

STUDIES OF ELECTRICAL RESISTIVITY (ρ) AND CHARGE-CARRIER MOBILITY (μ) OF CdS THIN FILMS DEPOSITED USING CHEMICAL BATH DEPOSITION METHOD

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ABSTRACT

Thin films of CdS were deposited on microscope glass substrate by chemical bath deposition technique using the reaction between CdCl₂, SC(NH₂)₂, NH₄OH and NH₄Cl in an aqueous solution. The parameters actively involved in the process of deposition have been identified and the methods used for production of CdS layers for use in thin film solar cells are also described. The pH value of the working solution was adjusted by pH meter and kept at a value of 9. It was confirmed by the hot-probe method to be n-type semiconductor and was orange in colour with mirror like gloss and adhered tightly to the substrate used. An average value of electrical resistivity, ρ of $1.8 \times 10^5 \Omega\text{cm}$ was obtained for CdS layers produced using the four point probe method, while charge-carrier mobility, μ of average value of $2.4 \times 10^3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ was obtained using the Hall Effect measurement.

KEYWORDS: CdS, electrical resistivity, charge-carrier mobility, CBD.

INTRODUCTION

Cadmium Sulphide (CdS) is among the binary compounds of group II-VI family and has direct bandgap of 2.42 eV at room temperature with high optical transition probabilities for absorption and emission. The density of CdS is 4.82 gcm⁻³ and its stable structure is wurtzite with lattice parameters $a_0 = 4.138 \text{ \AA}$ and $c_0 = 6.7490 \text{ \AA}$ (Sze et al., 2007). The group II-VI family is formed by the metallic element Cd, Zn, Hg or Mn and the elemental S, Se or Te. The bandgap ranges from 0.2 eV for HgTe to 3.6 eV for ZnS (Pandey, et al., 1996).

CdS thin films are widely used in various materials such as light emitting diodes (LEDs), solar cells, electronic and optoelectronic devices (Izgorodi et al., 2009, Bicer et al., 2010, and Peabहार et al., 2009). In thin film solar cells, CdS being an n-type window material can be combined with CuInGaSe₂ (CIGS) or CdTe to form a good heterojunction after annealing temperature at 400°C for 20 minutes in air. The annealing temperature of the window layer is very crucial in forming this junction (Nair et al., 2001). These two materials are now under intense research and development worldwide. CIGS-based solar cells are currently leading with the record efficiencies of 19.9% (Repins et al., 2008), whereas CdTe-based solar cells have achieved 16.5% (Wu et al., 2001) for small scale laboratory devices to date.

Various methods have been employed to deposit CdS thin films such as spray pyrolysis (Yadav et al., 2010) chemical vapour deposition (CVD) (Barreca et al., 2004), metal-organic

chemical vapour deposition (MOCVD) (Tsuji et al., 2000), vacuum evaporation (Senthil et al., 2001), Electrodeposition (Diso et al., 2010), sputtering (Fraser et al., 1972), rf magnetron sputtering (Har et al., 2008), close space sublimation (Bouchenaki et al., 1991) and chemical bath deposition (CBD) (Cortes et al., 2004, Dharmadasa et al., 2002, Chaure et al., 2003, and Pauporte et al., 2005). CBD techniques depend on the action of a chemical reducing agent in solution to reduce metallic ions to the metal, and it differs from homogenous chemical reduction. It takes place linearly with time in a manner similar to electroplating at constant current density. The aim of this work is to study the electrical resistivity and charge-carrier mobility of chemically deposited thin films CdS.

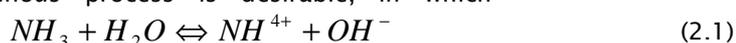
Experimental Procedure

CdS thin films have been deposited on microscope glass substrate of dimension (5 × 3) cm by reacting CdCl₂, SC(NH₂)₂, NH₄OH and NH₄Cl using chemical bath deposition method. The substrates were cleaned using methanol to remove the surface contamination and to make the surface more conducive for uniform film deposition. After rinsing with distilled water, the cleaned substrate was inserted into the mixed solution and continuously stirred with constant speed to obtain homogenous heat transfer to the total surface for uniform growth. Ammonium solution was used to adjust the pH value of the bath to 9. The optimal deposition parameters of the as deposited CdS thin films are given in table 1.

Table 1: chemical bath conditions

Reactants	Molar Concentration
CdCl ₂	0.01
SC(NH ₂) ₂	0.17
NH ₄ Cl	0.036
NH ₄ OH	0.73

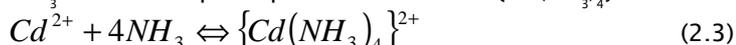
The solution is mixed in a beaker immersed in a water bath after heating at approximately 70°C and the microscope glass substrate was placed inside the mixed solutions. The solution was continuously stirred and thin films of CdS formed within the above temperature were orange in colour with mirror like gloss and adhered tightly to the substrate. Three samples were deposited on various microscope glass substrates and the deposition time was chosen to be 40 minutes. To obtain higher thickness of the films, the same procedures were repeated. The formation of CdS takes place heterogeneously on the microscope glass surface or homogeneously in the solution due to spontaneous precipitation of CdS. The homogenous process is desirable, in which



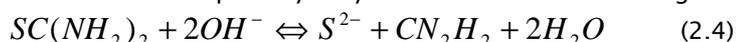
The source of Cd²⁺;



Cd²⁺ and NH₃ form a complex species of cadmium {Cd(NH₃)₄}²⁺ which slowly release Cd²⁺;



Thiourea the source of sulphur hydrolyzes in alkaline solution to give S²⁻;



The thickness of the films, t measured using the equation below:

$$\rho = \frac{m}{At}, \Rightarrow t = \frac{m}{A\rho} \quad (2.6)$$

where, ρ is the density of CdS, m is the mass of CdS deposited, A is the area of CdS layer and t is the film thickness.

A thermometric (hot-point probe) was carried out in order to identify the type of electrical conductivity of the deposited CdS thin film. It consists of two probes, one of the two probe tips is heated several degrees centigrade above ambient while the other is at room temperature. The hot probe heats the sample immediately under it, with a consequent rise in the kinetic energy of the free carriers. The polarity of the voltage determined the Seebeck effect indicates the conductivity type as described in the literature (Schroder, 1998, and Pirret, 1996).

$$\rho = 2\pi s \left(\frac{V}{I} \right) \quad (2.7)$$

where, V/I is the slope of the graph and s is the probe-to-probe spacing.

The Hall Effect principle was used for the measurement of charge-carrier mobility. This principle is based on the fact that an electromotive force (e.m.f) is set up across a current carrying conductor (or semiconductor)

adsorption of Cd²⁺ and S²⁻ ions take place followed by the addition of S²⁻ or Cd²⁺ ions (Chu *et al.*, 1992).

The rate of formation of CdS is determined by the concentration of Cd²⁺ provided by {Cd(HN₃)₄}²⁺ and the concentration of S²⁻ from hydrolysis of CS(NH₂)₂. The rate of this hydrolysis depends on the pH and the temperature of the solution, promoting the formation of S²⁻, however, the concentration of {Cd(HN₃)₄}²⁺ is also increased, reducing the concentration of Cd²⁺ and the rate of CdS formation (Chu *et al.* 1994). The reaction mechanism for the formation of CdS could be understood as follows.

Ammonia hydrolyzes in water to give out OH⁻;

The collinear four-point array probe was used for the resistivity measurement of the CdS samples. In the standard four-point probe technique, four collinear, evenly spaced probes are brought into contact with the surface of the CdS sample. A known current I was passed through the outer two probes and the potential V thereby developed is measured across the inner two probes. The semiconductor resistivity, ρ is calculated using;

when a magnetic field is applied normal to the direction of flow of current. The sample was held with a wooden stand and placed between the opposite poles of the magnet.

Using the variable control of the direct current (d.c) power supply, the applied voltage, V_L was increased in steps and the corresponding Hall voltage, V_H were recorded. The charge-carrier mobility, μ can be calculated using;

$$\mu = \frac{V_H}{V_L} \left(\frac{w}{l} \right) B \quad (2.8)$$

where, V_H/V_L is the slope of the graph, B is the magnetic field strength = 0.03 T, w is the width of sample and l is the sample length.

RESULTS AND DISCUSSION

From the hot-point probe measurement, it was found that all the CdS films prepared in this work showed n-type in electrical conduction. Figures 1 - 3 are the results of resistivity values measured for three samples and the slope of the graph (V/I) is used to calculate the value of ρ using equation

(2.7) above. Similarly, Figure 4 - 6 represent the result for the charge-carrier mobility and their slopes give the value of V_H/V_L which is used to calculate the value of μ from equation (2.8). Table 2 presents the summary of thickness, resistivity and charge-carrier mobility of the three samples.

Table 2: Results of thickness, resistivity and charge-carrier mobility for the three samples.

Samples	Time of dipping (hrs)	Thickness (μm)	Resistivity (Ωcm)	Charge-carrier mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
DP-27	13.5	10.7	2.6×10^5	2.0×10^3
DP-32	16	20.0	1.9×10^5	2.5×10^3
DP-49	24.5	36.6	1.0×10^5	2.8×10^3

Average value of resistivity

$$= 1.8 \times 10^5 \Omega\text{cm}$$

Average value of charge-carrier mobility = $2.4 \times 10^3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$

From the table, it is clear that the thickness of the films increased with increasing time the substrate was left in the solution. However, from these results it is observed that there is also progressive decrease in resistivity values and progressive increase in charge-carrier mobility values for CdS samples as the thickness increases. This is because when thickness increases, the grain boundaries decreases which leads to the increase of the grain size and hence the resistivity becomes low. From the theory of photovoltaic principles, the internal resistance of

solar cells results in internal voltage drops by reducing the series resistance in practical solar cells. Electrical resistance and hence the resistivity of semiconductor is desired to be as low as possible in order to separate electrons and holes formed by irradiation with light in the space charge layer of the semiconductor surface. It is also observed that, as the temperature and thickness increases the resistivity decreases which confirmed the semi-conducting behaviour of the material (Yadar et al., 2010, Kundakci et al., 2008).

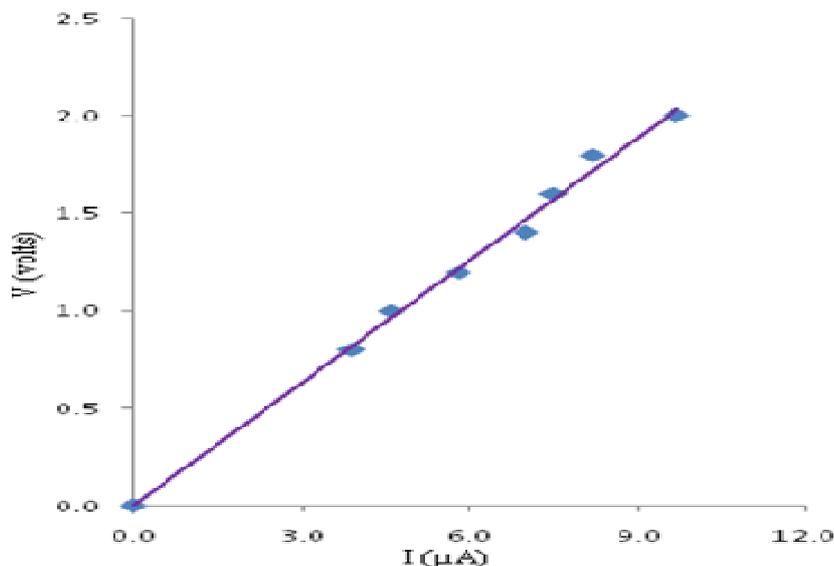


Figure 1: Graph of V (volts) against I (μA) for sample DP-27 (Thickness = $10.7 \mu\text{m}$).

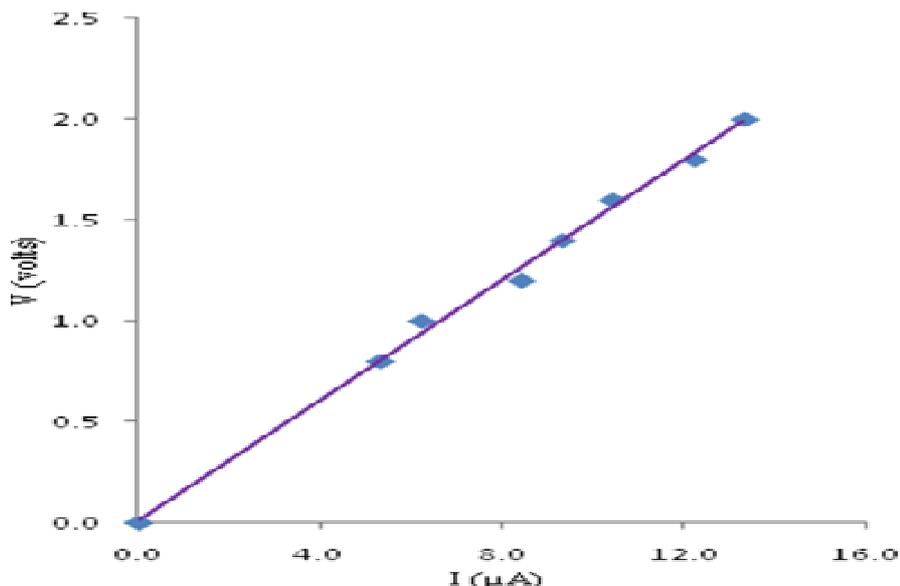


Figure 2: Graph of V (volts) against I (µA) for sample DP-32 (Thickness = 20.0 µm).

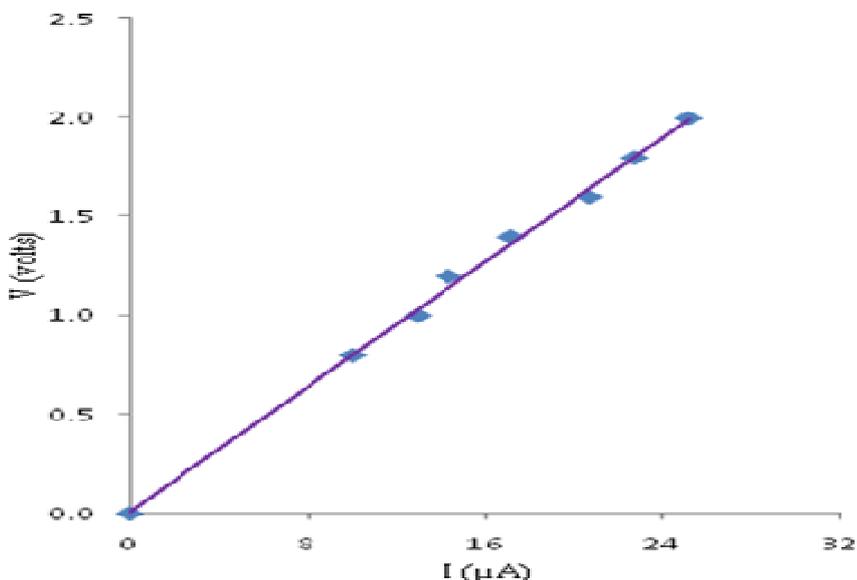


Figure 3: Graph of V (volts) against I (µA) for sample DP-49 (Thickness = 36.6 µm).

To achieve the maximum electrical power conversion efficiency, a semiconductor material with a very low resistivity is required. Pure CdS crystals have a high resistivity about $10^{12} \Omega\text{cm}$ and it is polycrystalline. Thin films can be reduced by doping with In, Sn, Al, Cr or Br using different growth techniques (Günel *et al.*, 1997). Furthermore, undoped CdS thin film is high resistive, the resistivity of such films are in the range $10^7 - 10^9 \Omega\text{cm}$ (de Melo *et al.*, 1994). The resistivity values of CdS thin film has been reported in the range $(1.48 \times 10^4) - 10^8 \Omega\text{cm}$ (Cha *et al.*, 2004, Uda *et al.*, 1990, and Ramaih *et al.*, 2001). The average value got in this work is therefore very close to those found by other researchers in this field.

For two given semiconductors, the charge-carrier mobility in the material of lower resistance has higher velocities than the materials of high

resistance for the same value of applied electric field. This is because of the less opposition to the flow of charge carriers for the case of the material of lower resistance. The higher charge-carrier values found for samples with lower resistivity value is then in agreement with this expectation. It is however, desired that charge-carrier mobility values for solar cell materials be high in order to achieve high conversion efficiency. The electron Hall mobility of CdS single crystals at room temperature and at 40°C was found to be $2.10 \times 10^2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $3.0 \times 10^3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ respectively (Kröger *et al.*, 1954). The average value of $2.4 \times 10^3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ found in this work is close to the one obtained as $2.83 \times 10^3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ by Cha *et al.*, 2004.

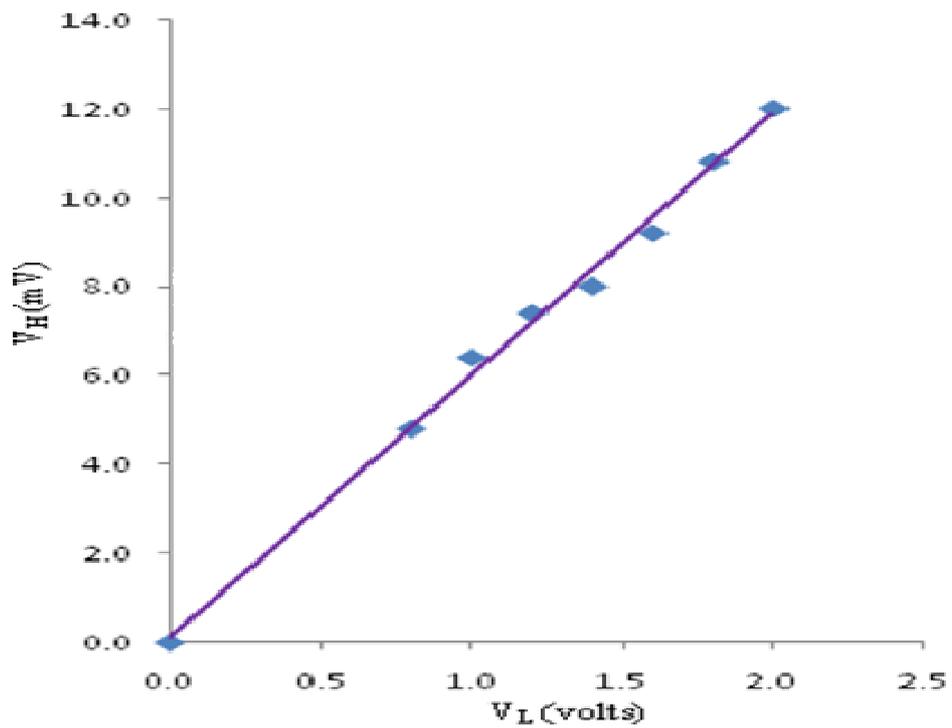


Figure 4: Graph of V_H (mV) against V_L (volts) for sample DP-27 (Thickness = 10.7 μm).

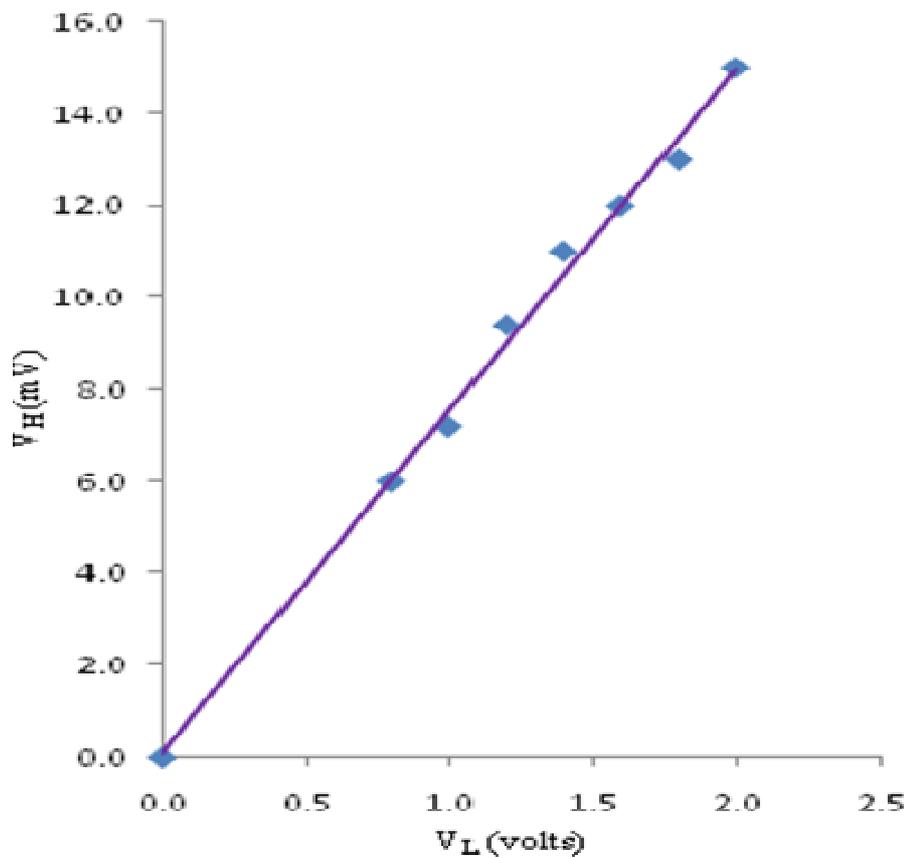


Figure 5: Graph of V_H (mV) against V_L (volts) for sample DP-32 (Thickness = 20.0 μm).

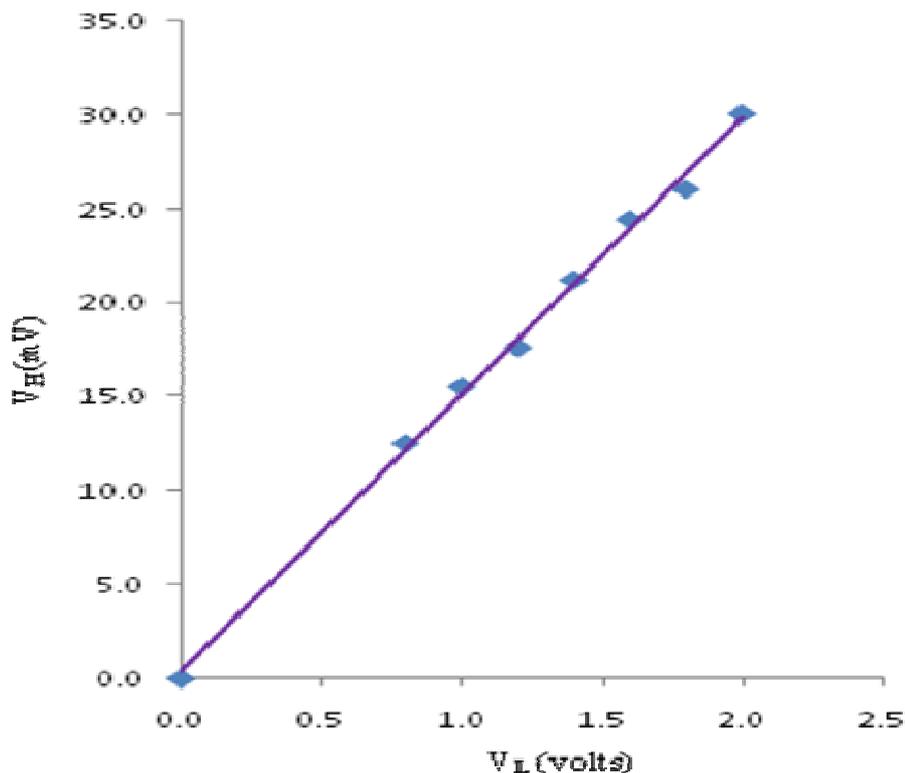


Figure 6: Graph of V_H (mV) against V_L (volts) for sample DP-49 (Thickness = 36.6 μm).

CONCLUSION

CdS thin film can be deposited using chemical bath deposition technique. The layers obtained have excellent adhesion to the substrate and orange in colour with mirror like gloss. It was confirmed by the hot-probe method to be n-type in electrical conduction. From the result obtained, as the resistivity decreases the charge-carrier mobility increases which confirmed the behaviour of semiconductors. An average value

of electrical resistivity, ρ of $1.8 \times 10^5 \Omega\text{cm}$ was obtained for CdS layers produced using the four point probe method, while charge-carrier mobility, μ of average value of $2.4 \times 10^3 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ was obtained using the Hall Effect measurement.

Acknowledgement

The main author wishes to acknowledge the financial support given by Kano University of Science & Technology, Wudil - Nigeria.

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