FABRICATION OF CADMIUM SULFIDE THIN FILMS BY AN AUTOMATED TRIGGER ENHANCED SPRAY TECHNIQUE AT TWO DIFFERENT SUBSTRATE TEMPERATURES

V.S. Nagarethinam [a, *], N. Arunkumar [b], A.R. Balu [a], M. Suganya [a], G. Selvan [c]
[a] Department of Physics, A.V.V.M Sri Pushpam College, Poondi, India
[b] Department of Physics, Parisutham Institute of Technology and Science, Thanjavur
[c] Department of Physics, Thanthai Hans Roever College, Perambalur, India
rajavelubalu@yahoo.com

ABSTRACT

Cadmium Sulfide (CdS) thin films were deposited onto ultrasonically cleaned glass substrates using a fully automated low cost trigger enhanced spray (TES) technique. CdS films were coated at two different substrate temperatures of 300ºC and 350ºC respectively with S/Cd at.% ratio kept constant as 1. The X-ray diffraction studies revealed the polycrystalline nature of the as-deposited samples. Films were found to have a mixture of hexagonal and cubic phases with hexagonal phase being predominant. The degree of preferred orientation of the coated films were found to be along the (111) plane. The crystallite size, strain, dislocation density and the number of crystallites corresponding to (111) plane for the as-deposited samples were calculated. The optical transmittance for the as-deposited samples show interference patterns with maximum transmittance of 80% and 87% for the films coated at 300 and 350°C respectively. Direct band gap values was found to be equal to 2.28 eV and 2.37 eV for the films coated at 300 and 350°C respectively. The resistivity of the as-deposited films was found to vary in the range of $0.591 – 1.131 \times 10^3$ ohm-cm and it decreases with increase in temperature indicating the semiconducting nature of these samples.

Keywords: Thin films; Semiconductors; X-ray; Thickness; Resistivity; Optical.

I. INTRODUCTION

The preparation of CdS thin films suitable for use in photo-conductors, photo detectors and photovoltaic applications, including photo electrochemical solar cells, is currently the subject of intensive research. The new technologies for massive production of solar cells are based on the use of materials with thin film geometry due to the low cost solar energy conversion, low materials consumption and the facility to obtain very small integrated modules [1 - 2]. Considering the different materials for photovoltaic applications, the hetero-structure glass / conductor-oxide / CdS / CdTe/ metal is one of the most low cost efficient converters of solar radiation in electricity (15.8%) [3, 4]. Actually, CdTe is one of the most important semiconductors because of the direct band gap energy (1.45 eV), and the high conversion efficiency of terrestrial solar light in electricity. However, CdTe does not grow stoichiometrically, having slight Cd vacancies deficiency, consequently growing as p-doped. Thus a natural n-doped material is required as a partner to achieve a good junction with high efficiency in solar conversion. An optimal partner for CdTe is cadmium sulfide, CdS. The wider band gap of CdS allows the sunlight to enter the CdTe material more readily, acting as a window.

Normally CdS thin films grow as n-type semiconductor. However, by means of thermal diffusion of impurities, such as Cu and In, after preparation it is possible to obtain p-type CdS [5, 6]. For optical window applications, band gap energy is an important parameter of transparent thin films. CdS polycrystalline films possess a direct band gap of 2.42 – 2.45 eV at room temperature. For solar energy applications, CdS films require to have: high optical transparency, low electrical resistivity and high structural orientation at room temperature.

There are various methods used for preparing CdS thin films, which includes thermal evaporation [7, 8], chemical bath deposition (CBD) [9], molecular beam epitaxy (MBE) [10], and spray pyrolysis [11], etc. In the conventional spray pyrolysis technique after a spray, the solution present in the spray gun flows down which was collected and reused. In doing so the purity of the solution is questioned as it reacts with surrounding atmosphere. So many researchers have modified their spray set up to circumvent this problem. One such effort was made in this work. Here we have designed a fully automated spray pyrolysis technique enhanced with trigger pulses to coat CdS thin films suitable for solar cell applications. The main advantages of this technique are: minimum volume of the solution is required for large area coating than the conventional spray technique, reusability of the solution is avoided as the solution which has been triggered gets completely sprayed, no need to maintain the spray rate of the solution as in the conventional spray technique. Cadmium sulfide thin films were prepared using this technique. The structural, morphological, optical and electrical properties of the coated films have been studied and the results are discussed.

II. EXPERIMENTAL DETAILS

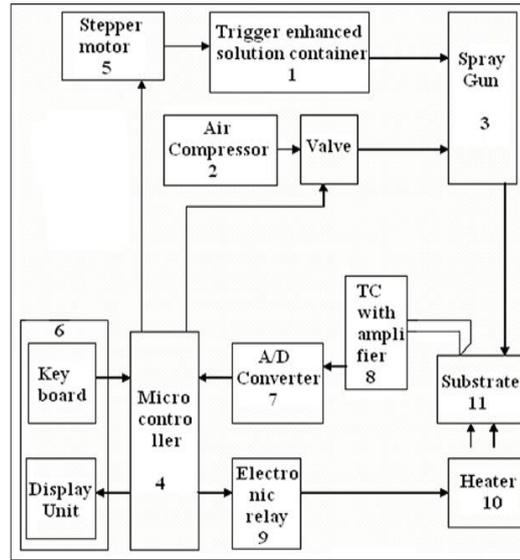The schematic block diagram of the trigger enhanced spray setup is shown in Fig. 1.

Figure 1: Schematic block diagram of automated trigger enhanced spray set up

Block 1 is the solution container with an arrangement to give trigger pulses. The stepper motor (block 5) interfaced with microcontroller is used to activate the trigger arrangement in block 1 so that one drop of the solution reaches the spray gun which is kept at block 3 for each triggering. The compressor in block 2 is used to give carrier air at desired pressure to the spray gun which is controlled by a valve arrangement activated by a solenoid arrangement. The solenoid activation is controlled by the microcontroller in block 4.

The spray gun has two inputs: one from the trigger enhanced spray container and the other from the compressor. When they are synchronized the solution gets sprayed onto preheated ultrasonically cleaned substrates kept at block 11. Substrate temperature is maintained constant by an automated temperature controller controlled by the AT89C55WD microcontroller (block 4). Chromel-Alumel thermocouple placed on the substrate (block 11) is used as a sensor for the measurement of substrate temperature. The analog equivalent voltage of the substrate temperature amplified by an instrumentation amplifier (Block 8) is converted into digital signal with the 12 bit A/D converter kept at block 7. The microcontroller processes the temperature equivalent digital value and controls the electronic switch at block 9 which will switch ON/OFF the heater in block 10. Block 6 consists of a keyboard through which the data can be given. A two row 16 character alpha numeric display in block 6 is used to display the temperature.

Software developed in C language is used to activate the stepper motor, to open/close the valve in the compressor, to read temperature of the substrate using A/D converter, to give set temperature through the key board, to switch ON/OFF the heater, to display the temperature in the LCD display. The set up is enclosed in an air tight glass chamber provided with an exhaust tube to remove the gases and vapours produced during the spray processes. Undoped films of CdS were prepared at two different substrate

temperatures of 300ºC and 350ºC respectively, using an aqueous solution consisting of 0.2 M of cadmium acetate and thiourea.

III. RESULTS AND DISCUSSION

III 1 Film formation

The precursor solution was atomized to form uniform stream of fine droplets with pneumatic glass nozzle. The pyrolytic decomposition of the fine droplets of aqueous solution of cadmium acetate and thiourea onto the glass substrates results into the formation of thin films of CdS. The possible chemical reaction that takes place is as follows:

$$Cd(CH_3COO)_2 + SC(NH_2)_2 + 2H_2O \rightarrow CdS\downarrow + 2CH_3COOH\uparrow + 2NH_3\uparrow + CO_2\uparrow$$
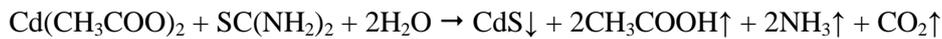
The thickness of the films measured by the weight difference-density consideration method was found to be equal to 0.95 μm and 0.77 μm for the films coated at 300°C and 350°C respectively. The thickness decreases with the increase in substrate temperature which shows that the amount of mass being deposited at lower temperature is more than that of the films coated with higher temperature.

III. 2 XRD studies

The X-ray diffractograms of the as-deposited samples are shown in Fig. 2(a) and (b). The observed interplanar distance 'd' for the coated films along with standard ASTM data is presented in Table 1. It can be inferred from the observed and ASTM data that pure CdS is a mixture of cubic and hexagonal phases [12 - 15]. From the ASTM data for CdS, the strongest diffraction peak corresponds to the (101) plane for the hexagonal phase and to the (111) plane for the cubic phase [15]. In the present work, the strongest diffraction peak is observed at d = 3.361 Å, which ordinarily can be indexed as (111) cubic and (002) hexagonal. It has also been reported that the cubic and hexagonal phases of CdS overlap. Such overlapping is also found at d = 1.761 Å.
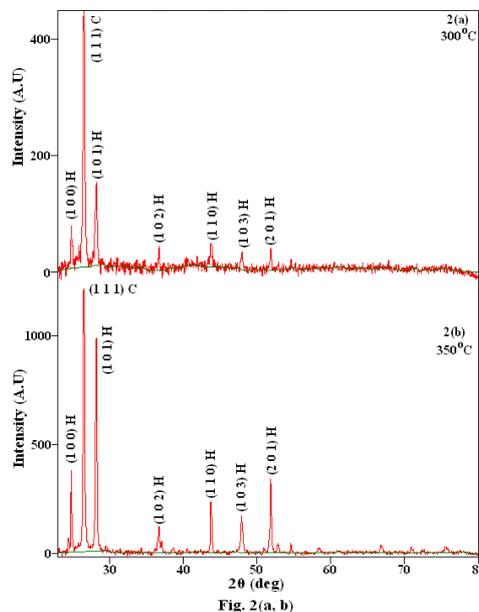

Fig. 2 (a, b): XRD patterns of CdS thin films with S/Cd ratio equal to 1 at 300 (a) and 350°C (b) respectively.

Table 1: Comparison of d values (Å) and hkl planes for the CdS films coated at 300°C and 350°C respectively

(hkl)		d standard (Å)		d observed (Å)	
CdS hex	CdS cubic	CdS hex	CdS cubic	300ºC	350ºC
100		3.583		3.584	3.583
002	111	3.357	3.361	3.362	3.3616
101		3.160		3.161	3.161
102		2.45		2.45	2.45
110		2.068	2.06	2.067	2.068
103		1.896		1.898	1.896
112		1.761	1.753	1.762	1.761
201		1.731		1.732	1.731

The XRD patterns show additional peaks, corresponding to distinctly hexagonal phases such as (100), (101), (102), (103), (112) and (201) and planes (220), (311) for the cubic phase. The results are similar to those reported by Amalnerkar et, al [15]. So the films coated using this technique is hexagonal oriented which is suitable for solar cell applications. It was further observed that as the substrate temperature increases from 300°C to 350°C, the intensity of the hexagonal phases increased to a large extent while the percentage of cubic phase remains move or less the same. The variation in preferential orientation factor f(hkl) for the planes (111), (101) and (100) as a function of substrate temperature is shown in Fig. 3, which shows that f(1 1 1) increases as the substrate temperature increases.

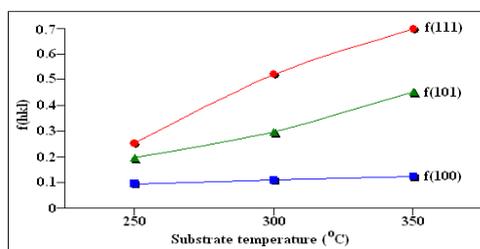Fig. 3: Variation of f(hkl) with substrate temperature

Thus the films coated at higher temperature have a better crystalline quality with preferential orientation in either the cubic (111) plane. The latter interpretation is further evidenced by additional peaks corresponding to (100), (101), (102), (103), (112) and (201) planes all of hexagonal phases. It is known that CdS structure has a stable hexagonal phase and a metastable cubic phase, but for solar cell applications, hexagonal structured films are preferable [16]. The results obtained here matches the results obtained at a temperature

greater than 400°C by other spray techniques. Thus device quality CdS films can be prepared at even low temperatures compared with the conventional spray technique. The crystallite size D and strain present in the samples have been calculated by the relations present elsewhere [17]. The values of various micro structural parameters are compiled in Table 2.

Table 2: Micro structural parameters for the (111) plane.

Microstructural parameters	Substrate temperature	
	300ºC	350ºC
Lattice parameter 'a' (Å)	4.139	4.139
Thickness 't' (μm)	0.95	0.77
Crystallite size 'D' (nm)	42.76	49.64
Strain 'ε' (x 10^{-3})	0.61	0.7815
Dislocation density 'δ' (x 10^{15} lines/m^2)	0.34	0.46
Number of crystallites 'N' (x 10^{21}/unit area)	7.05	7.59

It has been observed that with an increase in substrate temperature, the crystallite size decreases, or in other words dislocation density increases, which in turn results in the increment of number of crystallites in the samples coated at higher temperature.

III.3 SEM studies

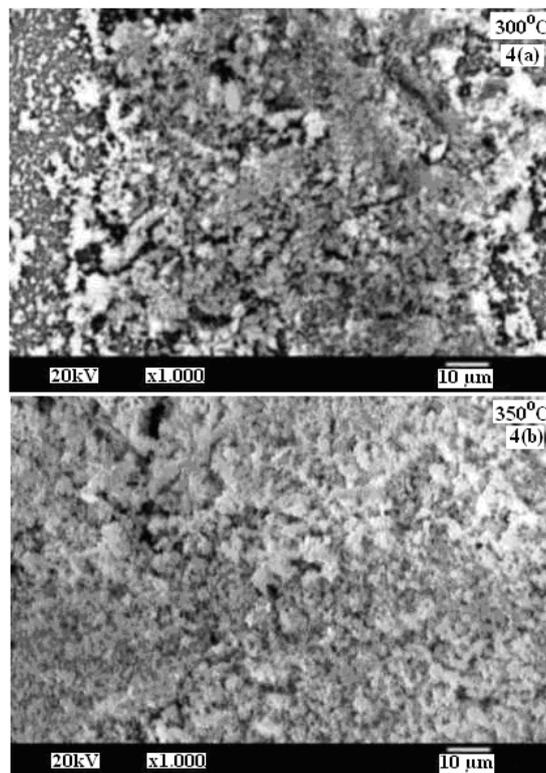Fig. 4 (a, b) shows the SEM micrographs of the coated CdS films.

Fig 4(a,b)

Fig. 4(a, b) SEM micrographs of the as-deposited CdS films.

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The film prepared at 300°C Fig. 4(a), has a high surface roughness and this value decreases as the temperature increases to 350°C. The variation in the surface roughness may be due to high growth rate at low temperature, probably because the size of droplets reaching the substrate surface may be quite large. This is due to the fact that the droplets may not be vaporized before reaching the substrate surface. At high temperature the size of the droplets reaching the substrate may be reduced owing to vaporization and a heterogeneous chemical reaction taking place just over the substrate surface in a well ordered manner. This may be the reason for the smoothness of the film coated at 350°C, as shown in Fig. 4(b), which consists of nano grains uniformly spread throughout the surface.

III.4 Optical absorption studies

Fig. 5 shows the optical transmission spectra of the CdS thin films coated with S/Cd at.% ratio equal to 1 and at substrate temperatures of 300°C and 350°C respectively.
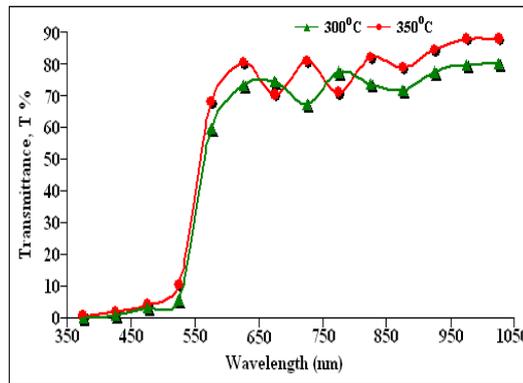

Fig 5

Fig. 5 Optical transmittance spectra of the as-deposited CdS films.

The maximum transmittance values obtained in the wavelength range 350 nm to 1050 nm was found to be equal to 80% and 87% for the films coated at 300°C and 350°C respectively. The spectra of both the films show a sharp fall in transmission near the fundamental absorption, which is an identification of the good crystallinity of these films. The transmittance spectra exhibit interference fringes. Similar behavior in the transmission spectra of the CdS films prepared by other techniques have been reported in the literature [18]. From the absorbance data, the absorption coefficient (α) was calculated using Lambert law [19]:

$$\ln(I_0/I) = \alpha.t \qquad\qquad (3)$$

where I_o and I are the intensities of the incident and transmitted light respectively, A is the optical absorbance and t is the film thickness, with

$$\ln(I_0/I) = 2.303\ A \qquad\qquad (4) .$$

The absorption coefficient (α) values calculated from the transmittance data are about 10^6 cm^{-1}. The variation of the absorption coefficient (α) with wavelength for the coated films is shown in Fig. 6 (the inset showing the variation of extinction coefficient with photon energy). The value of α decrease as the substrate temperature increases to 350°C. This decrease in α might be due to the increase in surface

smoothness which might be due to the improved crystallinity of the film coated at 350°C, as confirmed from SEM analysis.
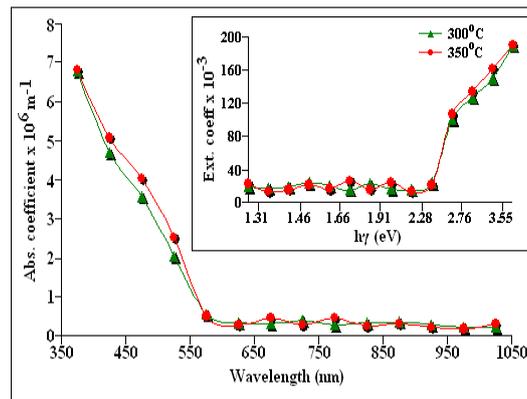

Fig 6

Fig. 6 Variation of absorption coefficient with wavelength.

The variation of the extinction coefficient is directly related to the absorption of light. In the case of polycrystalline films, extra absorption of light occurs at the grain boundaries. This leads to non-zero value of k for photon energies smaller than the fundamental absorption edge. The absorption coefficient was found to follow the relation [20]:

$$\alpha = A (h\nu - E_g)^{1/2} \tag{5}$$

where A is a constant which is related to the effective masses associated with the bands and E_g is the band gap energy.

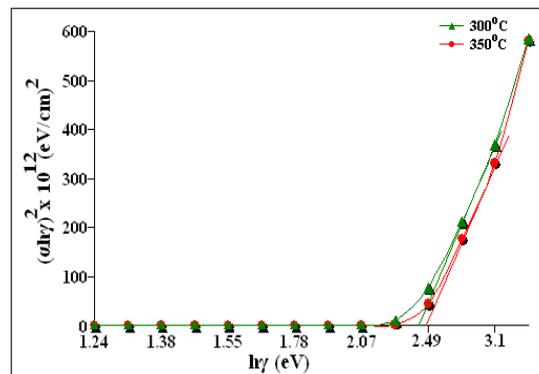Plots of $(\alpha h\nu)^2$ vs the photon energy (hν) for the as-deposited samples is shown in Fig. 7.

Fig 7

Fig. 7 Plot of $(\alpha\nu)^2$ versus hυ for the as-deposited CdS films.

Linearity of the plots indicates that the material is of direct band gap nature which on extrapolation to the energy axis at α =0 gives the band gap energy E_g, which is equal to 2.28 eV and 2.37 eV for the films coated at 300°C and 350°C respectively. These values are in good agreement with the values reported by others [21, 22]. The band gap energy increases for the films coated with higher substrate temperature which might be due to improved crystallinity of the films coated at that temperature due to reduced thickness of these samples.

III.5 Electrical studies

The electrical resistivity of the coated CdS films were measured in the temperature range of 303 K to 503 K by the Vander Pauw four point probe method [23] with the appropriate correction factor. Fig 8 shows the variation of log ρ with inverse of temperature for the as deposited samples.
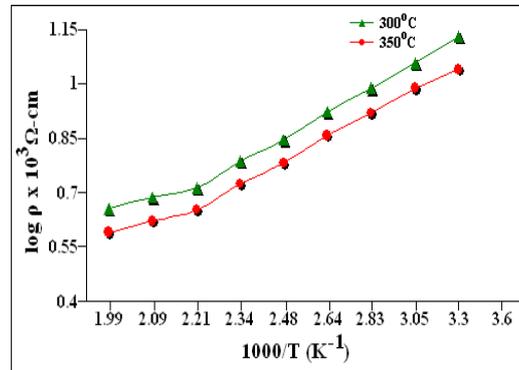

Fig 8

Fig. 8 Variation of electrical resistivity with inverse temperature

It is observed that as temperature increases the resistivity decreases, indicating the semi conducting behavior of the material. The film coated at 350°C has the low resistivity compared to the film coated at 300°C which may be due to reduced grain size and the improvement in film stoichiometry as indicated by the XRD pattern in Fig. 2(b). All the films have resistivity values in the range of {0.591-1.131} 10^3 ohm cm.

IV. CONCLUSIONS

A new automated spray technique enhanced by trigger pulses has been developed to coat thin films. Using this technique CdS thin films have been coated at two temperatures. The X-ray diffraction studies showed that the films are polycrystalline in nature with a mixture of hexagonal and cubic phases with hexagonal phase being predominant. The microstructural parameters corresponding to the (111) plane was calculated. The optical transmittance for the as-deposited samples showed interference patterns. Direct band gap values was found to be equal to 2.28 eV and 2.37 eV for the films coated at 300°C and 350°C respectively. The resistivity of the as-deposited films was found to vary in the range of {0.591–1.131} 10^3 ohm-cm. The high transmittance and low resistivity values obtained for the films coated using this technique is best suited for solar cell applications. From these results, it is evident that using this spray technique, device quality CdS films can be successfully prepared and this technique can be considered as a desirable alternative to conventional spray technique for the production of device quality CdS films.

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