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TIME DEPENDENCE OF ENERGY BAND GAP OF ELECTRODEPOSITED ALUMINUM SELENIDE Al_2Se_3

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Abstract

In this paper, Aluminum selenide (Al_2Se_3) thin films are synthesized electrochemically using cathodic deposition technique in which graphite was used as a cathode while carbon as an anode. Synthesis is done at 70^0 C temperature from an aqueous solution of analytical grade selenium dioxide (SeO_2), and Aluminum chloride ($AlCl_2.7H_2O$). Aluminum selenide thin films from a controlled medium (pH =2.5) are deposited on fluorine doped tin oxide (FTO) substrate using different time of deposition 3mins, 6mins, 9mins, 12mins and 15mins. Further investigation was done to study the effect of deposition time. The films are characterized for their; electrical conductivity, structural, morphological, and optical properties of the deposited films have been studied using photoelectrochemical (PEC) cell measurement, X-ray diffraction, scanning electron microscopy (SEM) and UV-visibile spectroscopy. These various characterizations reveal the successful fabrication of Al_2Se_3 thin films.

1.0 Introduction

Aluminum selenide (Al_2Se_3) is a promising material in the fabrication of optoelectronic devices due to its direct energy band gap, better charge transport, good absorption coefficient and highly transmittance material. Despite its potential in device applications, it has received relatively low research attention when compared to other members of the III-VI family of semiconductors [1-4]. Aluminum (Al) as an elemental semiconductor has been extensively studied because of its ease of growth, promising optical, electrical properties and abundance in the earth's crust, after oxygen and silicon [5-6]. Since compound semiconductor has more functionalities than elemental semiconductor, compound semiconductors such as cadmium telluride (CdTe), zinc oxide (ZnO), zinc sulfide (ZnS), lead sulfide (PbS) etc., are therefore received scientific attention. We chose to form aluminum selenide because of the potential of selenium in compound semiconductors such as zinc selenide (ZnSe) [7], copper selenide (CuSe) [7], lead selenide (PbSe) [8] etc. The band gap of Al_2Se_3 has been reported as 3.1 eV at wavelength of 401 nm which make it possible to be potentially used in photoemitter [9-10]. Various deposition techniques have been employed in the synthesis of compound semiconductor materials [11-16]. Since the primary aim of synthesizing material for device applications is to minimize cost, Electrodeposition technique (ED) has rendered significant help to achieve the goal. ED is cost effective, scalable, capable of re-engineering material energy band gap and has electrolytic bath longevity with self-purification. Moreover, the synthesis of nanomaterials can be controlled over the properties by changing the ionic concentration (electrolyte), pH value, temperature, deposition time and cathodic voltage [17-25]. In this study, Al_2Se_3 was electrodeposited on a conducting substrate/FTO of 2.3 by 4 cm^2 in dimension. Different samples of Al_2Se_3 were synthesized by varying the cathodic potential [26]. The films were characterized for their optical properties using UVs spectrophotometer and electrical conductivity using photoelectrochemical cell measurement.

2.0 Methodology

Procedure: 400 ml of deionized water will be put in a beaker having a lid. The cathode electrode ((graphite) will be tied to an electrodeposited substrate S_1), and the anode electrode (carbon) will be arranged into the beaker containing the deionized water in parallel to each other and then connected to the PEC. At a constant time of 20s, the readings of voltage will be taken under dark and under light. The PEC will be repeated to the other four electrodeposited substrates and their readings of voltage under dark and light will be recorded. In order to ascertain the conductivity type of the electrodeposited compounds, photoelectrochemical cell measurements was used. Figure 2.0 show the schematic diagram for photoelectrochemical cell measurement techniques.

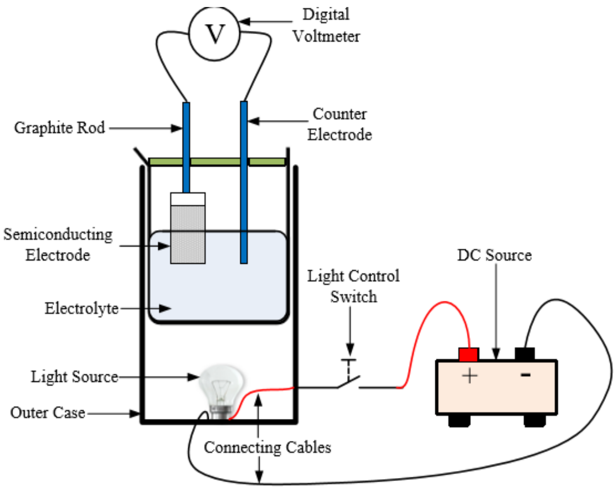

Figure 2.0: Typical schematic diagram of the experimental set-up for PEC cell measurement (Olusola., 2016)

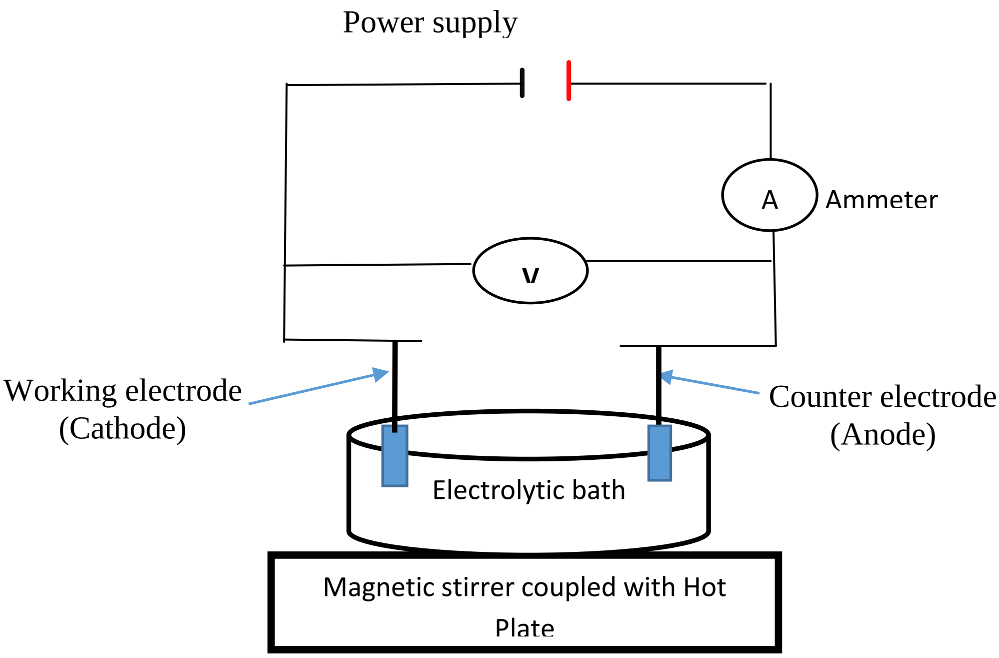

Figure 2.1: Schematic diagram of two-electrode system used for electrodeposition of Al_2Se_3.

The films optical properties such as energy band gap, percentage of transmittance, absorbance, extinction and absorption coefficients were obtained using ultraviolet visible spectroscopy with wavelength ranged from 200 -900 nm. Equation 2.0 to 2.2 was adopted in the determination of film thickness, optical properties and electrical conductivity.

$$T = \frac{JtM}{\rho nF} \qquad (2.0)$$

The film thickness is denoted as T, J is the current density of the electrodeposited Al_2Se_3, t is the deposition time, ρ is the density of Al_2Se_3, n is the total number of electrons transferred per ion of the deposited material and F is Michael faraday's constant with numerical value of 96,485 $Cmol^{-1}$ and M is the molar weight of the deposited Al_2Se_3. The absorption coefficient can be calculated with;

$$(\alpha h v)^2 = A(hv - E_g) \quad (2.1)$$

Where α is absorption coefficient, hv is photon energy, A is a constant usually equal to one, E_g is the energy band gap. The photoelectrical chemical signal may be analyzed using the relation;

$$PEC\ Signal = V_L + V_D \quad (2.2)$$

Where V_L is voltage under illumination and V_D is voltage under dark

2.1 Morphology characterization

SEM as a characterization technique in the investigation of a material microstructural properties was used to investigate the size, shape and level of agglomeration of the deposited film.

The shape and the sizes of the deposited compound semiconductors were analyzed using scanning electron microscopy (SEM) that situated at The University of Ibadan, Oyo State, Nigeria. SEM Jeol Tescan model coupled with EDS with images taken at an accelerating voltage of 15kV was used to determine the shape and the size of the deposited Al_2Se_3.

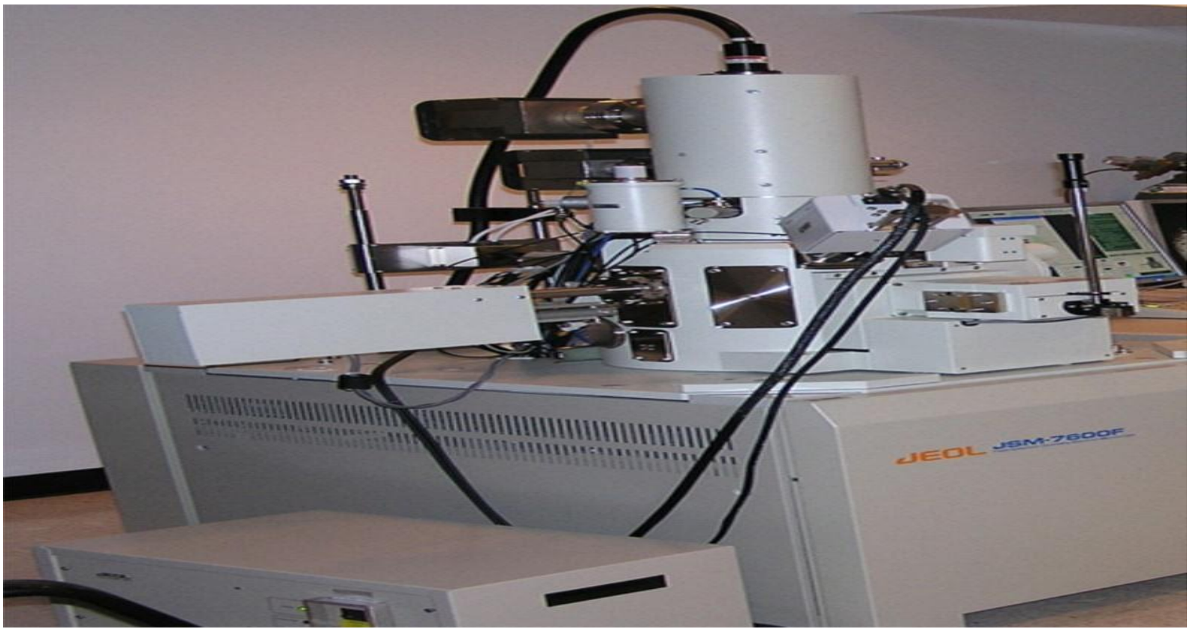

Figure 2.2: Photograph of a Scanning Electron Microscope (SEM)

3.0 Results and Discussion

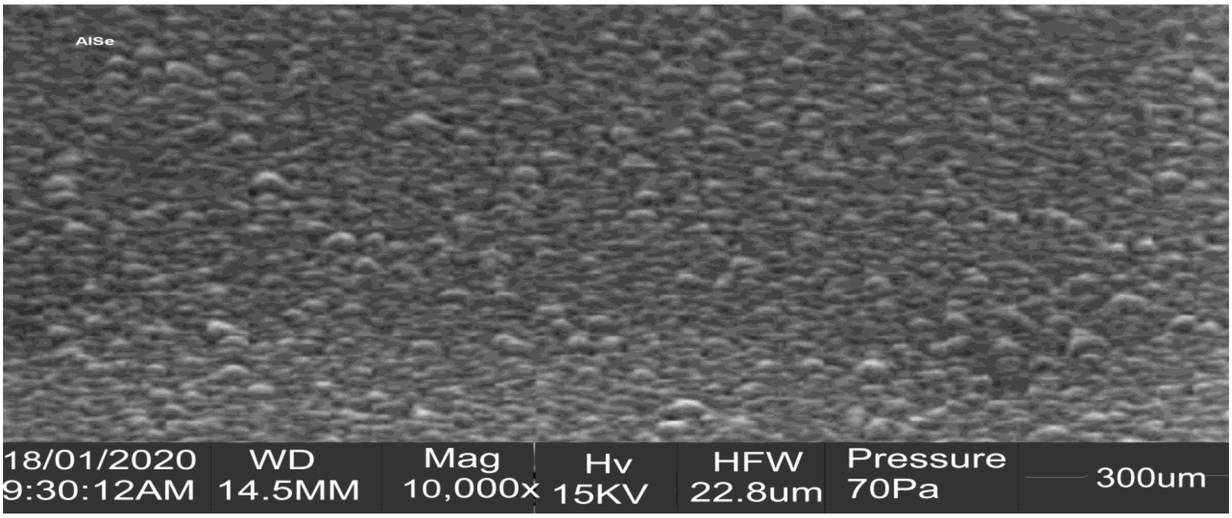

Figure 3.0: Scanning Electron Microscopy (SEM) of 1200 mV cathodically deposited Al_2Se_3

The following tables show the results gotten from the electrolysis and the corresponding electro-deposited values of the five substrates.

Table 3.0: Potentiostat results of conducting substrate

Conducting substrate 1. Time: 3min V: 1200mV Temp: 70˚C pH:2.3		Conducting substrate 2. Time: 6min V: 1200mV Temp: 70˚C pH:2.5		Conducting substrate 3. Time: 9min V: 1200mV Temp: 70˚C pH:2.5		Conducting substrate 4. Time: 12min V: 1200mV Temp: 70˚C pH:2.5		Conducting substrate 5. Time: 15min V: 1200mV Temp: 70˚C pH:2.5	
Time	Current (µA) × 10	Time	Current (µA) × 10	Time	Current (µA) × 10	Time	Current (µA) × 10	Time	Current (µA) × 10
0	675	0	650	0	418	0	593.33	0	550, 490, 480
10	635	20	527	30	269	30	458	30	455
20	592	40	476	60	242	60	396	60	360
30	569	60	445	90	223	90	367	90	321

40	537	80	411	120	214	120	352	120	285
50	510	100	389	150	212	150	339	150	256
60	495	120	370	180	202	180	334	180	238
70	472	140	353	210	192	210	332	210	229
80	454	160	341	240	183	240	328	240	217
90	444	180	333	270	174	270	324	270	209
100	430	200	323	300	173	300	320	300	197
120	418	220	317	330	175	330	318	330	180
130	407	240	314	360	172	360	316	360	175
140	399	260	309	390	164	390	312	390	166
140	390	280	305	420	156	420	310	420	156
160	377	300	300	450	158	450	310	450	148
170	371	320	297	480	158	480	309	480	137
180	364	340	296	510	156	510	307	510	140
-	-	360	295	-	-	540	305	540	145
-	-	-	-	-	-	570	303	570	144
-	-	-	-	-	-	600	302	600	138
-	-	-	-	-	-	630	302	630	149
-	-	-	-	-	-	660	300	660	151
-	-	-	-	-	-	690	301	690	150
-	-	-	-	-	-	720	300	720	147
-	-	-	-	-	-	-	-	750	146
-	-	-	-	-	-	-	-	780	140
-	-	-	-	-	-	-	-	810	132
-	-	-	-	-	-	-	-	840	130
-	-	-	-	-	-	-	-	870	133
-	-	-	-	-	-	-	-	900	134

Table 3.1: PEC result for electro-deposited substrate 1 Time taken: 20s

V_D	V_L
-0.483	-0.487
-0.490	-0.493
-0.490	-0.498

$$\text{Vd: } -0.483 + (-0.490) + (-0.490) = -1.463$$

$$\text{Vl: } -0.487 + (-0.493) + (-0.498) = -1.478$$

V_{PEC} (V_L - V_D): -1.478 - (-1.463) = -0.015 (which is a N type material)

Table 3.2: PEC result for electro-deposited substrate 2 Time taken: 20s

V_D	V_L
-0.386	-0.386
-0.383	-0.384
-0.380	-0.379

$$\text{Vd: } -0.386 + (-0.383) + (-0.380) = -1.145$$

$$\text{Vl: } -0{,}386 + (-0.384) + (0.379) = -1.149$$

V_{PEC} (V_L – V_D): -1.149 – (-1.145) = -0.004 (which is a N type material)

Table 3.3: Result for electro-deposited substrate 3 Time taken: 20s

V_D	V_L
-0.599	-0.601
-0.591	-0.595
-0.582	-0.587

$$\text{Vl: } -0.601 + (-0.595) + (-0.587) = -1.783$$

$$\text{Vd: } -0.599 + (-0.591) + (-0.582) = -1.772$$

V_{PEC} (V_L - V_D) = -1.783 - (-1.782) = -0.001 (which is a N type material)

Table 3.4: Result for electro-deposited substrate 4 Time taken: 20s

V_D	V_L
-0.570	-0.572
-0.558	-0.556
-0.551	-0.553

$$Vd: -0.570 + (-0.558) + (-0.551) = -1{,}679$$
$$Vl: -0.572 + (-0.556) + (-0.553) = -1.68$$

V_{PEC} (V_L – V_D): -1.681 – (-1.679) = -0.002 (which is a N-type material)

Table 3.5: Result for electro-deposited substrate 5 Time taken: 20s

V_D	V_L
-0.546	-0.554
-0.560	-0.562
-0.566	-0.567

$$Vd: -0.546 + (-0.560) + (-0.566) = -1.672$$
$$Vl: -0.554 + (-0.562) + (-0.567) = -1.683$$

V_{PEC} (V_L- V_D): -1.683 – (-1.672) = -0.011 (which is a N-type material)

Table 3.6: Electrical conductivity of electrodeposited Al_2Se_3 at a fixed cathodic voltage of 1200 mV while varying the time of deposition.

Sample at various time	Under illumination (V_L)	Under dark (V_D)	Pec signal $=V_L-V_D$	Conductivity type
3 minutes	-1.478	-1.463	-0.015	n-type
6 minutes	-1.149	-1.145	-0.004	n-type
9 minutes	-1.783	-1.772	-0.009	n-type
12 minutes	-1.681	-1.679	-0.003	n-type
15 minutes	-1.683	-1.672	-0.011	n-type

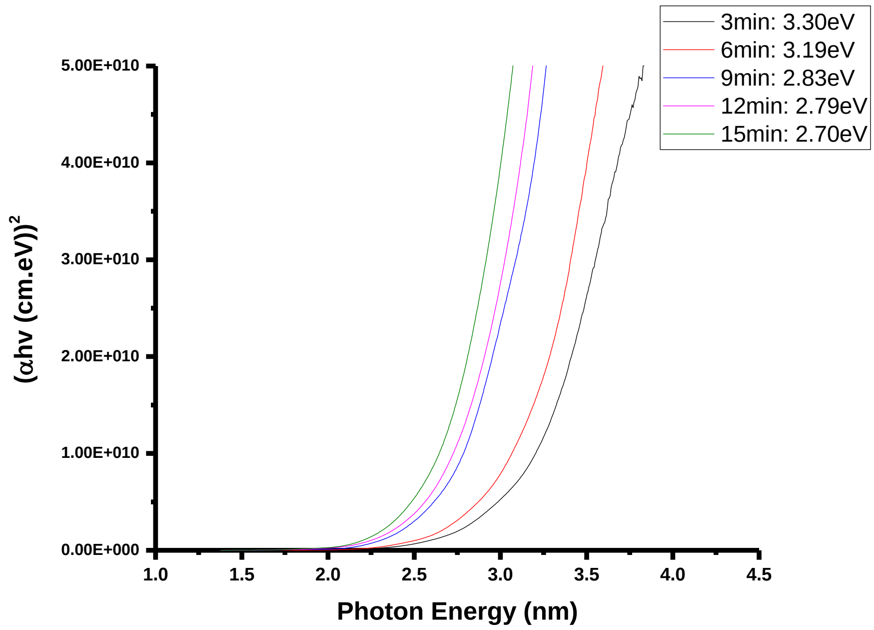

Figure 3.1: Energy band gap of electrodeposited Al_2Se_3 at various time of deposition

The energy band gap of the films decreases as the cathodic voltage increases (Figure 3.1). The increase in time of deposition resulted to increase in the films thickness. Such a behavior can be attributed to quantum conferment. The quantitative band gap of the films as given as an insert of figure 4 was obtained by extrapolating the linear part of the plots using tauc equation. The obtained agrees with previously reported work on the time of deposition during material growth.

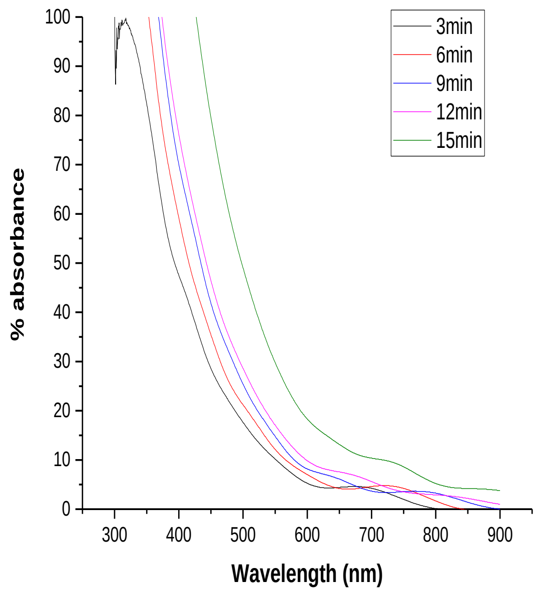

Figure 3.2: absorbance spectrum as a function of wavelength of the electrodeposited Al_2Se_3 at various time of deposition.

There is decrease in the absorbance with increase in wavelength which showed blue shift. The plot shows absorption spectrum at the visible region with relatively low values in the infrared region of the spectrum. The absorption characteristic revealed the potential applications of the material in the fabrication of solar cell.

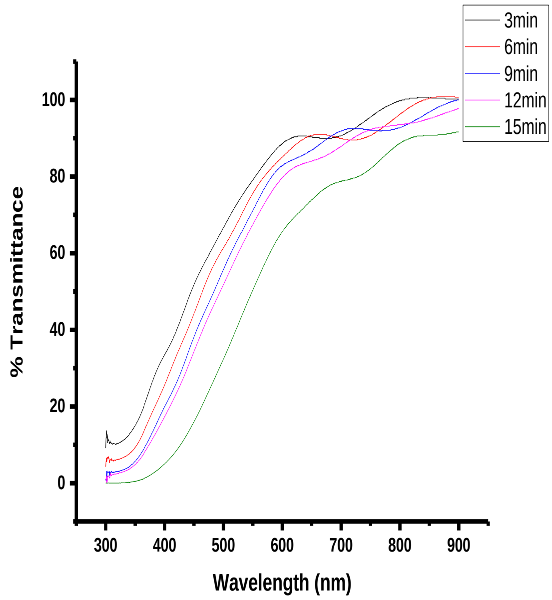

Figure 3.3: Transmittance spectrum as a function of wavelength of the electrodeposited Al_2Se_3 at various time of deposition.

The percentage of transmittance as a function of wavelength showed high transmittance throughout the UV/ VIS/NIR regions as the time of deposition decreases. The high transmittance in the visible region reveal the usefulness of the material as a good window layer capable of providing receptive surface to any absorber layer. A material with high transmittance can reduce reflection of solar radiation but transmit radiant energy.

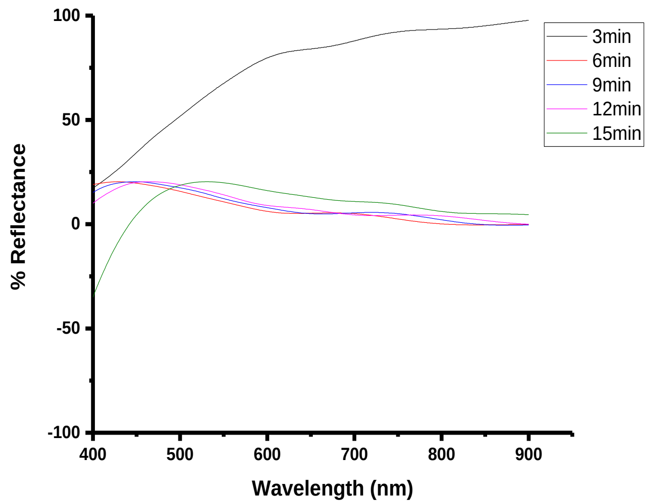

Figure 3.4: Reflectance spectrum as a function of wavelength of the electrodeposited Al_2Se_3 at various time of deposition

As the spectrum of the wavelength increases the percentage of reflectance increase from negative to positive within the UV/VIS/NIR region but very low at the positive side of the plot. Since the positive side gives the account of the transmission spectrum, it can be inferred that the films show a very low reflectance throughout the UV/VIS/NIR region. This low reflectance value reveals the potential of the films as good anti-reflection coating suitable for optoelectronic applications.

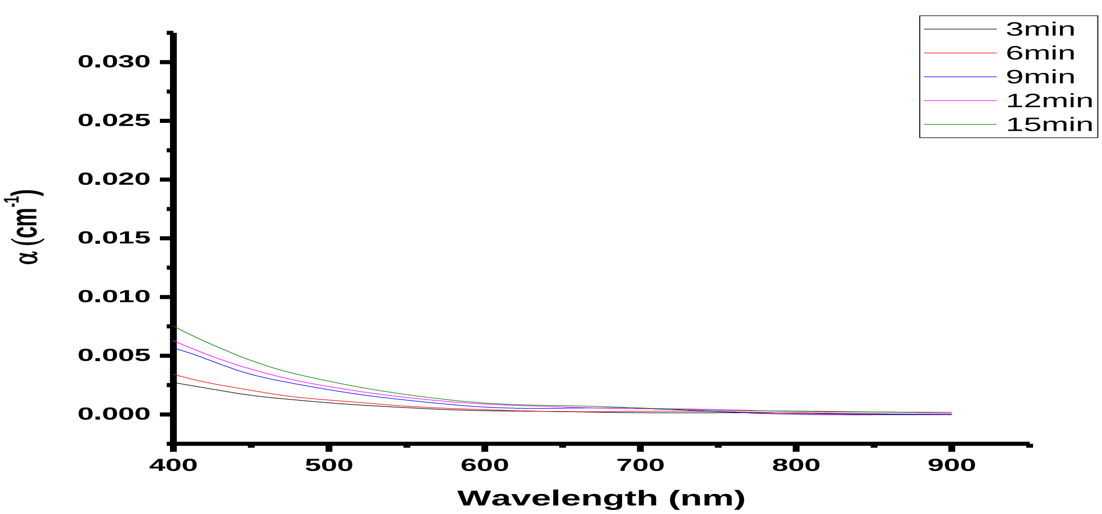

Figure 3.5: Absorbance co-efficient as a function of wavelength of the electrodeposited Al_2Se_3 at various time of deposition.

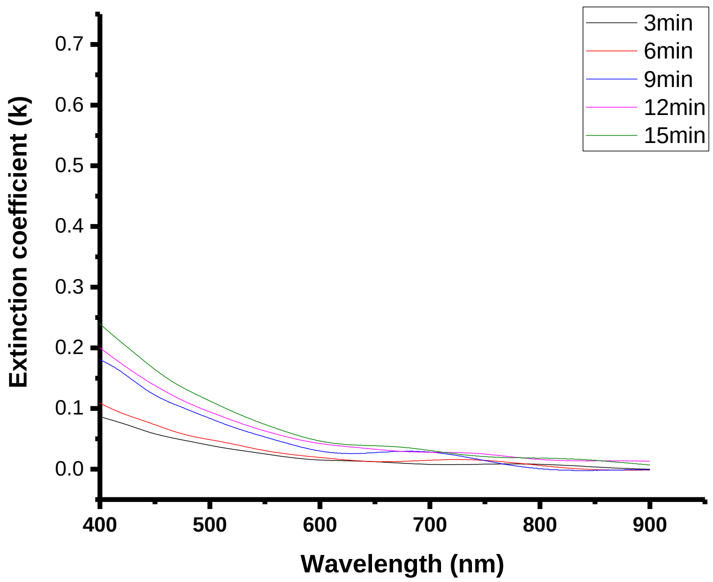

Figure 3.6: Extinction co-efficient as a function of the electroplated Al_2Se_3 at various time of deposition.

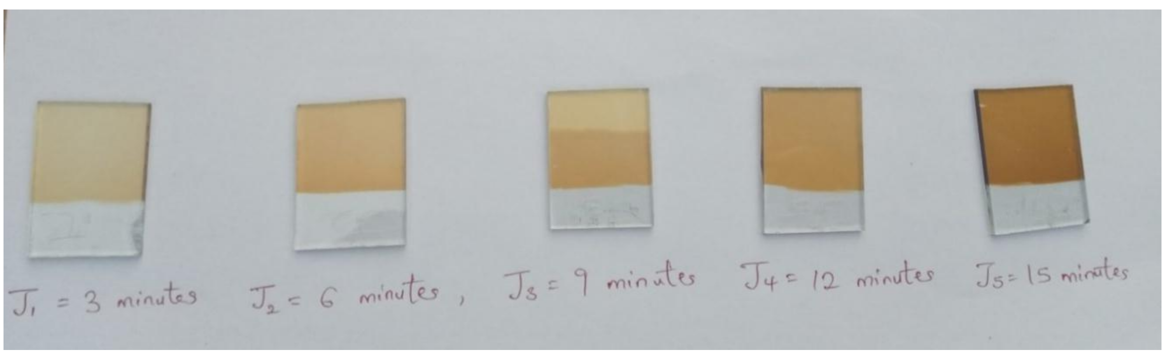

Figure 3.7: Photograph of electrodeposition Aluminum Selenide (Al_2Se_3)

4.0 Conclusion

In order to ascertain the conductivity type of electrodeposited aluminum selenide, a photoelectrochemical cell measurement was carried out which was achieved by forming a liquid junction between the substrate and the electrolyte. The PEC signal as measured under dark and illumination conditions, revealed the transition from p-type to n-type Al_2Se_3. From table 4, it can be observed that at fixed cathodic voltages of 1200mV the PEC signal falls within the negative region indicating that the conductivity of Al_2Se_3 and as the time of deposition increased, the PEC signal does not change. So it can be inferred that material electrical conductivity type transition does not depend on the time of deposition. These results confirmed the work of other researchers who reported the possibility of growing either p- or n- type compound semiconductors.

The achievement of aluminum selenide thin films from aluminum chloride as source of aluminum and selenium dioxide as a source of selenium using electrodeposition technique has been reported in this research work. The work further revealed the effect of varying time of deposition on the band gap of the films. It can be concluded that material can exhibit various energy band gaps and constant conductivity types by the variation of deposition parameters. The optical properties of the films at varied time of deposition showed that the films are interesting material in the formation of optoelectronic devices such emitters and collectors. The decrease in the current density as the cathodic voltage increases showed that the adopted growth technique, electrodeposition obeys two laws in physics that Michael Faraday and Ohm's law.

The interest in the synthesis of cost-effective material suitable for energy conversion has attracted researcher's attention recently. Aluminum selenide as a promising material in the energy conversion has been synthesized using electrodeposition technique. In view of this, I will recommend that various deposition techniques and characterization should be employed in order to harness the potential of the material.

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