# Design and Development of an Electrodeposition System and Application to Deposition of a Thin-Film Semiconductor Material (CdZnSeS) for Solar Cell Application

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**Abstract:** *Electrochemical deposition is a cheap means to produce solar cell materials compared to the clean-room deposition facilities needed for silicon solar cells. We showed that an electrodeposition system can be built cheaply in Africa using materials that are readily available and that such a system can be used to produce thin films of materials that have scientific and technological merits. In this work, two-electrode electrodeposition system is designed, fabricated and used for electrodeposition of CdZnSeS thin film on indium tin oxide (ITO) substrate. Two distinguished thickness were achieved by choosing two different deposition times, 6mins and 3mins respectively. The optical transmittance and absorbance of the thin films are determined by Ultraviolet-Visible spectrophotometer, achieving 71% to 88% transmittance depending on the wavelength of the incident radiation. The results indicate that the sample with longer time of deposition yields higher transmittance than the one with lower deposition time, but the difference in band gaps between the two samples is not significant.*

**Keywords:** *Absorbance, band gap, electrodeposition, thin film, transmittance, UV-spectrophotometer.*

## 1. INTRODUCTION

Electrodeposition is a unique technique of producing in situ metallic coatings by the action of electric current on a conductive material in a solution of a salt of the metal to be deposited [1]. Electrodeposition is also often called "electroplating," a short version of electrolytic deposition [2] and the two terms are usually used interchangeably. It's a process using electric current to reduce cations of a desired material from a solution and to coat the material as a thin film onto a conductive substrate surface [3]. Presently, much emphasis is laid on the fabrication of thin films and nanoparticles due to their potential applications in the emerging technologies such as optoelectronics, solar cells, electrochromic windows, chemical sensors and so on [12-15].

Electrodeposition is one of the most practicable ways of growing nanostructure and thin film deposition. However, many electrodeposited samples are obtained by three-electrode electrochemical cell, having saturated calomel electrode as reference electrode, which has been widely employed for the growth since 1996 [4, 11]. Electrochemical deposition of metals typically begins with oxidation or reduction of species in a solution. The standard electrode potential for an electrochemical reaction is the potential in which the rate of the oxidation and the reduction reactions are equal at standard conditions of concentrations, pressure and temperature [5]. The Nernst equation relates the standard electrode potential $E_s$ to the electrode potential E:

$$E = E_S + \frac{RT}{nF}\ln\frac{\{ox\}}{\{red\}} \quad 1$$

where R is the standard gas constant (8.314510 $J\cdot K^{-1}\cdot mol^{-1}$), T the absolute temperature in Kelvin, n the number of electrons transferred and F the Faraday's constant (96485.309 C $mol^{-1}$) [6].

Electrodeposition is a cheap means to produce solar cell materials compared to the clean-room deposition facilities needed for silicon solar cells. Research has deepened the understanding of the deposition processes, and electrochemical deposition today provides many exciting routes for the synthesis of metals, alloys, thin films and nanostructured materials [7]. The merits of electrodeposition method include low cost, required no clean room and large area semiconductor growth technique which is used for applications in macroelectronic devices as in solar cells and large area display devices. Electrodeposition is capable of producing high quality materials for electronic device applications when materials are grown with right conditions [8].

In this work, we successfully designed a much simpler two-electrode electrodeposition cell and apply to deposit CdZnSeS thin film.

Table 1: Deposition parameters obtained for CdZnSeS thin film by electrochemical deposition

| **Substrate** | **Voltage (V)** | **Deposition Time (min)** | **Film Thickness (nm)** | **pH (±0.1)** | **Transmittance (%)** |
|---|---|---|---|---|---|
| ITO | 6.5 | 6.0 | 587.34 | 7.62 | 88 |
| ITO | 6.5 | 3.0 | 295.93 | 7.53 | 71 |

## 2. METHODOLOGY

### 2.1 Design and Fabrication Mechanism

In this design, a normal 500ml beaker with 82mm inner diameter was used as the solution glass container. Two copper rods of 6mm thickness and 140mm long were also used as electrode holders. The separation between the two electrodes is 40mm fixed but the height and relative orientation can be adjusted by the cork embedded in the stopper. The electrode sheets are fastened to the electrode holders by crocodile clips made of stainless steel. Small holes are drilled on the upper sides of the copper rods for easy connections of power supply and multimeter. The rubber gasket cover is designed in such a way that is closely tight to the beaker so that the air would be able to escape in or out of the cell. This is because the electrodeposition process would be affected.

Figure 1: Two-electrode electrochemical cell

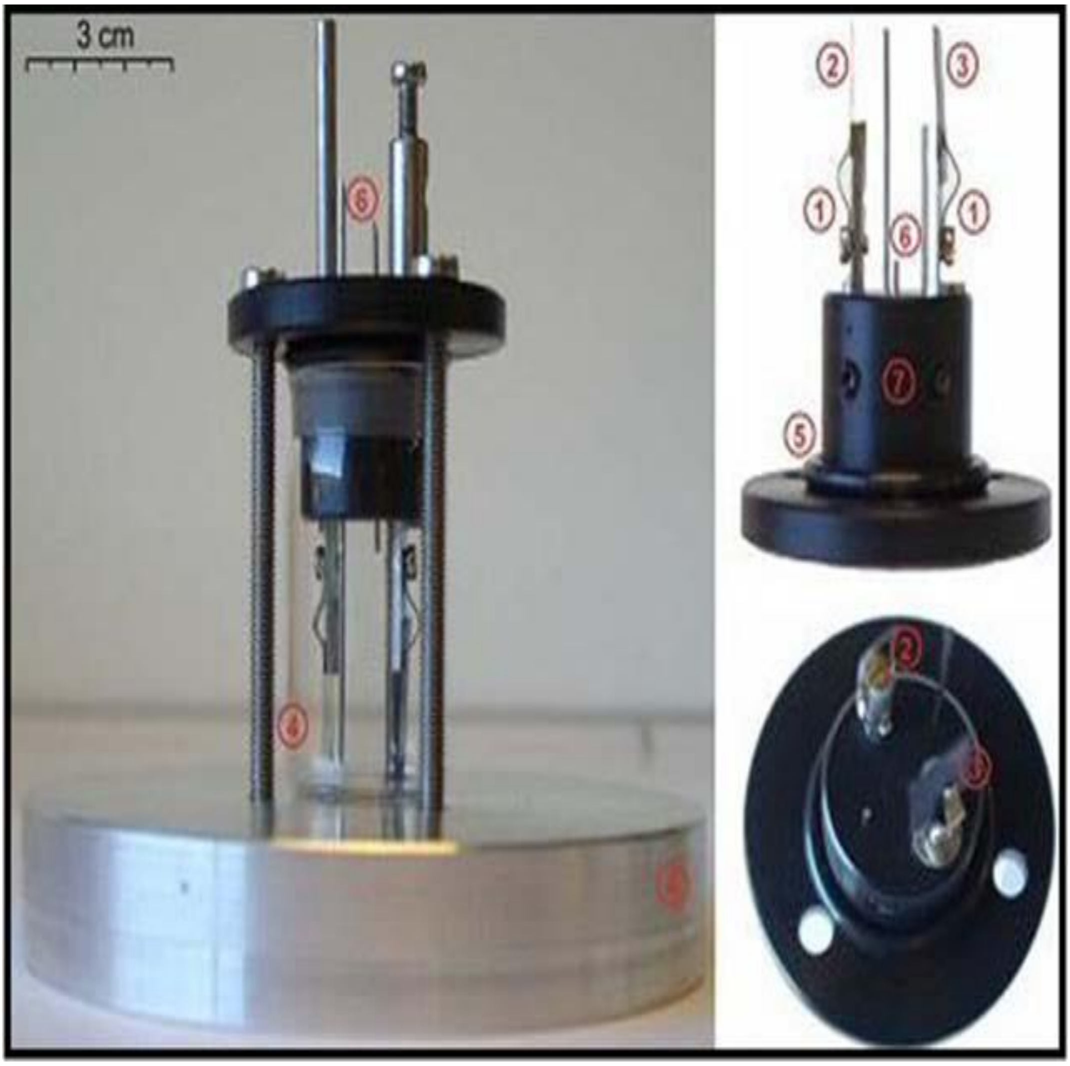

Figure 2: Parts of two-electrode electrochemical cell. (1) Electrode holders with stainless steel crocodile clips, variable in height, (2) working electrode: substrate for sample growth (ITO) (3) Counter electrode: graphite. (4) Glass container. (5) Rubber cork. (6) Connecting wire (7) Inlet tubes and holes for gases and liquids [4]

Little quantity (100 – 200 ml) of solution is sufficient for running the deposition process depending on the substrate surface area to be coated. The substrate used acts as the working electrode while a piece of graphite as the counter electrode. The two electrodes are held firmly to the holders (separation of 32.28 mm) with the coating surface of the working electrode facing directly the counter electrode. Two stainless steel tubes of different lengths with extra holes in the stopper provide flexible possibilities for filling in solution. For the construction, the followings are the necessary requirements fulfilled: two electrode setup for easy reproducibility of results, possibility of using different electrode materials, flexible adjustment of height and relative orientation of the electrodes, Minimize amount of solution needed for running the cell and in-situ nitrogen bubbling of the solution for degassing where and when necessary.

The following materials were required for the construction of electrochemical cell used in the research work.

Table 2: List of materials used and the cost

| S/N | Material | Quantity |
|---|---|---|
| 1 | Glass Beaker (500ml) | 1 |
| 2 | Copper Rod | 2 |
| 3 | Crocodile Clip | 2 |
| 4 | Rubber cork | 1 |
| 5 | Connecting Wire | 2 |
| 6 | Graphite sheet (cathode) | 1 |
| 7 | Conducting glass e.g. ITO (cathode) | 1 |

### 2.2 Thin Film Fabrication

There are many diverse ways of producing thin film materials. In this work, samples were prepared on the substrates (ITO) using electrochemical deposition method. Prior to deposition, the substrates preparation and treatments were carried out to obtain contaminant free samples. The thin film of this compound, $CdZnSe_xS_{1-x}$ was prepared at the same ratio of concentration of 0.1 and 0.9 molar for Selenium and Sulphur, respectively, while the concentrations of Cadmium and Zinc ions were kept constant. The mass of the salt required for the concentration was obtained as follows:

Mass (g) = Conc. (mol/dm$^3$) x Mol. Weight (g/mol) x Volume (dm$^3$)
50ml of 0.05M Cadmium Nitrate + 50ml of 0.005M Zinc Acetate + 50ml of 0.1M Sodium Selenite + 50ml of 0.9M Thiourea

The calculated mass of the salt was weighed using a Laboratory analytical weighing balance and then dissolved in a certain amount of distilled water to form the salt solution. However, other processes like varying the pH and concentration were carried out on the solution but only two samples of the solution used as electrolyte for electrochemical deposition process.

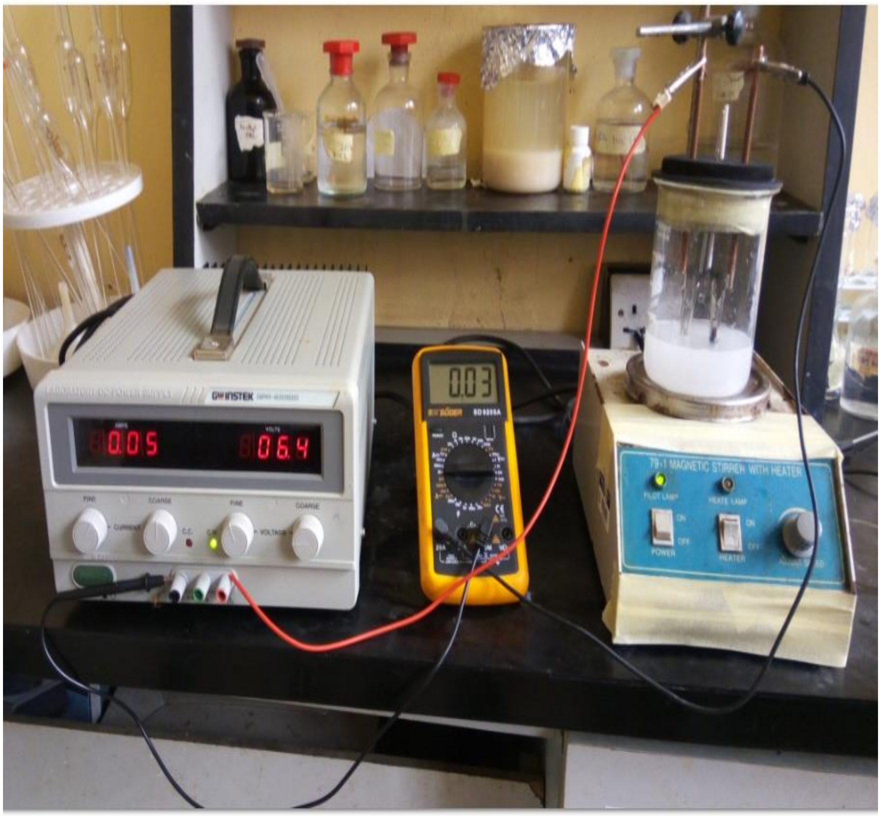

Figure 3: Electrical connections and Experimental Setup for electrodeposition

### 2.3 Electrical connections of the electrochemical deposition system (EDS)

In fig 2.2, electrochemical deposition system is a low power device powered by dc power supply regulated at 6.4 V. EDS consists of two terminal electrodes; the working (-) electrode and the counter (+) electrode. The positive (+) terminal of the power supply is connected to the counter electrode while the negative (-) terminal of the power supply is connected to the multimeter, and from there to the working electrode of the EDS. The multimeter in this connection is used to monitor the current during the electrochemical deposition. The EDS is filled with chemical solution which is the thin film material, closed and the two electrodes are immersed in the solution. The electrochemical deposition process starts immediately the power supply is switched on, and the current is reducing as shown on the multimeter. The electrochemical deposition is complete as soon as the current becomes zero.

## 3. RESULTS AND DISCUSSION

### 3.1 Optical Properties

Several studies have been carried out in the last few decades concerning the electrodeposition technique as a result of its merit over others [9]. In this work, it is found that the electrodeposition system worked perfectly and effectively when used to deposit $CdZnSe_xS_{1-x}$ thin film on a conducting substrate (ITO). The characterization of the deposited film is carried out by Uv-vis spectrophotometer. Spectroscopy is a technique based on the absorption of light by an unknown substance.

Light absorption from the spectroscopy is used to analyze and characterize the quantitative determination of the samples. The samples are illuminated with electromagnetic rays of different wavelengths in the visible and ultraviolet (UV) of the spectrum. Depending on the sample, light is partially absorbed and the remaining transmitted light is recorded as a function of wavelength by the detector, giving the samples' uv-vis spectrum. The results of the optical transmittance and absorbance of the films indicate that sample with longer time of deposition yields higher transmittance than the sample with lower deposition time which may be due to difference in thickness of the film deposited. Figure 4 shows the graphs of optical transmittance against the wavelength while Figure 5 shows the absorbance against the wavelength for samples deposition for 6 mins and 3 mins respectively. The transmittance $T$ is the ratio of the intensity $I$ to the original intensity $I_o$, while the absorbance $A$ is the negative logarithm of the transmittance as given in the Equations 2 and 3.

$$T = {}^{I}/_{I_o} \qquad (2)$$

$$A = -\log T \qquad (3)$$

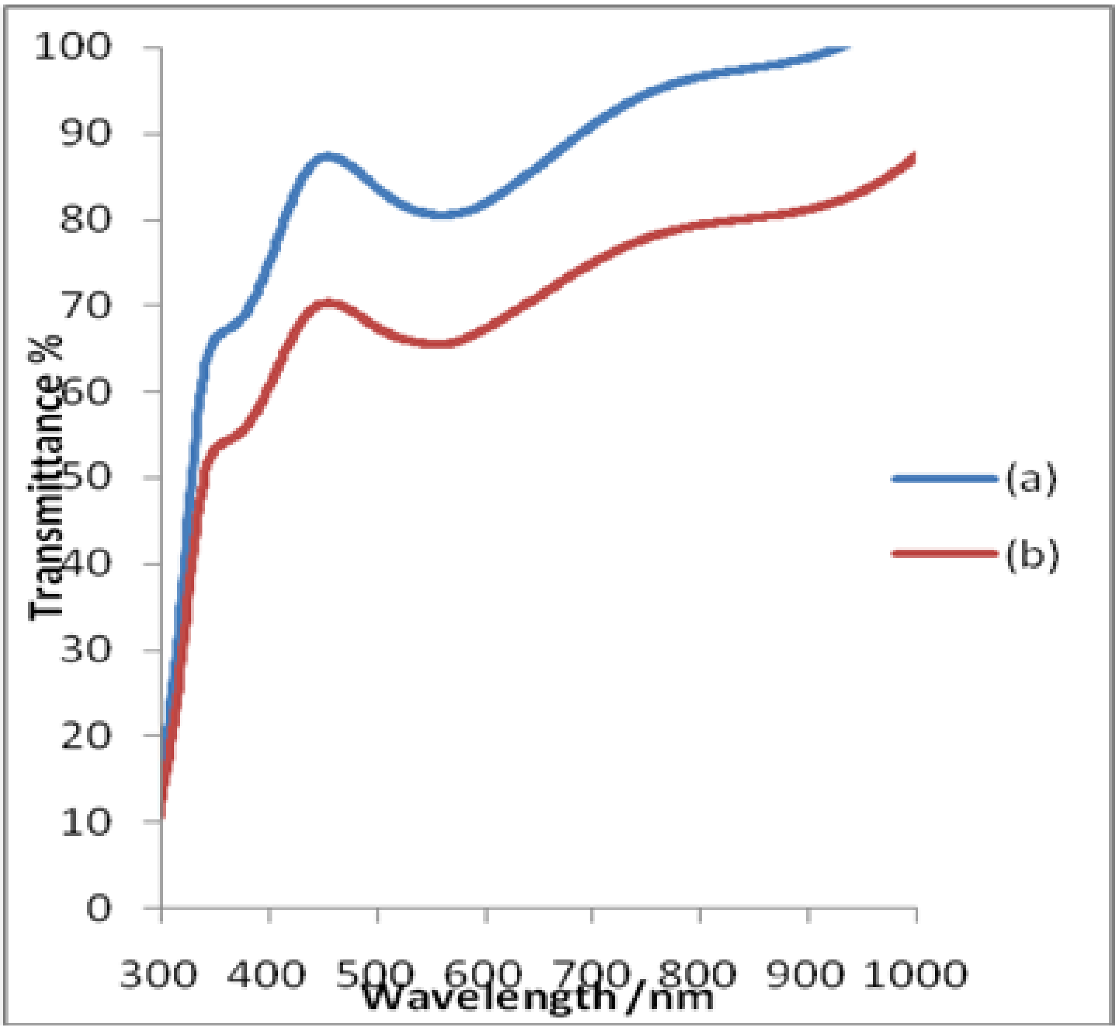

Figure 4: Optical transmittance of samples deposited for 6 mins and 3 mins

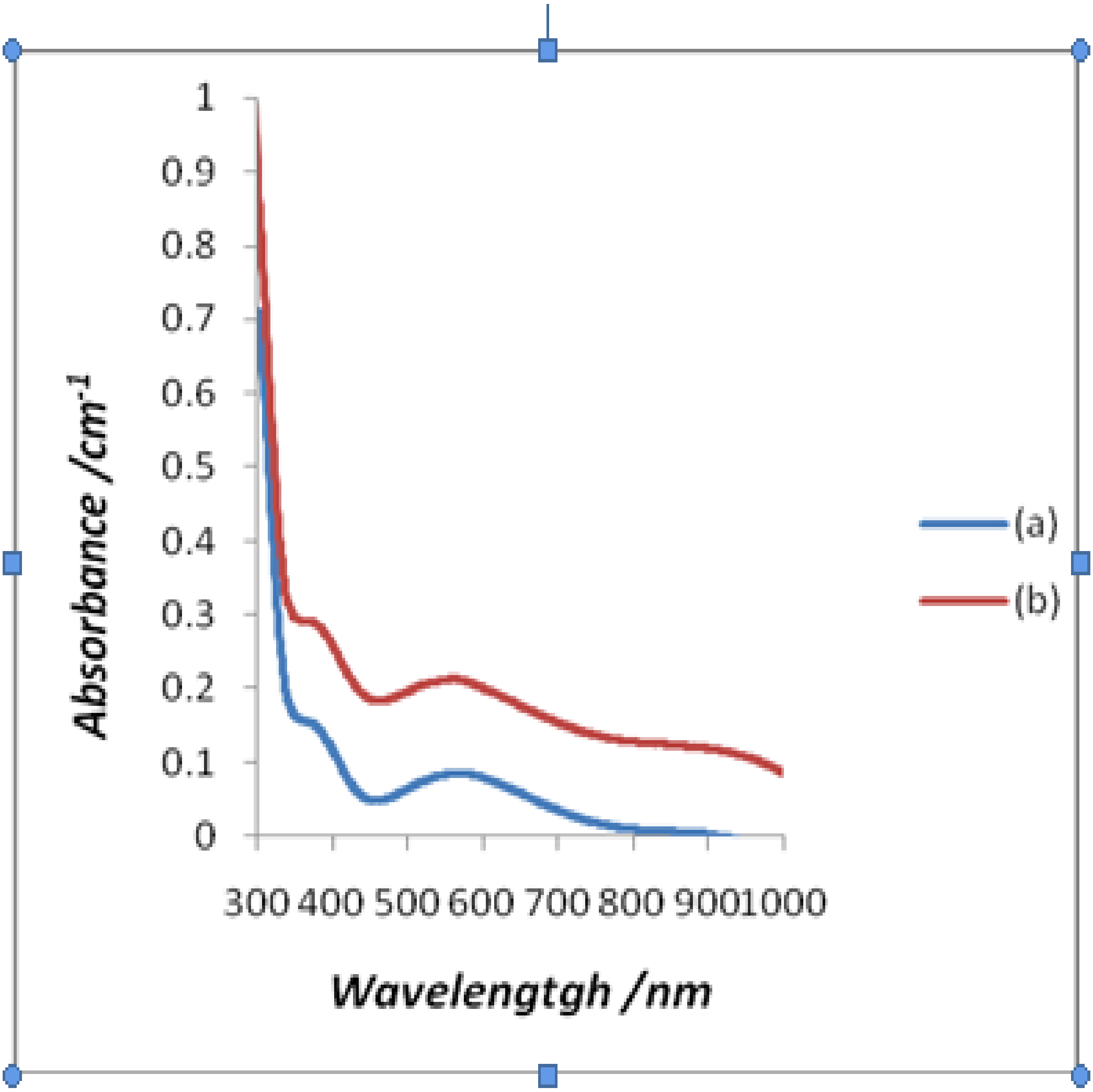

Figure 5: Optical Absorbance of samples deposited for 6 mins and 3 mins

### 3.2 Energy Band Gap

The band gap is obtained by plotting $(\alpha h\upsilon)^2$ against energy E = hv (eV) from the Uv-visible data using conventional Tauc equation ($\alpha h\upsilon\ =\ A\ (\ h\ \upsilon - Eg\ )\ ^n$) [10]. Where n = 2 for a direct and n = $\frac{1}{2}$ for an indirect band gap, A is an empirical optical constant, α is the absorbance coefficient ($\alpha = -lnT$), where T is the transmittance, hυ is the photo energy while Eg is the energy band gap. For a direct semiconductor material like this, energy band gap is calculated by extrapolating the linear fit of $(\alpha h\upsilon)^2$ curve to zero-crossing value of the abscissa (energy axis). Therefore, the values of energy band gap of the thin films are determined from the graphs shown in Figure 6 and 7. It was found that the energy band gap is about 3.72eV for both graphs above and this showed that the thickness has very small effect on the band gap. This is because the thinner film at $\approx 300nm$ is thick enough to be considered as a bulk material.

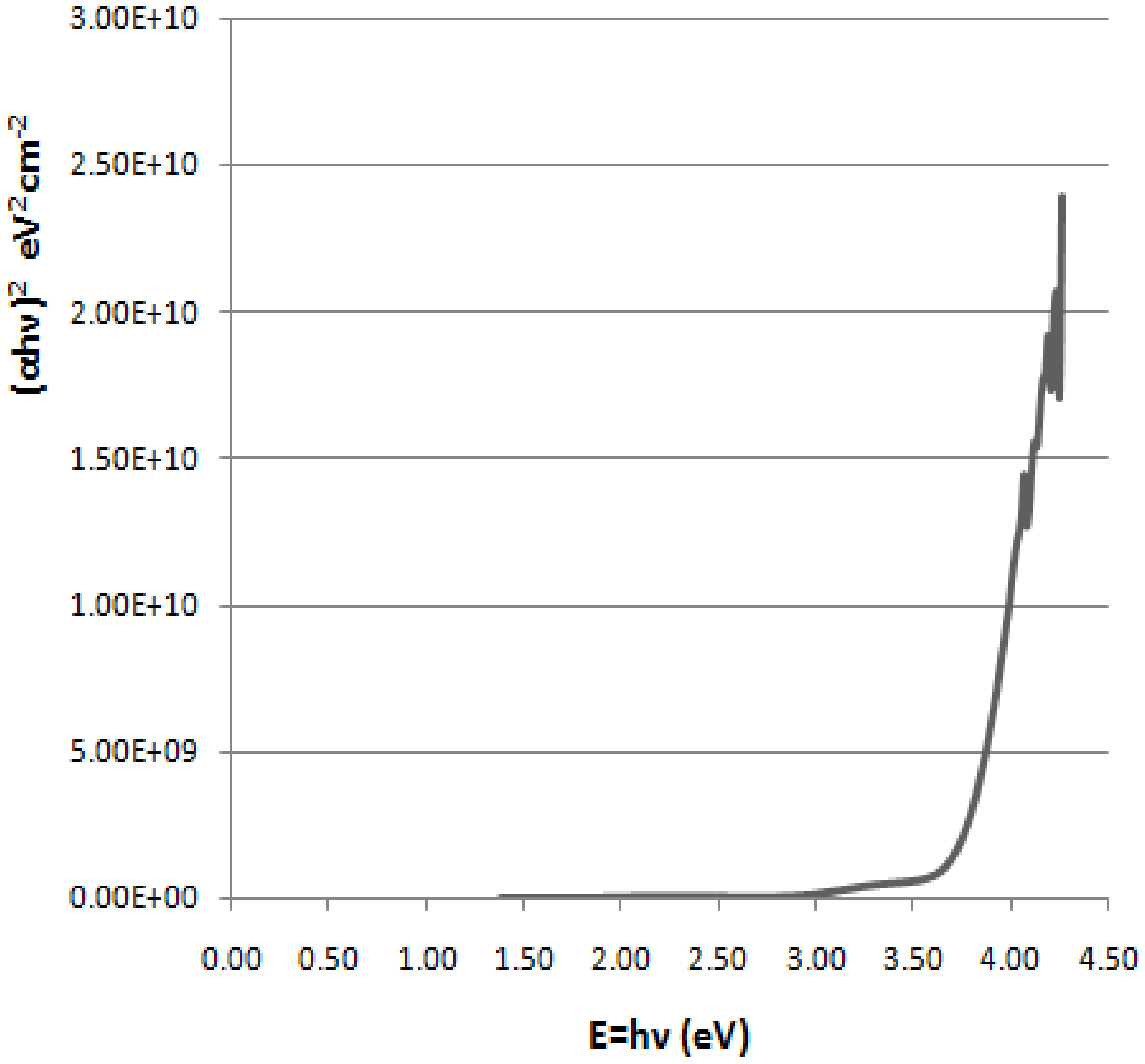

Figure 6: Energy gap of a sample deposited for 6mins

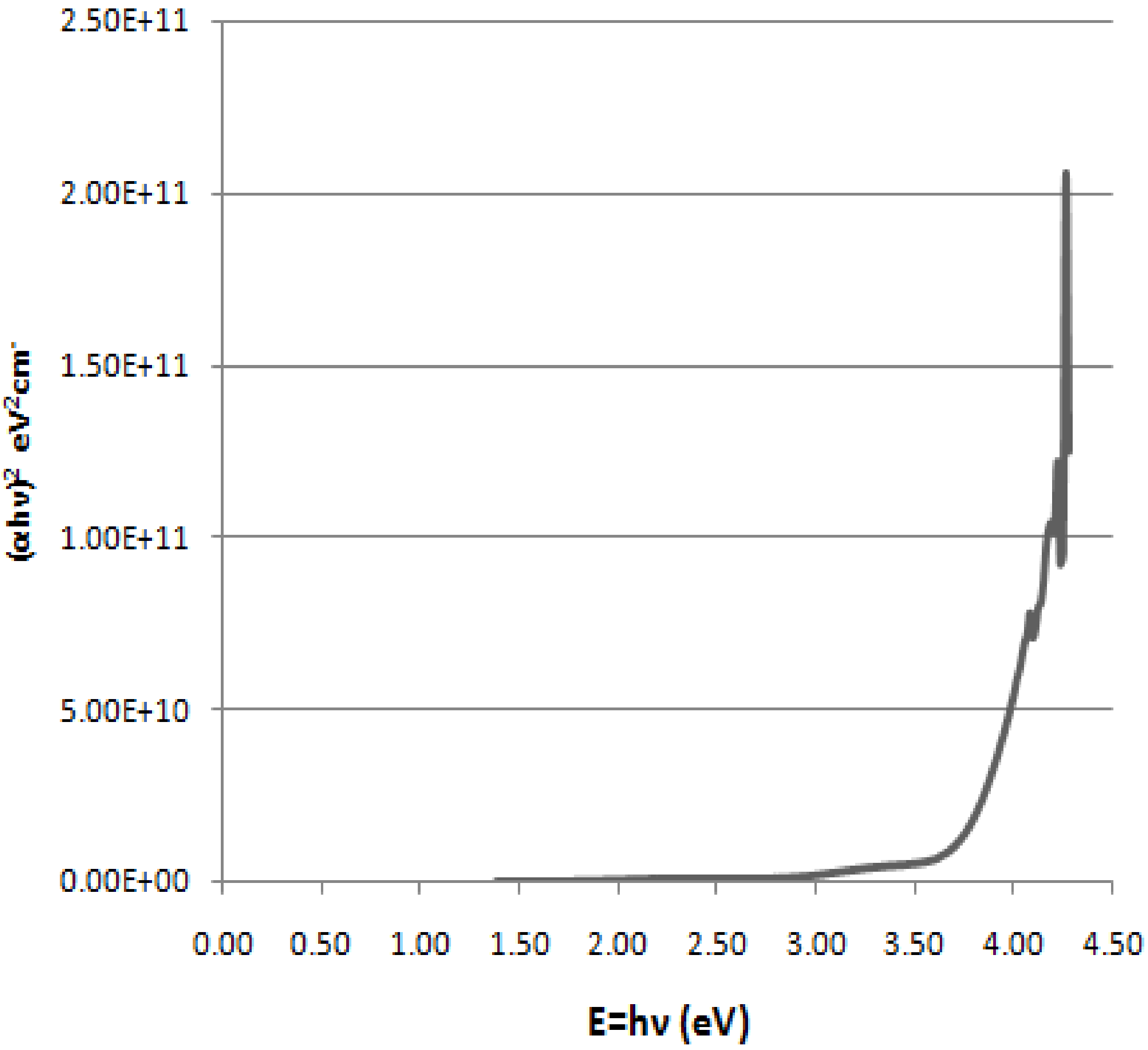

Figure 7: Energy gap of a sample deposited for 3mins

## 4. CONCLUSION

A simple locally fabricated two-electrode electrochemical deposition system was designed and applied to deposit CdZnSeS thin film at room temperature. The result indicates the ease and flexibility of this cell to grow thin films and nanostructures based of semiconducting compounds on conductive substrates from electrolytic solution.

The experimental method is projected to be simple and easily manipulated by varying the thickness based on deposition time as well as carrying out the appropriate post deposition annealing for desired results. The samples are deposited on ITO for 6-mins and 3-mins, the transmittance was determined and shown that the samples started transmitting above a wavelength of about 300nm (absorption edge) and gradually progressed across the visible region. The ease and flexibility of two-electrode electrochemical cell to grow diverse thin films and nanostructures of semiconducting compounds at room temperature have to be demonstrated on the morphological studies. The high voltage applied at cathode compensated for the non-inclusion of reference electrode (third electrode) in the cell arrangement.

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