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SYNTHESIS OF STRUCTURED ZINC SELENIDE FOR OPTOELECTRONIC APPLICATIONS

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Abstract
In this paper, synthesis of Zinc Selenide (ZnSe) based photovoltaic materials deposited by electrode position method. The material films have been characterized for their optical properties using UV-VIS spectrophotometer with wavelength range of 300 nm – 900 nm and electrical conductivity using photoelectrochemical (PEC) cell measurement. The conductivity type of the electrodeposited materials was investigated together with the tuning of the optical phenomena. The materials deposited were obtained by varying deposition time from 5 minutes to 15 minutes for ZnSe. It was observed that the optical properties of the materials increased with an increase in the time of deposition. The optical band gap of ZnSe was found to be in the range between 2.03 and 2.46 eV. The PEC signal results revealed ZnSe as an n-type material.
Keywords: Electrodeposition, Thin Film, Characterization, Deposition time variation, Optical properties.

Introduction

Solar energy which is a free and abundant form of energy has the potential to provide sufficient power to the growing number of industries and population especially in the developing world (Akimoto *et.al*, 2006). Its maximum exploitation has however been hindered by the high cost of silicon based solar cells which currently dominate the market (Asaduzzaman *et.al,* 2017). The available fossil fuels that currently power society will not meet up with demand over the long term, and the continued use of these conventional energy resources causes harmful side effects such as pollution that threatens human health and greenhouse gases (GHG) associated with climate change (Xia *et.al,* 2015). It has been stated that the warming and precipitation trends due to anthropogenic climate change during the past 30 years already claim over 150,000 human lives annually (Slonopas *et.al,* 2017). The sun is Earth's natural power source, driving the circulation of global wind and ocean currents, the cycle of water evaporation and condensation that creates rivers and lakes, and the biological cycles of photosynthesis and life (Balitskii *et.al,* 2013). Presently, solar and other alternative energy resources are being harnessed for various applications such as power generation, air-conditioning, space heating, domestic hot water system (Ikhioya *et.al*, 2020). In order to meet up with the world energy demand using the eco-friendly method (Mittal *et.al,* 2017), this work takes a look at how we can effectively harness the Zinc Selenide (ZnSe) for optoelectronic devices. Zinc Selenide (ZnSe) is an inorganic compound that belongs to the transition metal dichalcogenides (TMDCs) class of materials, and it has one atom of zinc and an atom of selenium. The choice for this compound (ZnSe) lies on the fact that its physical, chemical, and electronic properties makes it a promising material to substitute previously used semiconductor and graphene devices (Beck *et.al,* 2005 and Manoharan *et.al,* 2016). The constituent materials are nontoxic and abundantly available (Salim *et.al,* 2015) and (Khan *et.al,* 2016), and that the ZnSe has a high absorption coefficient in the wavelength range 350-800 *nm* and low-cost of production (Olusola.*et.al,* 2020). This makes it a good absorber layer in solar cell devices. ZnSe seems to solve many problems facing many semiconductor materials used for solar cell devices (Echendu *et.al,* 2016). It has a wide energy band gap of 1.8 eV which changes from an indirect band gap to a direct one in thin structures (Ceviz *et.al,* 2013). Thus, it is ideal for thin-film transistors with excellent on/off switching characteristics and high efficiency (Pandey, 2015), electrical and optoelectronic applications. Its fabrication is simple which means large production yield and low cost (Khan *et.al,* 2016). The covalent bonds between molybdenum and Sulfur and the Van der Waals bonds between its layers make it optimal for gas sensing and a lubricant in aerospace industry. It has a direct energy band gap, better charge transport, good absorption coefficient and highly transmittance material (Al-Hadeethi *et.al,* 2019).

Olubosede *et al,* (2020) in the study, Aluminum Selenide (Al_2Se_3) thin films were synthesized electrochemically using cathodic deposition technique in which graphite was used as a cathode while carbon as an anode. Synthesis was done at 353 K temperature from an aqueous solution of analytical grade selenium dioxide (SeO_2), and Aluminum chloride ($AlCl_2.7H_2O$). The films are characterized for their optical properties and electrical conductivity. The optical properties of the films at varied voltages showed that the films are good materials in the formation of optoelectronic devices.

Faremi *et.al,* (2021) worked on optoelectronics applications of electrodeposited p- and n-type Al_2Se_3 thin films. In the report, energy band gaps and electrical conductivity based on aluminum selenide (Al_2Se_3) thin films were synthesized electrochemically using cathodic deposition technique, with graphite and carbon as cathode and anode, respectively. Synthesis was done at 353 K from an aqueous solution of analytical grade selenium dioxide (SeO_2), and aluminum chloride ($AlCl_2.7H_2O$). Junctions-based Al_2Se_3 thin films from a controlled medium of pH 2.0 were deposited on fluorine-doped tin oxide (FTO) substrate using potential voltages varying from 1,000 mV to 1,400 mV and 3 minutes -15 minutes respectively. The films were characterized for optical properties and electrical conductivity using UV-vis and photoelectrochemical cells (PEC) spectroscopy. The PEC reveals a transition in the conduction of the films from p-type to n-type as the potential voltage varies. The energy band gap reduces from 3.2 eV to 2.9 eV with an increase in voltage and 3.3 eV to 2.7 eV with increase in time. These variations indicate successful fabrication of junction based Al_2Se_3 thin films with noticeable transition in the conductivity type and energy band gap of the materials. Consequently, the fabricated Al_2Se_3 can find useful applications in optoelectronic devices.

It has been reported that Zinc Selenide (ZnSe) based thin film solar cell technology is known to be 40% cheaper than silicon based solar cells (Wang *et.al,* 2014). In order to effectively exploit solar energy, research into new materials for production of cheaper and efficient solar cell must be intensified (Olusola *et.al,* 2020). This paper, studies the properties Zinc Selenide (ZnSe) for possible applications in optoelectronic devices, determine the conductivity type of the material and improve and optimize optical properties of materials by the variation of time of deposition.

Materials and Methods

These materials and experimental methods used on ZnSe were analyzed in this section. The materials used in this research work are potentiostat, magnetic stirrer, electrodes, substrate, pH meter and weigh balance. The reagents used consist of ammonium molybdate (NH_4MoO_4), Sodium thiosulfate ($Na_2S_2O_3$). All these reagents were of analytical grade, purchased and used without further purification. The FTO substrate of 2.3 cm^2 by 2.5 cm^2 was cleaned with liquid soap, methanol, and acetone in order to get rid of any oily residue and other contaminants from its surface. The substrate was then rinsed with acetone and methanol after washing. A graphite plate was attached to one of the electrodes, this electrode was taken as the working electrode, as the adhesive surface of the substrate was attached to the graphite plate after these three (carbon rod, graphite plate, and substrate) have been joined together with the PTFE, a multimeter is used to test the conductivity of the working electrode by putting negative pin of the multimeter at bottom of the carbon rod and the positive pin of the multimeter on any part of the adhesive surface of the substrate in figure 1, a reading from the multimeter shows that current can pass through from the substrate to the bottom of the carbon rod.

A buffer solution was prepared using a buffer of 4. The buffer of 4 was mixed and stirred with 200ml of deionized water for 30 minutes for the pH meter calibration and pH for the ZnSe electrolytic bath was 2.5±0.1 The molarity of the chemical reagent was first calculated to ascertain the amount of the chemical reagent needed to achieve the desired molarity in the solution. For this research, the desired measurement for the deionized water which was the solvent used was 400ml.

$$\text{Molarity of solute} = \frac{\text{Mass of solute X 1000m}}{\text{Molar mass of solute x volume of solvent}} \quad (1)$$

Synthesis of ZnSe

The synthesis of zinc selenide (ZnSe) was prepared by the electrodeposition method. Zinc (Zn) from Zinc sulfate tetrahydrate and selenium (Se) from selenium dioxide. Totals of 20 grams of Zinc sulfate tetrahydrate and 20 grams of selenium dioxide were dissolved in 400ml of de-ionized water contained by 500 ml beaker to form 0.214 mole of zinc sulfate tetrahydrate and 0.451 mole of selenium dioxide. The mixture was then stirred on a magnetic stirrer for one hour; a magnetic bar was added to the magnetic stirrer in order to increase the stirring rate of the solution. The electrolyte was formed at pH of 2.5. The electrochemical deposition technique was adopted in depositing the films of ZnSe. Deposition also took place at bath temperature of 70°C but in the variation of time at 20, 15, 10 and 5 minutes of deposition durations.

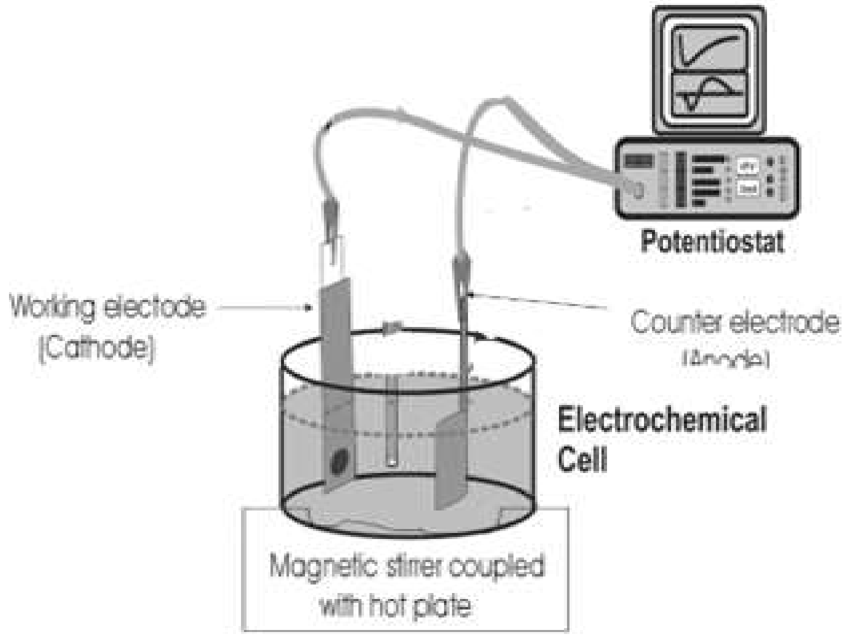
$$SeO_2 + H_2O \longrightarrow H_2SeO_3 \quad (2)$$

$$H_2SeO_3 + 6H^+ + 6e^- \longrightarrow H_2Se + 3H_2O \quad (3)$$

$$Zn^{2+} + H_2Se \longrightarrow ZnSe + 2H^+ \quad (4)$$

Table 1: The molarity, mass and molar mass of solutes in the electrolytic bath of ZnSe

Solute	Molarity (mol)	Mass (g)	Molar mass (g/mol)
Zinc Sulfate tetrahydrate	0.214	20	233.19
Selenium Dioxide	0.451	20	110.97



Fig, 1.0 Schematic diagram of two-electrode System used for electrodeposition of ZnSe

$$\text{Absorbance (A)} = \frac{t}{\text{in } 10} \quad (5)$$

$$\text{Transmittance } T = 10^{-A} \quad (6)$$

$$\text{Reflectance } R = 1 - (A + R) \quad (7)$$

$$\text{Photon energy (eV) } E = hv = \frac{hc}{\lambda} \quad (8)$$

$$A + T + R = 1 \quad (9)$$

$$\alpha = \frac{2.303A}{t} \quad (10)$$

$$k = \frac{\alpha\lambda}{4\pi} = \frac{\alpha\lambda}{12.57} \quad (11)$$

$$(ahv) = A\,(hv - E_g)^n \quad (12)$$

$$\text{PEC Signal} = V_L - V_D \quad (13)$$

where τ is the optical depth, h is plank constant, v is frequency, c is the speed of light and λ is wavelength, A is absorbance, T is transmittance, R is reflectance, α is absorption coefficient, t is thickness of the film, A is absorbance, k is extinction coefficient, λ is wavelength of photon.

Result and Discussion

Optical characterization of electrodeposited ZnSe thin films

The absorbance of the deposited thin film decreases with increasing wavelength, the materials have a good absorbance in the visible spectral region which indicate the material possess good absorption edge and may be suitable in optoelectronic applications. The transmittance of the deposited thin film increases with decreasing wavelength, the material have a good transmittance in the visible spectral region which indicates that the material possesses good transmittance edge which makes it suitable in optical electronic applications. The energy band gap of the films decreases with increase in deposition time; this increase is due to increase in the films thickness. Therefore, the energy band gaps of the films are inversely proportional to the thickness as a result of the varied preparative parameters arising from the quantum conferment effect. Absorption coefficient is a characteristic that describes how far light a travel in materials before it is being absorbed. The higher the absorption coefficient of a material, the more photon energy absorbed. Zinc Selenium (ZnSe) is a very good absorber layer material capable of absorbing more photon energy which is suitable for heterostructured based devices. . The relationship between the extinction and absorption coefficients of ZnSe as established by the mathematical equation used revealed the suitability of ZnSe material in fabrication of solar cells.

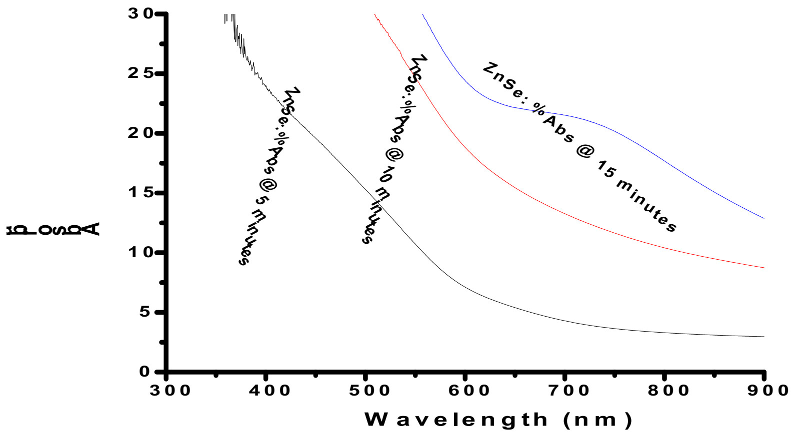


Figure 2: Percentage of absorbance of electrodeposited ZnSe films at varied time of deposition as function of wavelength.

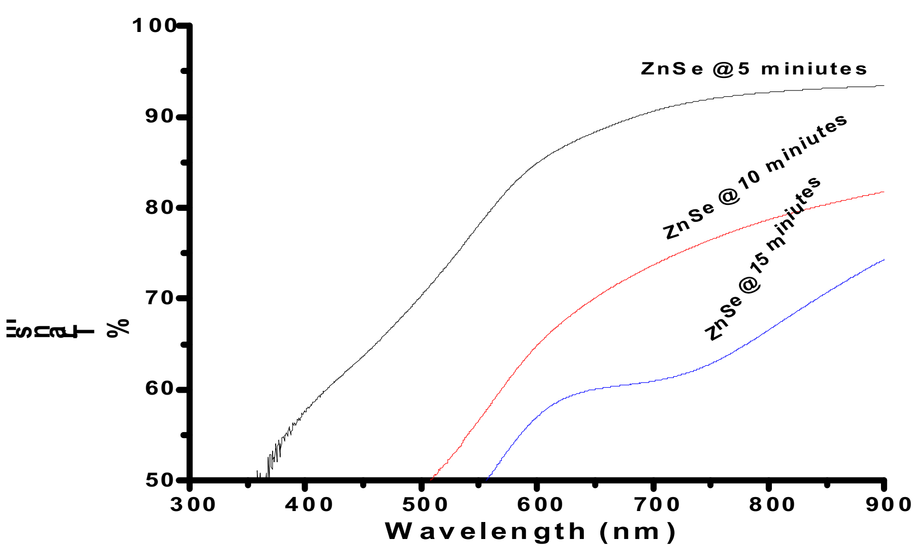


Figure 3: A percentage of Transmittance of ZnSe thin film as a function of wavelength

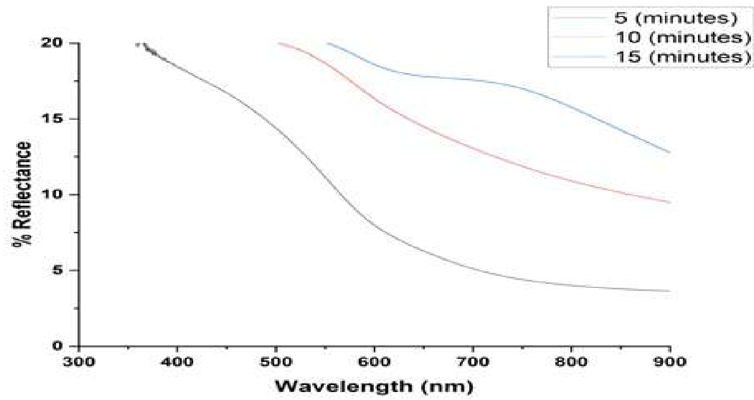


Figure 4. Reflectance versus the wavelength of the ZnSe

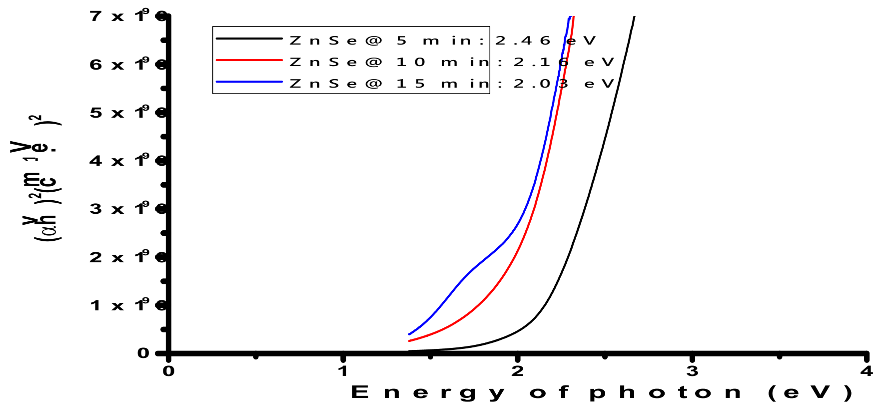


Figure 5: Energy band gap of ZnSe

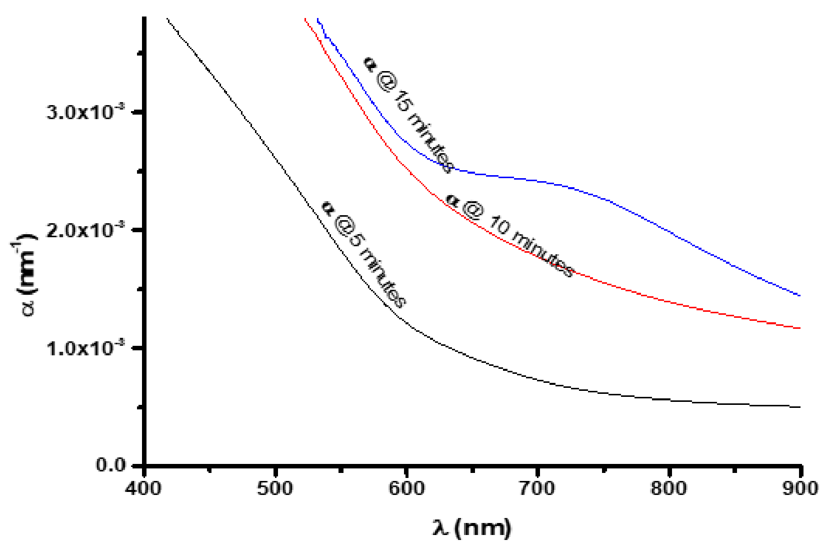


Figure 6: Graph of absorption coefficient versus wavelength for ZnSe

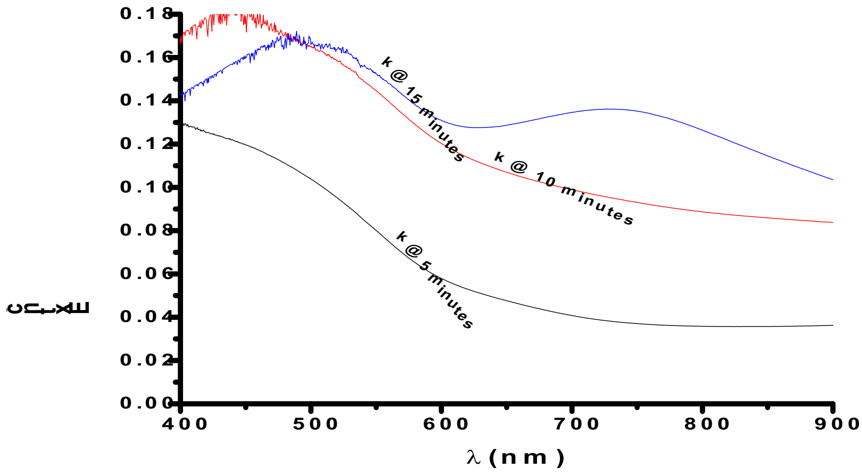


Figure 7: Graph of Extinction coefficient versus wavelength for ZnSe

Table 2. Optical measurements of ZnSeat deposition time

Time of Deposition	Absorbance	Transmittance	Reflectance	Total = A+T+R
5 minutes	0.1654	0.7168	0.1178	1
10 minutes	0.2537	0.5809	0.1654	1
15 minutes	0.2962	0.5188	0.1850	1

Table 3. Energy band gap for ZnSe

Time of deposition (minute)	Thickness (nm) MoS_2	Energy band gap (eV) MoS_2
5	135	2.46
10	172	2.16
15	205	2.03

Photoelectrochemical (PEC) cell Analysis of ZnSe thin films

The PEC signals analysis was done to characterize the semiconductor type of the materials which gave access to the type of semiconductor the materials exhibited. The PEC was formed by forming a liquid junction between the substrate and reference electrode. When light is onto the liquid junction, the voltage reads and when light was on off, the voltage was also taken. When the light was switched on for 5, 10, 15 and 20 minutes, the voltage was taken. In the same process as the light was switched off 5, 10, 15 and 20 minutes, the voltage was also taken. The voltages taken for 5, 10, 15 and 20 minutes when the light was switched off were subtracted from the voltages taken at the same time intervals when the light was switched on as depicted in table 3. The qualitative PEC signal of ZnSe as depicted in figure 8, revealed the material is positive which is an indication of n-type layer materials.

Table 4: PEC results for electrodeposited ZnSe

Substrate	Deposition time (minute)	V_L	V_D	V_L - V_D (V)	PEC signal (mV)
B1	20	-0.422	-0.414	-0.008	-8
B2	15	-0.417	-0.413	-0.004	-4
B3	10	-0.415	-0.412	-0.003	-3
B4	5	-0.413	-0.411	-0.002	-2

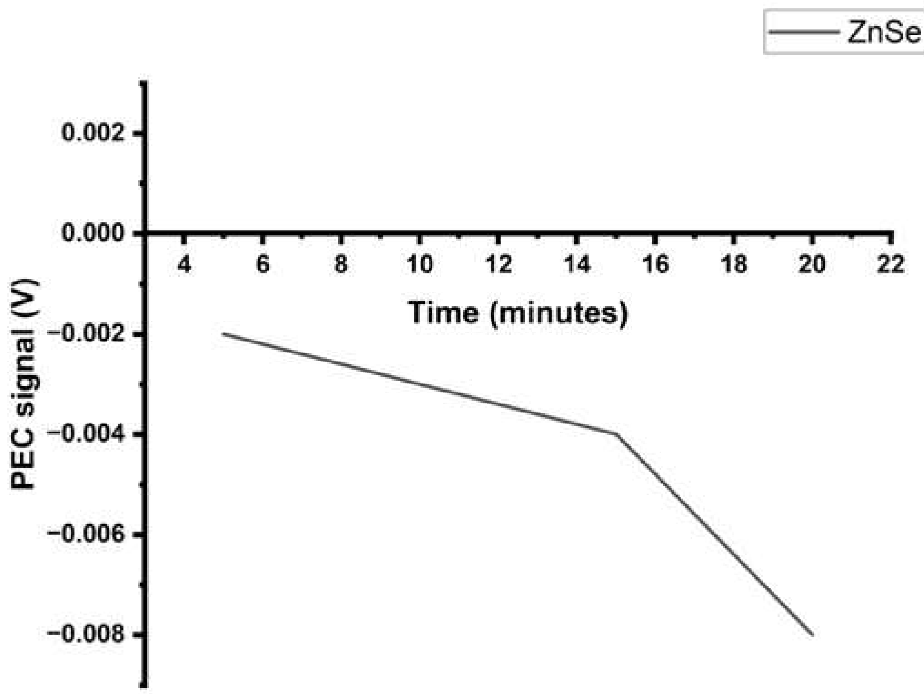


Figure 8: Graph of PEC signal as a function of time for ZnSe.

Conclusion

The various characterizations carried out in the analysis of both the optical and conductivity type of the materials reveal the successful fabrication of ZnSe thin film through the application of electrodeposition technique. The optical phenomena such as reflectance showed clearly that ZnSe thin film has less reflectance properties of light which is good for the absorption of light energy from the sun suitable for solar cells applications. Also, the low reflectance values make the thin films of ZnSe an important material for anti-reflection coating. The energy band gap of ZnSe and the thin film at deposition time of 5, 10 and 15 minutes are 2.46 eV, 2.16 eV and 2.03 eV which provided information about the proportionality of the Synthesised material energy band gap to both the time of deposition and the thickness of the films. The electrical conductivity type of the Synthesised material through the PEC analysis showed that the material is n-type semiconductor suitable for junction-based devices. Electricity is needed for both p-type and n-type solar cells because they operate on the principle of the photovoltaic effect, which involves absorbing photon energy and directly converting it into usable energy. Our research has revealed that the type of conductivity of the material depends not only on the cathodic potential but also on the deposition time. Considering that the material's characteristics are similar to those of cadmium telluride, the investigation has yielded valuable insights regarding the electrodeposition technique and the tunability of zinc selenium properties. The greatest substitute for CdTe would be electrodeposited materials because CdTe thin films, despite its intriguing optoelectronic potentials, are known to be poisonous.

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