ELECTRICAL CHARACTERIZATION OF CHEMICALLY GROWN CdS AND $CdTe$ THIN FILMS FOR SOLAR CELL APPLICATION.

ABSTRACT

Thin films of Cadmium Sulphide (CdS) and Cadmium Telluride ($CdTe$) have gained a great deal of interest due to their potential applications in solar cells. Deposition of CdS and $CdTe$ thin films were performed on Soda Lime glass and FTO substrate at $400℃$ and $300℃$ respectively using spray pyrolysis technique. The Hall Effect property was measured for the deposited CdS and $CdTe$ films. These results shows the resistivity and mobility of CdS films deposited at $400℃$ were $1.588 \times 10^4 \Omega cm$ and $5.619 \times 10^2 cm^2/Vs$, respectively, The annealed $CdTe$ thin film had a resistivity value of $1.016 \times 10^4 \Omega cm$, while the annealed and etched $CdTe$ thin film had a resistivity value of $4.52 \times 10^4 \Omega cm$, The resultant films are observed to be good to make a solar cell with CdS as a window layer and CdTe as absorber layer

Key Words: Cadmium Sulphide, Cadmium Telluride FTO, P-type and N-type

1. INTRODUCTION

Thin films of Cadmium Sulphide (CdS) and Cadmium Telluride ($CdTe$) have gained a popular of attention because of their potential uses in solar cells(Fang et al., 2013). These are all direct band-gap semiconductors, which means they can ingest solar power at a far smaller thickness than silicon wafers used in crystalline silicon (Si) solar cells (Morales-Acevedo, 2006). CdS is an n-type semiconductor with a large direct band gap (2.42 eV) that is commonly employed as the window layer in hetero-junction thin film solar cells coated over p-type $CdTe$(Rahman et al., 2019; Tiwari, Verma, Jain, & Bajpai, 2014) or Copper Indium Selenide ($CuInSe_2$)(Sajedur et al., 2019). The value of 1.45 eV band gap of $CdTe$ suited the Air Mass (AM) of 1.5 solar spectrums. Although only a few millimetres of absorber film were needed for solar cell functioning, the high absorption coefficient was attributable to this phenomenon(Ahmad et al., 2022). CdS and $CdTe$ Thin films are widely acknowledged as two of the most promising prospects for second-generation solar cells due to their wide range of inexpensive production methods and great efficiency (Kulkarni *et al*, 2017). Mobility, resistivity, carrier concentration, and the types of semiconductors are all key issues in the electrical properties of semiconductor measurements (Seboui *et al*., 2013). The two important criteria that affect whether CdS and $CdTe$ Thin films could be used as window layer or absorber layer in $CdS/CdTe$ heterojunction solar cells are electrical resistivity and carrier concentration (Garba, 2011).

There are many techniques identified to be successful in deposition CdS and $CdTe$ Thin films The most significant ones are Close Space Sublimasion CSS(Sobayel *et al*., 2020), Chemical Bath Deposition CBD (Ikhmayies & Ahmad-Bitar, 2010), Other techniques used to deposit material include Electrodeposition, Vacuum Evaporation, Sputtering, Vapor Transport Deposition (VTD), Metal organic Chemical Vapor Deposition (MOCVD), Molecular Beam Epitaxy (MBE), Screen Printing, and Spray Pyrolysis Deposition. However, it has been discovered that layers produced using the Spray Pyrolysis method are among of the most effective second-generation solar cells to date (Ashour, 2003). Additionally, this method appeals to researchers since it is simple to use, has a rapid deposition rate, and can easily produce large quantities of commercial modules (Dharmadasa *et al*., 2014). More over the use of this methodology, specialized materials can be quickly and efficiently deposited across enormous regions. It has been used for many years in the photovoltaic and solar cell industries for this reason, according to Ojeda-Barreto *et al*, (2018).

This study examine the electrical properties of CdS and $CdTe$ Thin film samples deposited using the Spray Pyrolysis process (at room temperature utilizing a Hall Effect Measurement instrument).The Hall effect measurement is a common, dependable, and more straightforward technique for determining the basic electrical characteristics of semiconductors (Miyake *et al.*, 2004).

Hall Effect is one of the most important techniques in determination of parameters that characterizes a semiconductor from electrical point of view (Kulkarni *et al*., 2017). The Hall Effect is a phenomenon that occurs when a semiconductor carrying current I is placed in a transverse magnetic field of flux density B. This phenomenon is: (i) to identify the charge carrier of a semiconductor, which may be N-type or P-type; (ii) find carrier concentration; (iii) measure the conductivity of the materials; and to identify carrier mobility.
Hall coefficient is mathematically given as;

$$R_H = \frac{1}{nq} \tag{1}$$

Charge carrier mobility;

$$\mu = \left|\frac{V_d}{E}\right| \ \ and\ its\ unit\ is\ m^{-2}V^{-1}s^{-1} \tag{2}$$

The Hall mobility,

$$\mu = \left|\frac{R_H}{\rho}\right| or\ \mu = |R_H|\sigma \tag{3}$$

The Resistivity is given as;

$$\rho = \frac{1}{N_e \mu} \quad (4)$$

Where ρ is resistivity, μ mobility, N_e bulk concentration(Mohammed, 2018).

2. MATERIALS AND METHODS

Spray Pyrolysis was used to deposit CdS and $CdTe$ layers on soda lime glass substrates. For CdS thin films, an aqueous solution of Cadmium acetate dihydrate $Cd(CH_3COO)_2.2H_2O$ and Thiourea $(NH_2)_2CS$ were employed as Cd and S sources, respectively. The pumping and exhausting gas scrubbing systems, the reaction chamber where the substrate was heated, the precursor solution and carrier gas (air) assembly connected to the spray nozzle and a temperature controller with a Copper-Constantan thermocouple to control the substrate temperature make up the deposition setup. The solution was sprayed onto a glass substrate that had already been cleaned. The temperature of the substrate was kept constant at 400℃. The normalized distance between the spray nozzle and the substrate was adjusted to 20 cm. The pressure of the carrier gas (air) was kept constant at 1 bar. The solution flow rate was kept constant at 0.5 ml/m throughout the experiment. The grown CdS films colour changes with the time from greenish yellow to bright yellow as shown on plate 1. The possible chemical reaction that takes place on the heated substrate to produce CdS is shown

$$Cd(CH_3COO)_2.2H_2O + (NH_2)_2CS + H_2O \rightarrow CdS \downarrow + CO_2 \uparrow + CH_4 \uparrow + steam \quad (5)$$

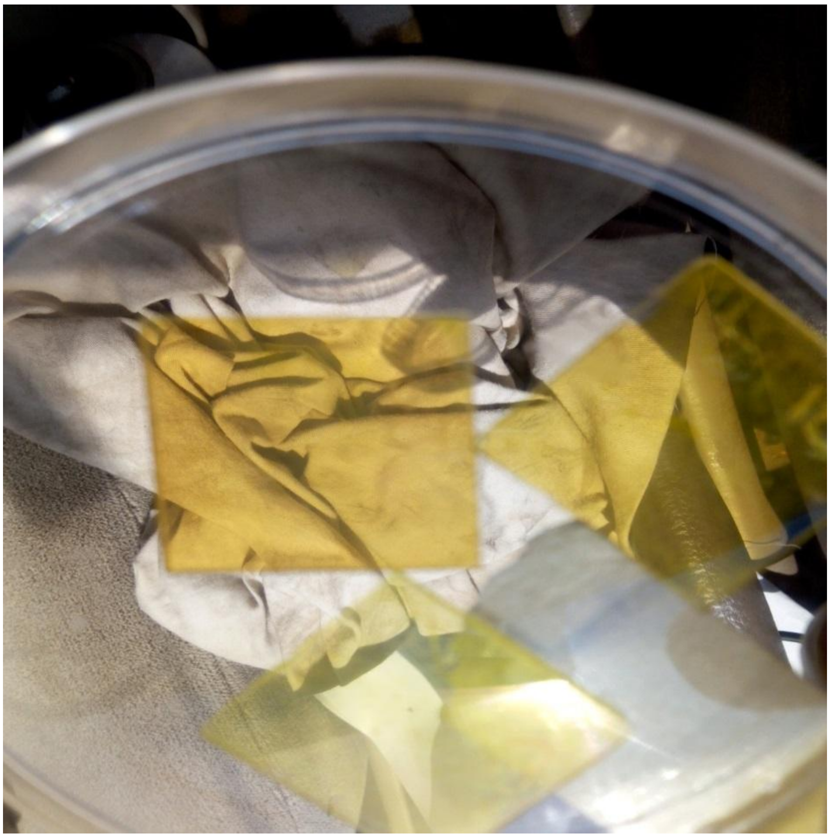

Plate 1. Optical study of CdS samples deposited at $30 minutes\ and\ 60 minutes$

2.1 CADMIUM TELLURIDE DEPOSITION

a. $CdTe$ deposition

$CdTe$ Was prepared by grinding $CdTe$ powder in a ceramic mortar mixed with $10\ wt\%CdCl_2 2 \cdot 5H_2O, ethylene\ glycol$ was added to the $CdTe$ powder which adjusted the viscosity for spray pyrolysis. The $CdTe$ paste was sprayed on the desired area. After completing the $CdTe$ thin films coating process which lasted $20 minutes$ by spray pyrolysis technique the films were naturally cooled at the room temperature. After deposition, samples were treated with a saturated Cadmium Chloride $CdCl_2$ in N-methyl-2 Pyridine NMP solution. The samples were submerged for 20 seconds in the solution.

b. $CdTe$ annealing

The spray pyrolysed films was dried on a hot plate at $150℃$ and was further annealed in flowing argon at $500℃$ for 1hr. Sample 2 differs from sample 1 in that the $CdTe$ layer after annealing was etched with a mix of nitric and phosphoric acid. The composition of the etching solution was 70% phosphoric acid, 1% nitric acid, and 29% distilled water. Etching time was 20 sec. The sample 2 was rinsed with distilled water and dried by spinning at $3000\ rpm$. The films were deposited on thoroughly cleaned substrates using the following processing parameters: (i) spray gun nozzle to substrate distance= $20cm$, (ii) spray solution concentration= $0.1M$, (iii) carrier N_2 gas flow rate=$10l/min$, (iv) deposition time= $20 minutes$, and (v) solution flow rate= $5ml/min$.The chemical reaction that took place in the chamber is presented as;

$$Cd^{2+} + Te + 2e^{-} \rightarrow CdTe \tag{6}$$

3. RESULTS AND DISCUSSION

3.1 ELECTRICAL PROPERTIES

For investigating the electrical properties of CdS and CdTe films, the resistivity and Hall Effect measurements with an incorporated resistivity/Hall measurement system (ECOPIA 3000) was used. For this purpose, the magnetic field was applied vertically to the surface of the samples and the magnitude and polarity of this were alternated periodically, while a direct current was passed across the sample using one diagonal pair of the four gold electrodes connected to a current source. After that, by using a frequency response analyzer (HMS-3000), alternating Hall voltage induced synchronously with the ac magnetic field was detected via the other pair of electrodes. The magnitude of the magnetic field and the current source was 0.55 T at the maximum and 20nA, respectively. The carrier concentration, mobility, resistivity and Hall coefficients were deduced from this study. The calculated bulk concentration, mobility, resistivity and Hall coefficients are presented in Table I..

Table 1. The Hall Effect measurements

SAMPLE	RESISTIVITY (Ωcm)	MOBILITY cm^2/Vs	BULK CONCENTRATION cm^{-3}	$AVERAGE\ HALL\ COEFFICIENT$ cm^3/C
$CdS\ at\ 1hr$	1.588×10^4	6.619×10^2	6.996×10^{11}	8.923×10^6
$CdS\ at\ 30mins$	2.234×10^4	7.262×10^2	3.629×10^{11}	-1.769×10^7

From the Table 1, the resistivity marginally decreases with respect to deposition time, ranging from $2{,}234 \times 10^4$ to $1.588 \times 10^4 \Omega cm$. Mousavi et al, (2014) reported that the rise in particle packing density with the increase in grain size causes the resistivity to drop.

Faraj, Eisa, & Pakhuruddin (2019) also reported that the nearer resistivity value for CdS film by Spray Pyrolysis technique. The CdS films deposited have the conductivity value about $4.106 \times 10^{-5}\ and\ 6.297 \times 10^{-5}((\Omega cm)^{-1})$ which are in good agreement with the previous report of (Ahmad *et al*., 2022). The prepared CdS thin film has $n - type$ conductivity(Kerimova, Bagiyev, Aliyeva, & Bayramov, 2017).

The bulk concentration was found to increase from 3.629×10^{11} to 6.996×10^{11} for the increasing of deposition time from 30minutes to 1hour and this was in agreement with the work of (Miyake *et al*., 2004). The film's thickness and crystallinity have a significant impact on the bulk concentration and mobility was improved. All CdS films displayed semiconducting activity, with resistivity's ranging from 10^{-3} to $10^{-5}\Omega cm$ (Ashour, 2003). The film's resistivity was seen to decrease with longer deposition times.

For $CdTe$ Thin films deposited on soda lime glass substrate at 1hour deposition time. The values of electrical resistivity, bulk concentration, mobility for the deposited films were presented in Table 2.

Table 2. The Hall Effect measurements.

SAMPLE	$RESISTIVITY$ (Ωcm)	$MOBILITY$ cm^2/Vs	$BULK\ CONCENTRATION$ cm^{-3}	$AVERAGE\ HALL$ $COEFFICIENT$ cm^3/C
$CdTe$ annealed	1.016×10^4	1.99×10^2	3.074×10^{12}	2.030×10^6
$CdTe$ Annealed and etched	4.52×10^4	2.58×10^2	0.98×10^{12}	6.820×10^6
$CdTe$ As deposited	4.85×10^4	3.15×10^2	7.2×10^{11}	8.47×10^6

From table 2 the resistivity value of the annealed $CdTe$ thin film was $1.016 \times 10^4\Omega cm$ and the resistivity value for the annealed and etched $CdTe$ thin film was $4.52 \times 10^4\Omega cm$. The order was in agreement with previous works of Rahman *et al*., (2019) and also the resistivity values of the $CdTe$ sample treated with $CdCl_2$ and annealed decreases. Miyake, *et al*,(2004) reported similar values of resistivity of the order $10^4\ to\ 10^8$. Hall effect measurement revealed that the $CdTe$ thin film exhibited $p-type$ conductivity as the average hall coefficient value was found to be positive(Nithyayini & Ramasesha, 2015). The bulk concentration of the $CdTe$ Thin film value was observed to be of the order$10^{11} \times 10^{12}cm^{-3}$. This was in agreement with previous work of (Ahmad et al., 2022). The annealed

$CdTe$ thin film had a resistivity value of $1.016 \times 10^4 \Omega cm$, while the annealed and etched $CdTe$ thin film had a resistivity value of $4.52 \times 10^4 \Omega cm$, according to table 2. The order agreed with earlier research by Rahman et al. (2019), and it also decreased with annealing and $CdCl_2$ treatment of the $CdTe$ sample's resistivity values. Therefore it was observed that

after the $CdCl_2$ treatment, annealed and etched it was noted that the values of mobility, resistivity, and Hall coefficient were decreased compared with the values of As-deposited sample.

5. CONCLUSION

CdS and $CdTe$ Thin films were deposited by a Spray Pyrolysis Technique. From Hall Effect measurements, it was observed that the electrical resistivity of CdS thin films decreased from 2.234×10^4 to $1.588 \times 10^4 \Omega cm$ with respect to deposition time while the conductivity increases. The annealed $CdTe$ thin film had a resistivity value of $1.016 \times 10^4 \Omega cm$, while the annealed and etched $CdTe$ thin film had a resistivity value of $4.52 \times 10^4 \Omega cm$, according to table 2. The order agreed with earlier research by Rahman et al. (2019), and it also decreased with annealing and $CdCl_2$ treatment of the $CdTe$ sample's resistivity values. Therefore it was observed that after the $CdCl_2$ treatment, annealed and etched it was noted that the values of mobility, resistivity, and Hall coefficient were decreased compared with the values of As-deposited sample. The negative sign and positive sign of the Average Hall coefficient confirmed the $n - type$ nature of the semiconducting CdS films and p-type nature of $CdTe$ Thin film.The resultant films are observed to be good to make a solar cell with CdS as a window layer and $CdTe$ as absorber layer.

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