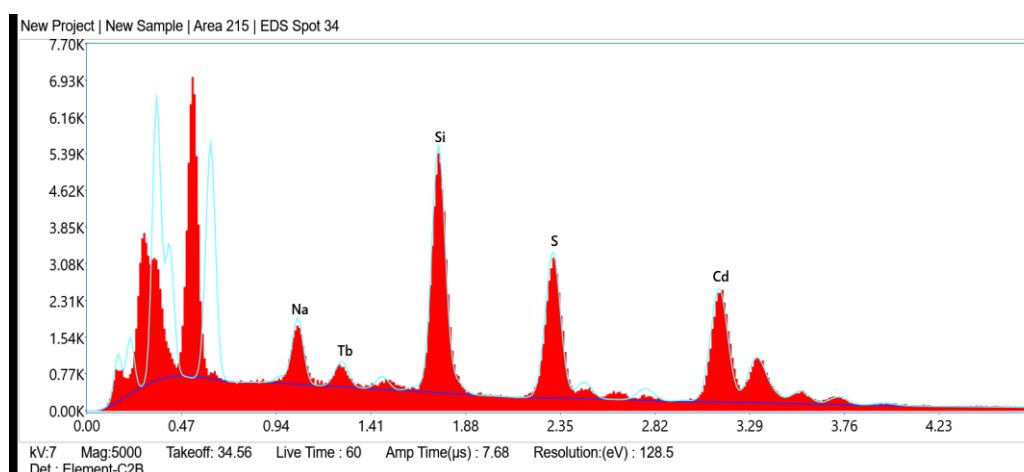**Fig. 2a. The micrograph of CdS nanofilm deposited for 9hrs and imaging magnified at 5kx**

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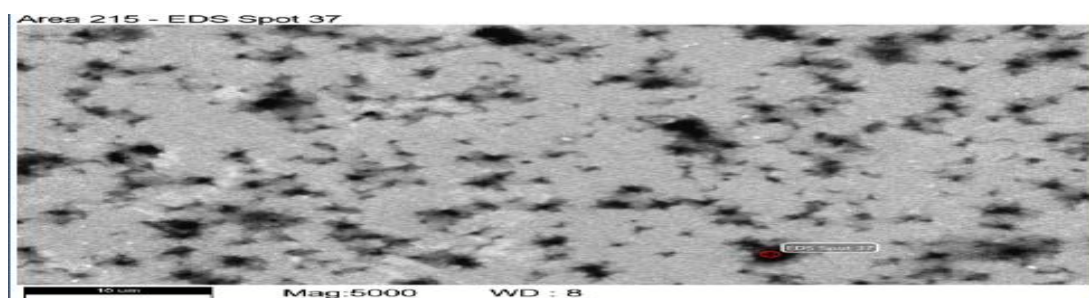

Fig. 3a. The graphical representation of compositional elements in the CdS thin film deposited for 9 hours
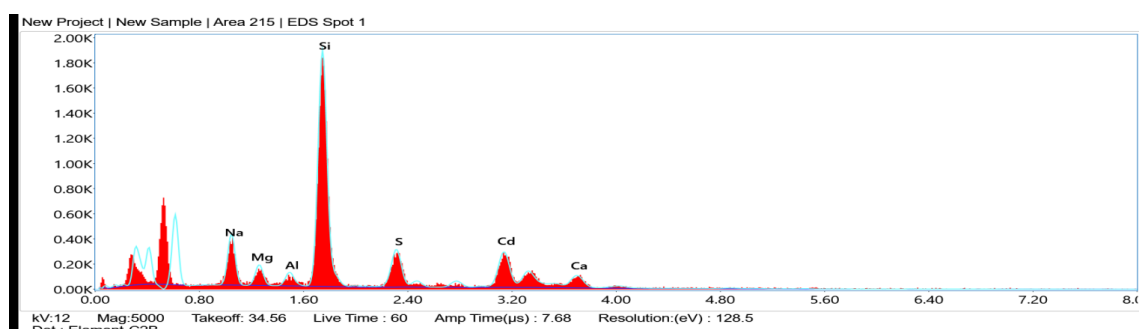

Fig. 3b. The graphical representation of compositional elements in the CdS thin film deposited for 12 hours

Table 4a. Compositional details of Cadmium, Sulphide and other elements present as illustrated by the spectrum for the 9 hours 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 12 hours CdS sample

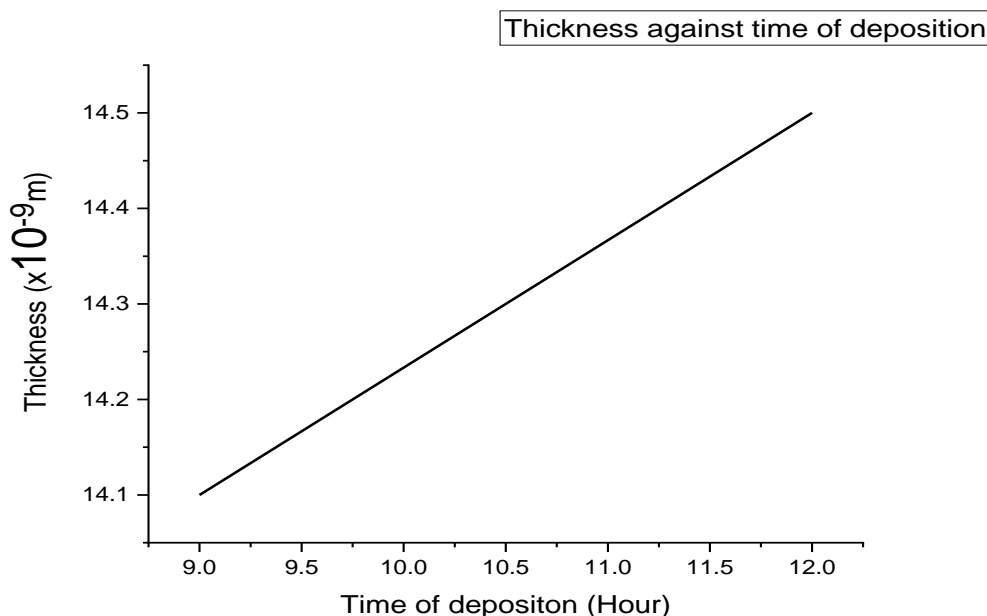| Element	Weight %	Atomic	Error	Net Int.	R	A	F
Na	3.73	9.06	8.41	158.50	0.8208	0.6472	1.0039
Si	15.29	30.43	5.33	710.46	0.8482	0.8646	1.0112
S	16.51	28.79	5.55	468.67	0.8680	0.9106	1.0178
Cd	62.15	30.91	6.78	414.75	0.9063	0.9507	1.0039
Tb	2.32	0.82	12.77	22.06	0.8296	0.7429	1.0146

Fig. 4. Plot of thickness against time of deposition for all the CdS film samples

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

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

Fig. 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.

The transmittance properties of the 9 and 12 hours CdS in various areas are compared in Fig. 5. The results show that both CdS films have little UV- Visible light transmission.

The transmittance of both samples were defined using the equation;

$$T = \frac{I}{I_0} \tag{6}$$

Where, T = Transmittance
I_0= Incident Light
I = Amount of light that passes through the sample.

Both the 9hrs and 12 hours samples of the CdS thin films have high spectral absorbance in the UV region, and relatively low in the visible and infrared region as shown in Fig. 6.

The optical bandgap for both 9 hours and 12 hours CdS thin film samples were obtained from Figs. 7a and 7b by the extrapolation of the best fit line between $(\alpha h v)^2$ against hv(ev) to intercept hv at $(\alpha h v)^2 = 0$.
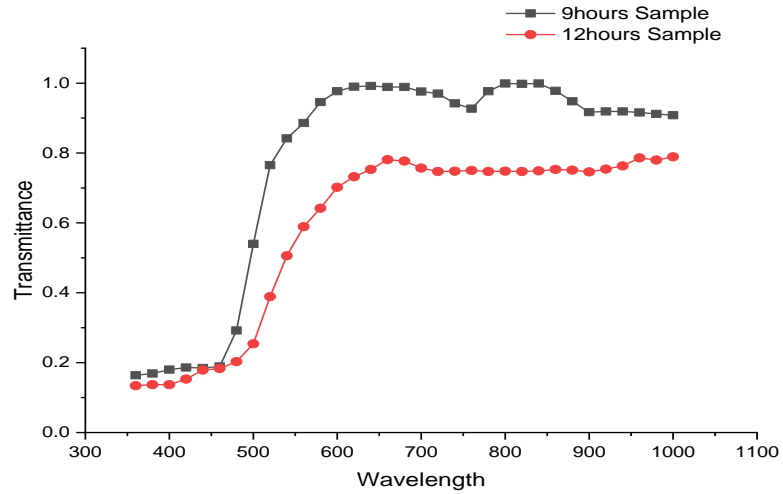
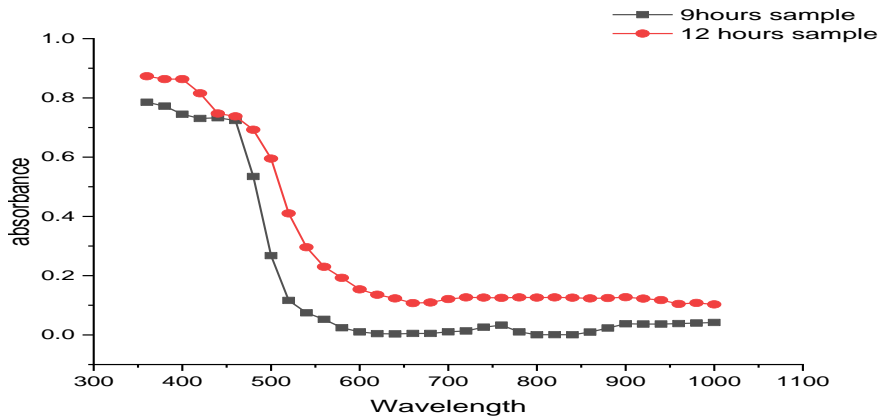**Fig. 5. Transmittance against wavelength of both 9 hours and 12 hours sample compared**

Fig. 6. Absorbance against wavelength of both 9 hours and 12 hours sample
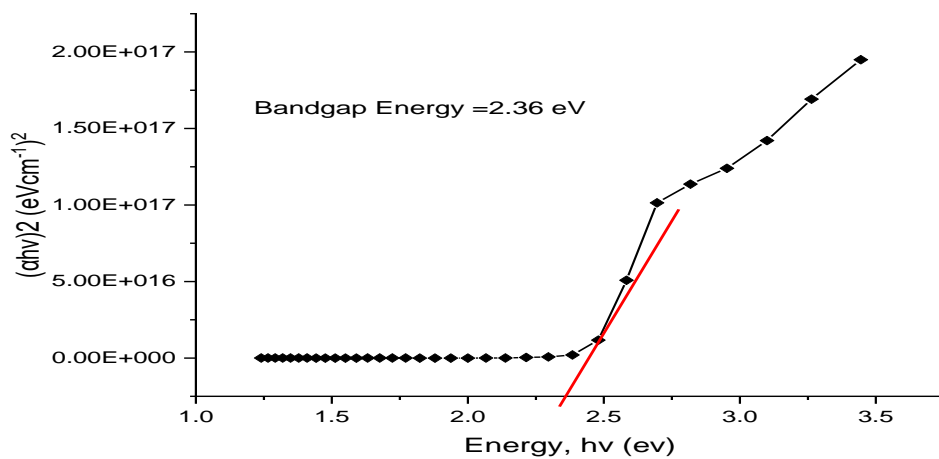

Fig. 7a. Bandgap Energy for 9 hrs CdS film sample
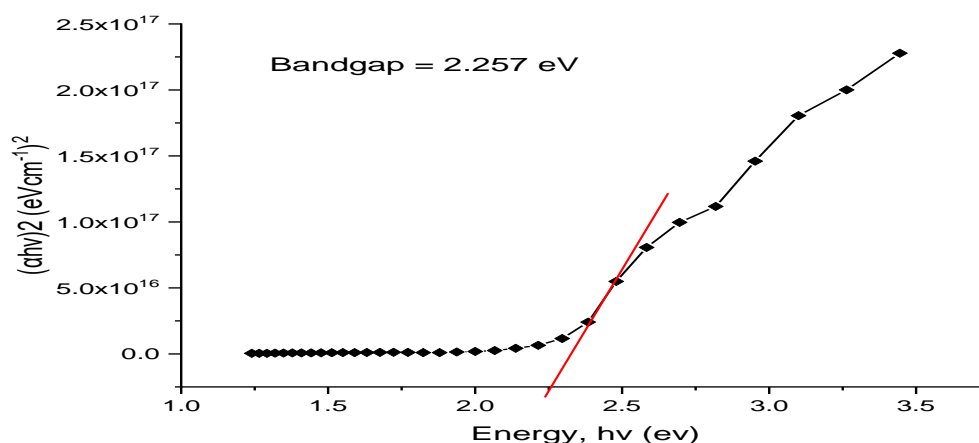
Fig. 7b. Bandgap Energy for 12 hrs CdS sample

The bandgap energies of the 9 hours 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.

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 9 hours and 12 hours samples respectively.

4. CONCLUSION

CdS Nanofilms were deposited using Chemical Bath Deposition (CBD) method. The X-ray diffraction pattern of the 9 hours 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 12 hours 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 9 hours CdS sample and 12 hours CdS although slightly similar, the 12 hours sample appeared to be more uniformly coated and more evenly distrubuted across the coated surface. With EDX, the 12 hours sample showed a higher percentage composition of both Cadmium and Sulphide compared with 9 hours sample, although other trace elements were also present such as Magnesium, Calcium, Silicon.

The bandgap energy of the 9 hours 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. These findings affirm the suitability of CdS nanofilms as a good potential material for the development of buffer layer in photovoltaic cell application.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Peer-review history:
The peer review history for this paper can be accessed here:
https://www.sdiarticle5.com/review-history/98235