

Electrical Behavior of $Cd_{0.3}Zn_{1.1x}S_{0.7}$ Thin Films for Non-Heat Light Emitting Diodes

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Abstract. In developing countries like Kenya, solution processing technique is the cheapest and simplest technique to grow inorganic composites thin films. This method was used to grow thin films of $Cd_{0.3}Zn_{1.1x}S_{0.7}$ on ordinary microscope Perspex substrate slides from aqueous solutions of Zinc chloride and cadmium chloride in ammonia solution. A solution of triethanolamine was used as a complexing agent while thiourea was used as source of sulphide ions. Electrical properties as a function of their thicknesses were obtained by varying deposition time while all other parameters were maintained constant. Using a resistance measurement device and a Gauss meter, resistivity and the conductivity of the films were found to be thickness dependent with semiconductor nature.

Keywords: complexing agent; zinc; cadmium; thiourea; resistivity; sulphur.

Introduction

A composite of inorganic thin films containing cadmium and zinc has been largely neglected en route to technological development though thin films containing sulphur has a significant solid state material of both scientific applications. It is ternary stable non-stoichiometric compound in which zinc and cadmium sulfides belongs to group II–VI compound semiconductor materials [4]. Depending on preparation conditions, they can occur in cubic or hexagonal or both crystal structures [14] with a large band gap of above 2.413 eV. This size of band gap has vast potential use in thin film devices especially in photoluminescent and electroluminescent devices. In most studies, only binary thin films of CdS and ZnS have been largely prepared using many deposition techniques such as Sol gel techniques [3], Metal Organic Vapor Deposition [15], Magnetron Sputtering Technique [18], Spray Pyrolysis

Technique [2], and Electrostatic Assisted Aerosol Jet Deposition [15]. Among most techniques, solution processing or what is commonly known as chemical both deposition methods has offered a better option. It is a technique that allows thin films to be grown on all kinds of hydrophilic substrates; very simple, inexpensive, suitable for large area deposition and impurities present in the initial chemicals can be removed by simply using of a suitable complexing agent [8]. This article chose to investigate electrical properties of $Cd_{0.3}Zn_xS_{0.7}$ ternary thin films grown chemical bath as a function their as deposited thicknesses.

Theory

Electrical Resistivity of thin films. When only two basic configurations of the film resistance are considered, their resistance R can be expressed be given as [9]:

$$R = \rho \frac{L}{\partial w}, \tag{1}$$

where R – is the resistance; ρ – is the resistivity; L – is the length of the rectangular substrate; ∂w – is the element of the width.

If $L = W$, then:

$$R = \frac{\rho}{d} = R_s, \tag{2}$$

is the resistance of the film layer and is expressed in ohms-square:

$$\rho = d \times R_s. \tag{3}$$

Therefore, the resistance R_s of one square of a film depends not on square the size but only on the resistivity and thickness though the figure's dimensions are shown in Figure 1.

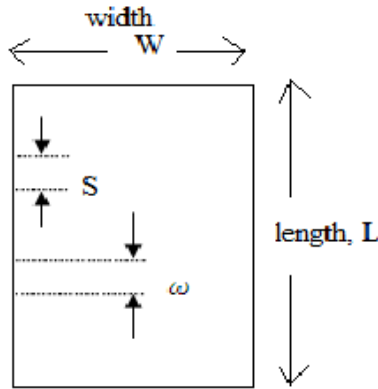


Figure 1 – Hypothetical dimensions for analysis of electrical resistivity section of thin films used for electrical characterization

This value is widely used for film comparison, in particular films of one material grown under identical conditions. If the thickness is known, the resistivity ρ can be obtained [1]. Any change in thickness causes variation of resistance changes without change in the basic properties of a material. This configuration is characteristic of many inorganic thin films [2]. Though it is known that resistivity and temperature coefficient of resistance depend on the surface resistance R_s

and the number of squares chosen N [3], hence the total resistance is given as:

$$R = R_s \times N. \tag{4}$$

The resistance of such material is determined by the equation are given by the relation:

$$R = R_s \left(\frac{LW}{n\omega^2} + \frac{1}{n\omega} - 2(0.46) \frac{L}{n\omega} \right), \tag{5}$$

$$\text{hence } \frac{R_s LW}{n\omega^2} \approx 1, \tag{6}$$

where $n = \frac{s}{\omega} + 1$, $\omega = s$ width of lines and S is the width of intervals between the lines giving the parameters of a thin film that can be used for operational development of resistance as:

$$R = \frac{\rho}{s} \times N. \tag{7}$$

Temperature coefficient of resistance TCR is described by the equations:

$$\alpha = \frac{1}{\rho} \frac{d\rho}{dT}, \tag{8}$$

$$\alpha = R - \frac{R_0}{R_0(T - T_0)}, \tag{9}$$

where R – is the resistance at certain temperature; T, T_0 – are the temperature at 0 K [4].

Measurement of Conductivity Type. The Hall Effect is observed when a magnetic field is applied at right angles to a rectangular sample of a material carrying an electric current. A voltage appears across the sample that is due to an electric field that is at right angles to both the current and the applied magnetic field. The Hall Effect can be eas-

ily understood by looking at the Lorentz force on the current carrying electrons. The orientation of the fields and the sample are shown in Figure 1 [5].

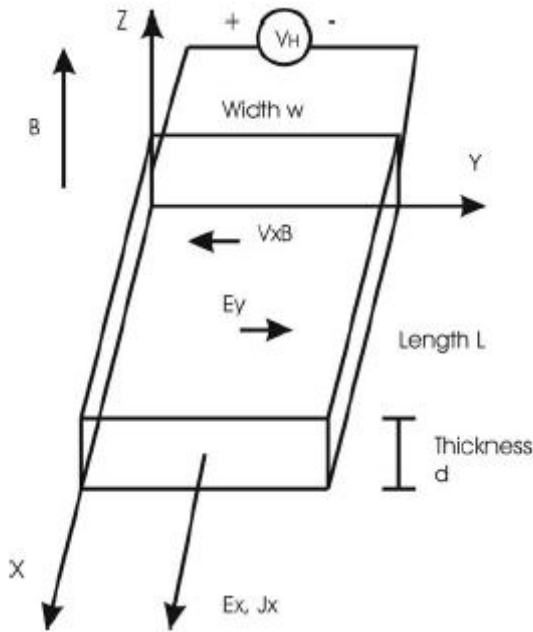


Figure 1 – Sign shown for the case of positive charge carriers

An external voltage is applied to the crystal and creates an internal electric field E_x . The electric field that causes the carriers to move through the conductive sample is called the drift field J_x and flows in the x-direction in response to the drift field. The carriers move with an average velocity given by the balance between the force accelerating the charge and the viscous friction produced by the collisions producing electrical resistance.

The drift velocity appears in the cross product term of the vector Lorentz force as shown below:

$$F = q(E + v \times B) \tag{10}$$

where F – is the force on the carriers of current; q – is the charge of the current carriers; E – is the electric field acting on the carriers; B – is the magnetic field inside the sample [8, 10].

The transverse (y) component of the Lorentz force causes charge densities to accumulate on the transverse surfaces of the sample. An electric field in the y -direction result which just balances the Lorentz force because there is no continuous current in the y -direction. The equilibrium potential difference between the transverse sides of the sample is called the *Hall voltage*. The charge may be positive (“holes”) or negative (“electrons”) depending on the material and the motion of the carriers is specified by the drift velocity v . The magnetic field is chosen to be in the z -direction [7]. The drift velocity is the result of the action of the electric field in the x -direction. The total current is the product of the current density and the sample’s transverse area $A(I = J_x A; A = wt$ as shown in Figure 2 gives a drift current J_x is given by:

$$J_x = n \times q \times v_x, \tag{11}$$

where n is the number density or concentration of carriers.

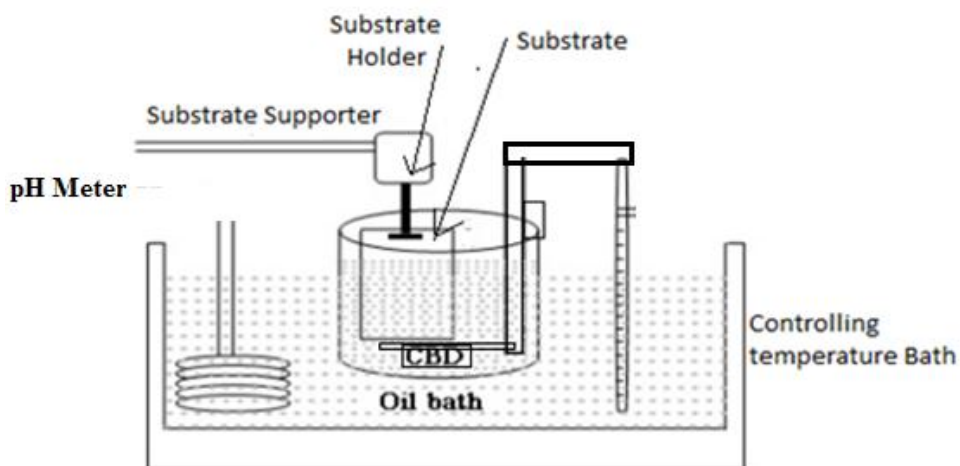


Figure 2 – Chemical bath Setup

The carrier density n is only a small fraction of the total density of electrons in the material. Thus we can measure the carrier density.

In the y -direction assuming a no load condition the free charges will move under the influence of the magnetic field to the boundaries creating an electric field in the y -direction that is sufficient to balance the magnetic force.

$$E_x = v_x B_z. \quad (12)$$

The Hall voltage is the integral of the Hall field $E_y = V_H$ across the sample width w such that $V_H = E_H \varpi$. Hence in terms of the magnetic field and the current, we have:

$$V_H = \frac{1}{nqd} BI = \frac{R_H BI}{d}. \quad (13)$$

Here R_H is called the Hall coefficient and the measurements will be of V_H as a function of drift current I and as a function of magnetic field B . You fix one parameter in order to intelligibly observe V_H . The mobility μ is the magnitude of the carrier drift velocity per unit electric field and is defined by the relation:

$$v = \mu E \text{ or, } \mu = \frac{v_x}{E_x}. \quad (14)$$

This quantity can appear in the expression for the current density and its practical form.

$$J = \sigma E \text{ or } J_x = nqv_x = nq\mu E_x \quad (15)$$

We have the relations:

$$\sigma = nq\mu = \frac{1}{\rho}. \quad (16)$$

Where σ is the conductivity and ρ is the resistivity. The total sample resistance to the drift current is:

$$R = \frac{\rho L}{\varpi d}. \quad (17)$$

Not only does the Hall coefficient give the concentration of carriers it gives the sign of their electric charge, by:

$$R_H = \frac{1}{nq}. \quad (18)$$

The dimensions of the sample are w , the width which is to be oriented in the y -direction, d the thickness which is to be oriented in the z -direction which is perpendicular to the magnetic field and L , the length of the sample which is to be located along the x -direction [12]. The sample should be about four times longer than it is wide so that the electric current streamlines have an opportunity to become laminar or the electric potential lines to become parallel and perpendicular to the edges of the sample. The Hall voltage should be zero when the sample is not in a magnetic field and the drift current is applied. A plot of Hall voltage as a function of drift current at constant magnetic field will have a slope equal to $R_H B / d$. Thus, the slope multiplied by d / B is the magnitude of the Hall coefficient. The Hall voltage is directly related to the magnetic field and the drift current, and it is inversely related to the thickness of the sample. The samples used for the measurement are made as thin as possible to produce the largest possible voltage for easy detection. The sample has no strength to resist bending and the probe is to be treated with great care. This applies to the probe of the Gauss meter as well.

Methodology

Reagents and Chemicals. Pure analytic grade chemicals (99.9 %) of zinc chloride ($ZnCl_2$) and cadmium chloride ($CdCl_2$), 25 % ammonia (NH_3), di-ionized water; triethanolamine (TEA), and thiourea (TU) were purchased. Ordinary microscope slides were bought and used as substrates without any further modifications.

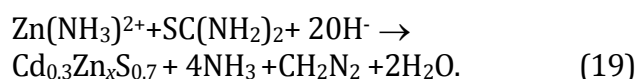
Cleaning of substrates. The following procedure was employed; scrubbing with liquid detergent; rinsing several times with distilled water; scrubbing again with detergent; Rinsing again with distilled water; scrubbing with trichloroethylene; rinsing with distilled water; scrubbing with acetone; rinsing with distilled water; scrubbing with alcohol; rinsing with di-ionized water and finally drying using an oven [9].

Experimental Procedures. All solutions were prepared using de-ionized water. 1 M of $ZnCl_2$, 10 M of ammonia solution, 1 M of TEA and 1 M of TU were prepared. 10 ml of the 1 M $ZnCl_2$ solution were measured into a 100 ml beaker and 6 ml of the 10 M Ammonia solution was introduced gradually into the beaker with thorough stirring until the white precipitates formed fully dissolved [8, 9]. This now followed an addition of 1 ml of the 1 M TEA and finally 15 ml of 1 M thiourea with continuous stirring to start the slow reaction for growth of the thin films. Di-ionized water was added to make up 49 ml of solution in the bath and then, 1 ml 0.3 M $CdCl_2$ was then added to top to 50 ml. The chemical bath composition was at pH of 10. Microscope perspex substrate slides were used as substrates and inserted at a small angle to the vertical and suspended vertically from synthetic foam and the beaker was covered with a glass cover and left to deposit at varying time intervals [6]. The initial period was 3 hours and then subsequent ones were taken out every after five hours labelled $S_1 \div S_{11}$ had deposition time of 3, 8, 13, 18, 23, 28, 33, 38, 43, 48 and 53 hours, respectively. They were dried and characterized as deposited for electrical resistivity using the direct current (DC) two point probe method and a Gauss meter.

Results and discussion

Chemical Processes in Optimization of $Cd_{0.3}Zn_xS_{0.7}$ thin films. Optimized concentration and volumes of sulphide ion source used was achieved with the concentration of 1 M zinc and 1 M cadmium chloride at pH of 10 at room temperature. This was kept constant and only the time of deposi-

tion was varied. It is generally accepted [11] that the reaction governing the formation of the $Cd_{0.3}Zn_xS_{0.7}$ deposits can be represented as:



Based on this expression, when the ionic product of Zn^{2+} and S^{2-} exceeds the solubility product of $Cd_{0.3}Zn_xS_{0.7}$, then $Cd_{0.3}Zn_xS_{0.7}$ deposits are formed. This means that the ions in $Cd_{0.3}Zn_xS_{0.7}$ nuclei start to coagulate onto the microscope slide substrate [8]. This then grows slowly with time at a rate complemented by the complexing agent (TEA). The rate of deposition becomes zero when $S < 1$ (where S = solubility) and the film attains terminal thickness [16] and stops to grow. It was noted that the rate of deposition was high at the initial process of growth. This was attributed to the high concentrations of Zn^{2+} and S^{2-} in the bath solutions [9]. As the deposition went on, a thicker film of $Cd_{0.3}Zn_xS_{0.7}$ was formed. The bath precursor solution becomes deficient in ions. This possible might have resulted into a slower rate of film growth [6] and finally the rate of deposition becomes zero when $S \leq 1$ and film attains terminal thickness stopping further deposition [10]. It was noted that at this final state, any further addition of thiourea does not increase the thickness of the film hence the optimized volume of thiourea was 17 ml.

Electrical properties of $Cd_{0.3}Zn_xS_{0.7}$ thin films. Using the direct current two point probe method, the variation of electrical resistivity, ρ (Ω -cm) as a function of thickness was obtained and tabulated in Table 1.

Table 1 – Variation of electrical resistivity and conductivity

Sample	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}
Thickness (nm)	69	120	143	156	166	189	214	237	269	283	300
Resistivity (Ω -cm) $\times 10^5$	1.822	1.623	1.212	0.976	0.803	0.747	0.697	0.613	0.502	0.407	0.363
Conductivity (Ω^{-1} -cm $^{-1}$) $\times 10^{-5}$	0.549	0.616	0.825	1.025	1.245	1.339	1.434	1.631	1.992	2.457	2.841

The resistivity of $Cd_{0.3}Zn_xS_{0.7}$ film decreases from 1.822×10^5 (Ω -cm) to 0.363×10^5 (Ω -cm) as the film thickness increases from 69 to 300 nm [7]. The results were plotted in figures 3–4. It can be noted from figure 3 that the conductivity of $Cd_{0.3}Zn_xS_{0.7}$ thin films increases from 0.549×10^{-5} (Ω^{-1} -cm $^{-1}$) to 2.841×10^{-5} (Ω^{-1} -cm $^{-1}$) as the film thickness increases from 69 nm to 300 nm.

These results are attributed to show that the decrease in resistivity or the increase in conductivity as the film thickness has a relationship with crystalline of the films. This was attributed to the increase in size of crystals that effected resistivity in semiconductor thin films [8, 9].

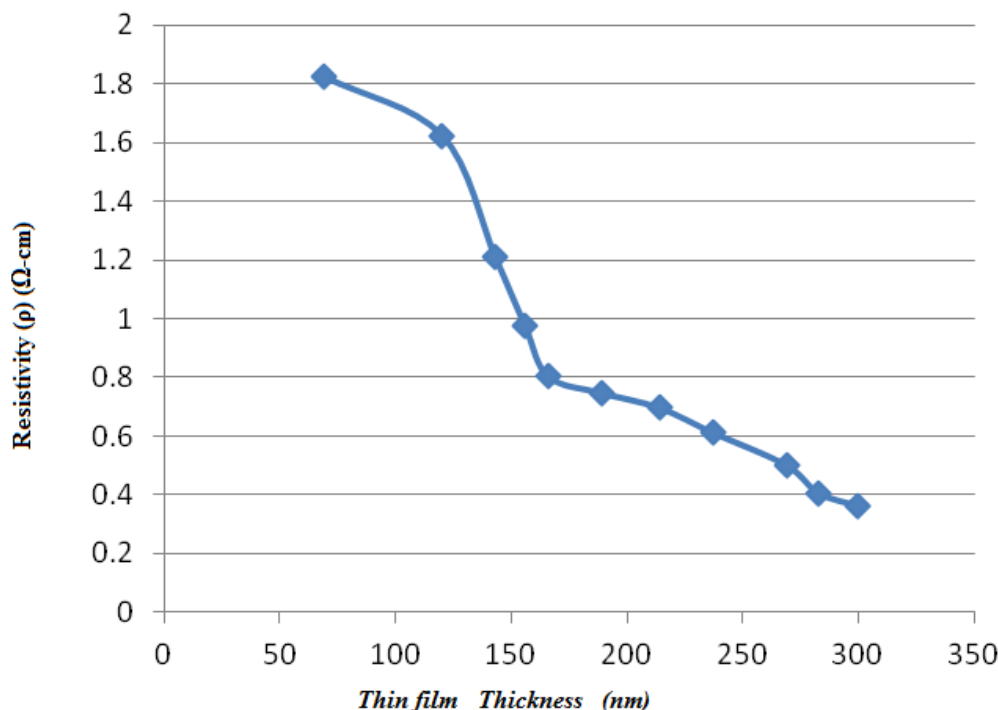


Figure 3 – Graph of resistivity against thickness

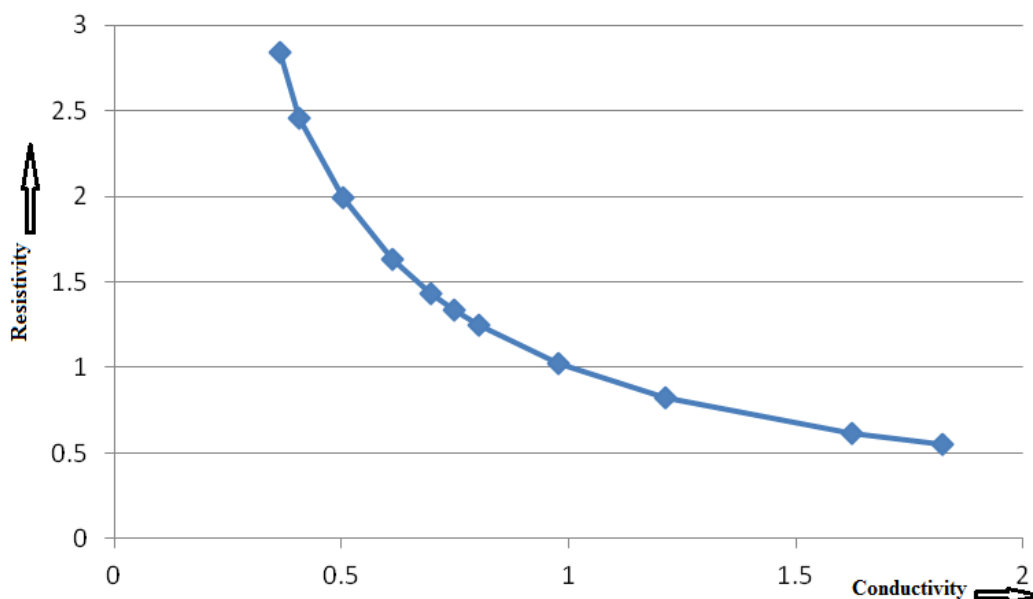


Figure 4 – Graph of conductivity and resistivity

Similar curves were observed by [12, 14, 16, 17] who used different deposition methods. Therefore the variation of $Cd_{0.3}Zn_xS_{0.7}$ thin film thickness with deposition time is optimized by taking a substrate out of bath at regular interval of 3 and not 5 hrs. Hence, film thickness increases exponential with deposition time since concentration decreases exponentially also.

Conductivity measurement of $Cd_{0.3}Zn_xS_{0.7}$ thin films. The Hall coefficient of a material is a function of the material and the impurity doping level in it. It

is best reported in meters cubed per coulomb (SI units). Unfortunately, it is usually reported in the units (cm^3 / C). In the determination of R_H , Lab-View was used to control the drift current in the Hall sample. In addition to controlling the drift current, the VI recorded data from the two volt meters in the gauss meter (Figure 5). One of the meters measured the voltage across the resistor in the drift circuit (bottom), while the other measured the voltage across the y-direction of the probe (the hall voltage).

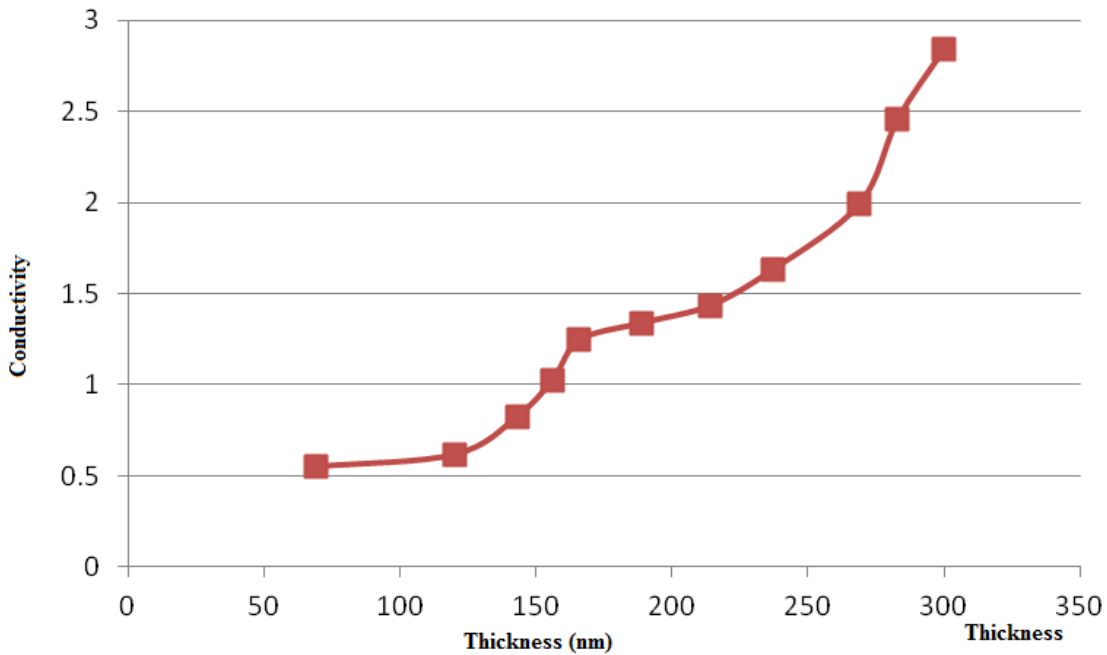


Figure 5 – Graph of thickness against conductivity

As the computer steps up the driving voltage (and therefore drift current) it recorded the value from each of these meters and the output them when the program finishes [13]. The probe is made of InAs (indium arsenide) who has a near

constant Hall coefficient so, hence giving a very close to a straight line (V_H vs I) with a slope that is related to the Hall constant R_H as shown in Figure 6.

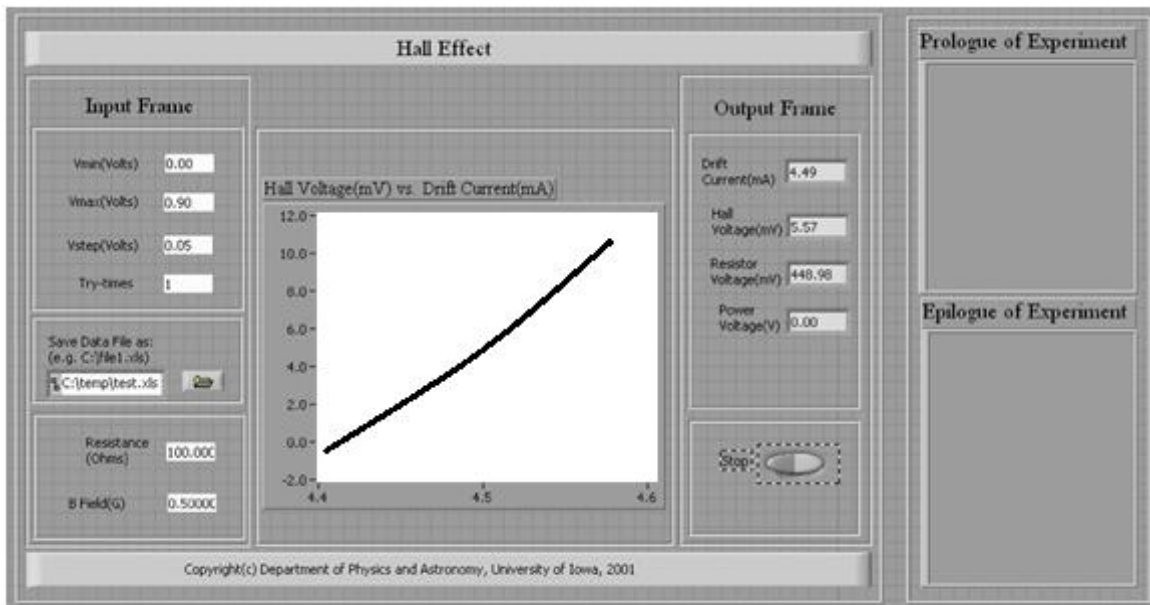


Figure 6 – Hall measurement

The Hall Effect probe is a thin slab of InAs, cemented to a piece of fiberglass and has a four lead cable is attached so that the necessary electrical circuit can be used to detect the Hall voltage. The white and green wires are used to measure the Hall voltage and the red and black wires carry the drift current [14].

The values for the dimensions used in our work were as follows $w = 0.152$ cm, width, $L = 0.381$ cm, length, $d = 69$ nm, thickness. $Cd_{0.3}Zn_xS_{0.7}$ has a relatively big band gap so the carrier density was estimated to be roughly the intrinsic carrier density by electrons hence a n-type semi-

conductor. These carriers are produced by the thermal excitation of the electrons from the valence band into the conduction band [15]. This was estimated that $Cd_{0.3}Zn_xS_{0.7}$ has the density of valence electrons was $7 \times 10^{28} \text{ m}^{-3}$) multiplied by the Boltzmann factor:

$$\exp\left[-\frac{E_g}{kT}\right], \quad (20)$$

where E_g is 2.41 eV and kT is room temperature which is about 1/40 eV [13, 16, 18].

Conclusion

In this work, $Cd_{0.3}Zn_xS_{0.7}$ thin films were grown by chemical bath method with thickness that ranged

from 69 to 330 nm on ordinary microscope perspex substrates at room temperature. Varying thin film thickness was obtained by changing the deposition time and their resistivity was found to be thickness dependent. Gauss meter measurement showed that the thin films were n-type and semiconducting in nature appropriate for light emitting diodes.

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