Transactions of the Nigerian Association of Mathematical Physics
Volume 13, (October – December, 2020 Issue), **pp69 –78**

THE EFFECT OF VARYING CATHODIC VOLTAGES, CURRENT AND TEMPERATURE ON OPTICAL PROPERTIES AND CONDUCTIVITY TYPE OF ELECTRODEPOSITED ALUMINUM SELENIDE (AL_2SE_3) THIN FILMS FOR OPTOELECTRONIC APPLICATIONS.

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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 353 K temperature from an aqueous solution of analytical grade selenium dioxide (SeO2), and Aluminum chloride ($AlCl_2.7H_2O$). Aluminum selenide thin films from a controlled medium (pH =2.0) are synthesized on fluorine doped tin oxide (FTO) substrate using varied potential voltages 1000 mV, 1100 mV, 1200 mV, 1300 mV and 1400 mV. The films are characterized for their optical properties and electrical conductivity. These various characterization reveals the successful fabrication of Al_2Se_3 thin films. Further investigation was done to study the effect of variation in the potential voltages.

Keywords: Electrodeposition; Thin Films; Cathodic graphite; Characterization; Varied potential voltages.

1. 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 [17-23]. 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. The films were characterized for their optical properties using UVs spectrophotometer and electrical conductivity using photoelectrochemical cell measurement.

Bicelli*et.al*[27] addressed the electrochemical growth of metals and alloys with nanometric structures controlling the functional properties of electrodeposited coatings and freestanding electroforms. Electrodeposition is starting to be regarded

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as a viable process for nanofabrication and - even though electrocrystallisation has received considerable attention from both the theoretical and experimental viewpoints - it is now worth focussing systematically on the role of processing and electrochemical engineering factors, in the tailoring of nanosized structural features. This information is currently scattered in the literature and a specific review would fill an information gap. This paper offers: (i) an overview of the tools currently avaliable for the description and in-situ and ex-situ assessment of the nanostructure of electrodeposited metals; (ii) a systematic discussion of the relationships among their nanostructure and mechanical and chemical properties; (iii) a rationalisation of the mechanisms of formation of the different types of nanoelectrodeposits; (iv) a critical presentation - ordered by chemical composition - of specific systems. An updated and comprehensive literature coverage is provided.

2. Material and Method

2.1 Material

Aluminum chloride ($AlCl_2$, 99%) from strem chemical, selenium dioxide (SeO_2, 99%) from shem chemical and ammonium solution were used without further purification.

2.2 Method

FTO of 2.3 by 4 cm^2 in dimension was first degreased using dilute hydrochloric acid and later immersed in deionized water for 30 minutes for removal of possible grease that might have injected onto the surface of the substrate. Electrolytic bath of Al_2Se_3 was prepared by dispensing 29 grams of aluminum chloride as a source of aluminum in 500 ml beaker containing 400 ml of deionized water to form 0.3 mol. 0.9 grams of SeO_2 as a source of selenium was added to the solution and the admixed solution was magnetically stirred for 2 hours to ensure homogeneous solution. Since the synthesis technique used is favoured by acidic medium, the electrolyte was adjusted to pH of 2.5 using ammonium solution. Deposition took place at bath temperature of 90^o C in 15 minutes of deposition duration. Two electrodes system were used to achieve the thin films by connecting the substrate to the graphite as a cathode and carbon anode was placed directly opposite the conducting surface of the substrate. Different films were achieved by the variation of cathodic potential ranged from 1000 -1400 mV. 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. In order to ascertain the conductivity type of the electrodeposited compounds, photoelectrochemical cell measurements was used. Figure 2 and 2.1 showed the schematic diagram for both electrodeposition and photoelectrochemical cell measurement techniques. Equation 2.0 to 2.2 was adopted in the determination of film thickness, optical properties and electrical conductivity.

$$T = \frac{JtM}{\rho nF} \tag{2.0}$$

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.

$$(\alpha hv)^2 = A\left(hv - E_g\right) \tag{2.1}$$

Whereα is absorption coefficient, hv is photon energy, A is a constant usually equal to one, E_g is the energy band gap and n is the transition between valence band and conduction band.

$$PEC\ Signal = V_L + V_D \tag{2.2}$$

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

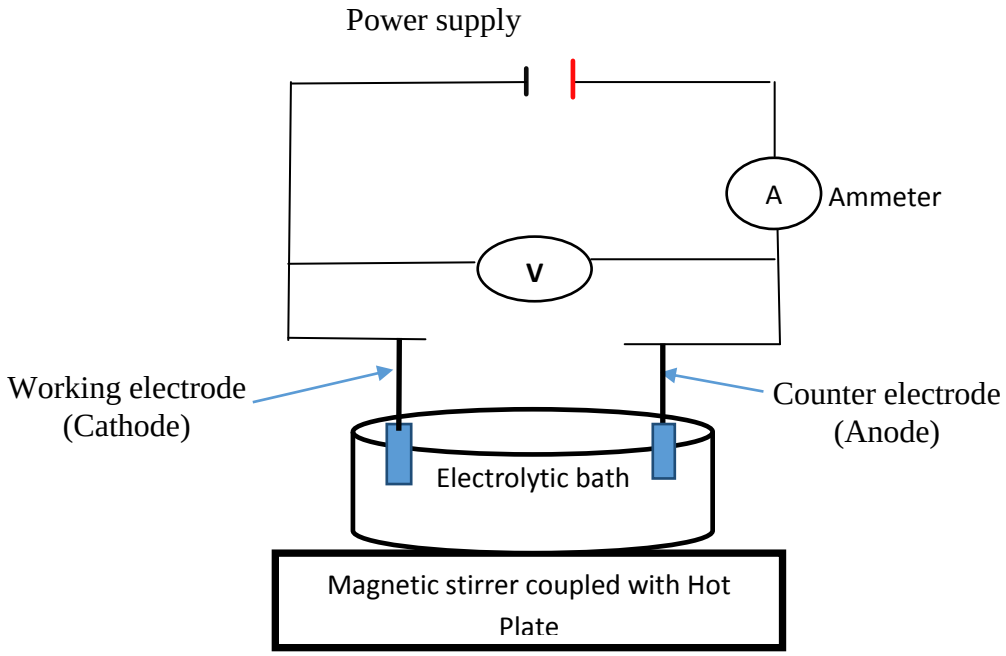

Figure 2.0: Schematic diagram of two-electrode system used for electrodeposition of Al_2Se_3.

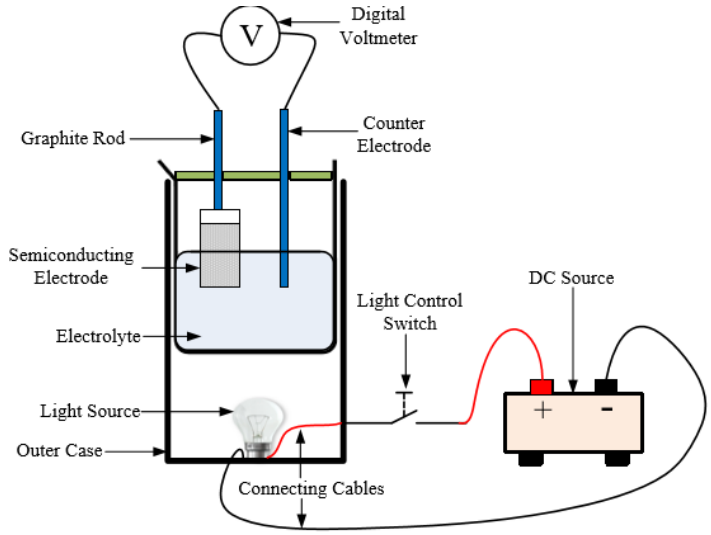

Figure 2.1: Typical schematic diagram of the experimental set-up for PEC cell measurement [24].

Morphology characterization

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 JeolTescan model taken at an accelerating voltage of 15kV was used to determine the shape and the size of the deposited Al_2Se_3 thin films with the help of image analyzer.

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

3.0 Results and Discussion

The optical properties of the electrodeposited aluminum selenide are revealed in figure 3-7. The various optical characteristics of the film hold potentiality to Al_2Se_3.

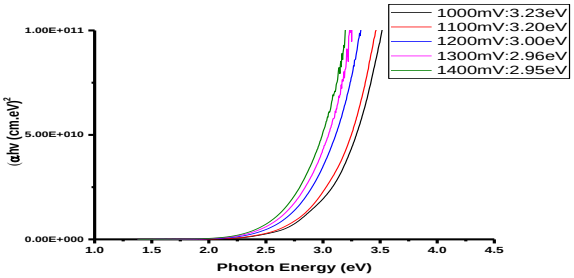

Figure 3: Energy band gap of Al_2Se_3 at varies cathodic potential

The energy band gap of the films decreases as the cathodic voltage increases (Figure 3). The increase in cathodic potential resulted to increase in the films thickness. Such a behaviour can be attributed to quantum conferment. The quantitative band gap of the films as given as an insert of figure 3 was obtained by extrapolating the linear part of the plots using tauc equation. The obtained agrees with previously reported work on the variation of growth voltage during material growth [25]

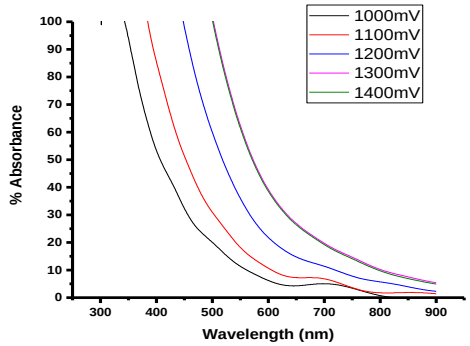

Figure 4: absorption spectrum as a function of wavelength

There is decrease in the absorbance with increase in wavelength which showed blue shift. The plot show 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.

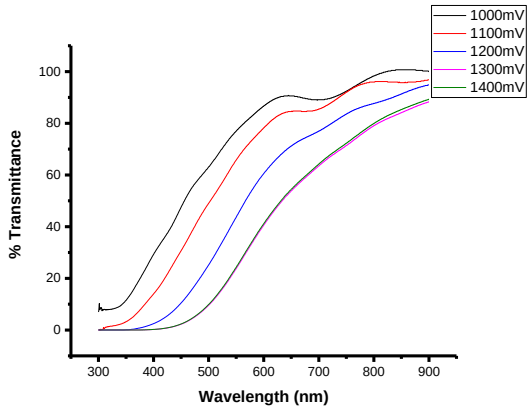

Figure 5: percentage of transmittance of Al_2Se_3 as a function of wavelength

The percentage of transmittance as a function of wavelength showed high transmittance throughout the UV/ VIS/NIR regions as the cathodic potential 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.

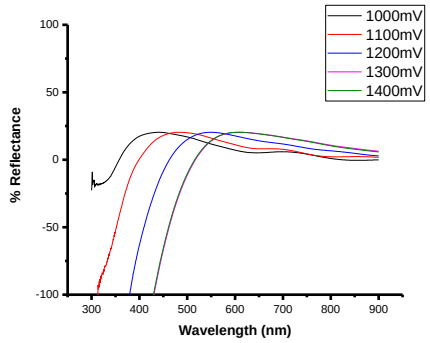

Figure 6: reflection spectrum as a function of wavelength

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.

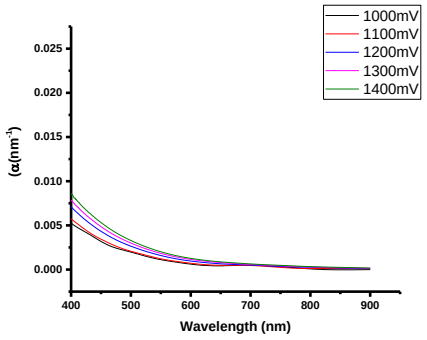

Figure 7: absorption coefficient as a function of wavelength

The absorption edge of the films as the wavelength increases show relatively low absorption edge within visible region.

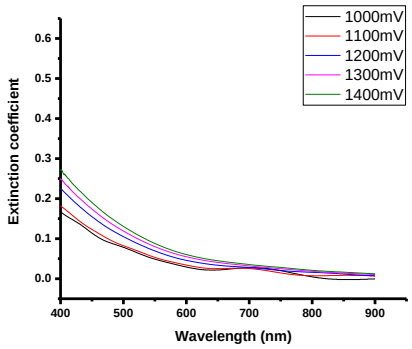

Figure 8: extinction coefficient as a function of wavelength

The extinction coefficient of the films as a function wavelength increases show relatively high extinction coefficient with the visible region.

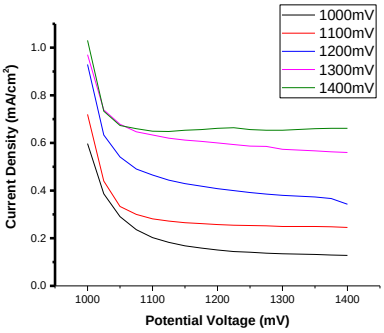

Figure 9: current density as a function of deposition voltage.

The current density reveals the quantity of electrical charges that passed through the electrolyte. The current decreases as the voltage increase. The increase in voltage can be attributed to ohm's law. Meaning that deposition take place as the resistance of the conducting surface is built up.

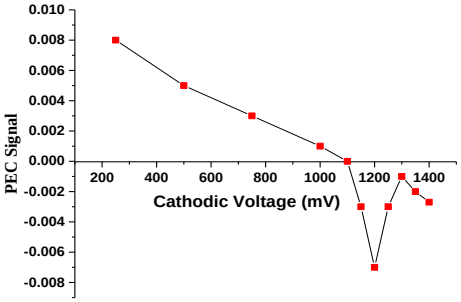

Figure 10: PEC signal as a function of growth voltage for glass/FTO/ Al_2Se_3 layers.

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 figure 10, it can be observed that at lower cathodic voltages the PEC signal falls within the positive region indicating p-type and intrinsic (i) Al_2Se_3 and as the cathodic voltages increased above 1100 mV, the PEC signal transited to negative region showing n- type Al_2Se_3. It can be inferred that material electrical conductivity type transition depends on the variation of growth voltage. These results confirmed the work of other researchers who reported the possibility of growing either p- or n- type compound semiconductors [26].

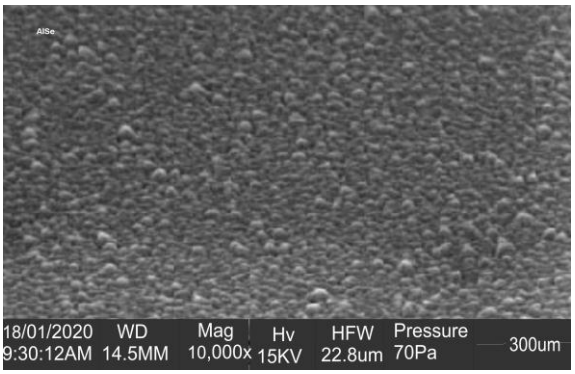

Figure 11: Scanning Electron Microscopy (SEM) of 1400 mV cathodically deposited Al_2Se_3

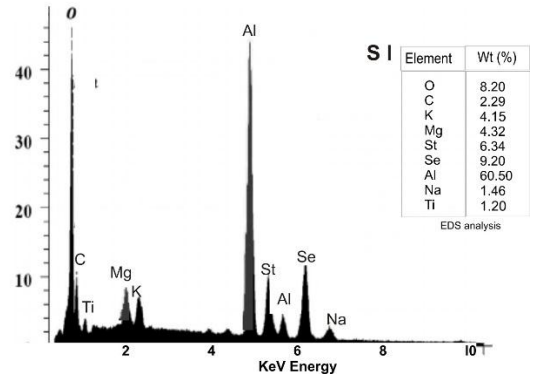

Figure 12: EDS analysis of structure S1

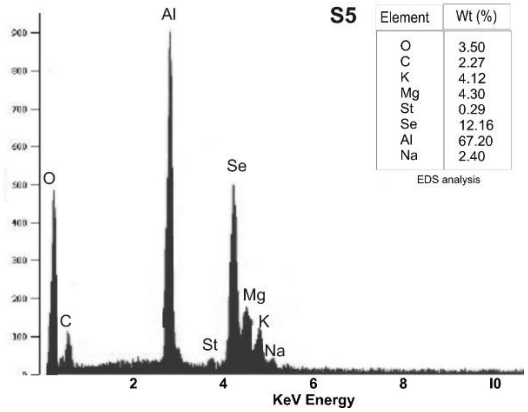

Figure 13:EDS analysis of structure S5

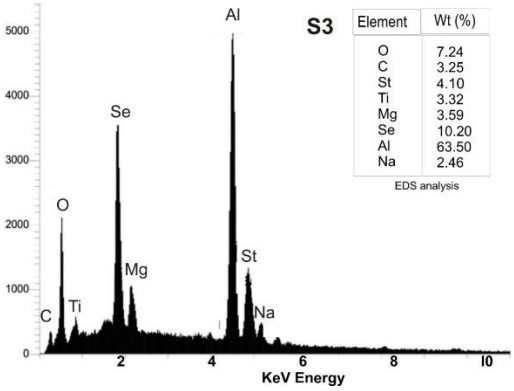

Figure 14:EDS analysis of structure S3

Table 3.1: Potentiostat results

Conducting substrate, E_1 ; Applied Voltage = 1000mV Temperature = 70^0C		**Conducting substrate, E_2;** Applied voltage = 1100mV Temperature = 70^0C		**Conducting substrate, E_3;** Applied voltage = 1200mV Temperature = 70^0C		**Conducting substrate, E_4;** Applied voltage = 1300mV Temperature = 70^0C		**Conducting substrate, E_5;** Applied voltage = 1400mV Temperature = 70^0C	
Time (min.)	**Current (μA) x10**	**Time (min.)**	**Current (μA) x10**	**Time (min.)**	**Current (μA) x10**	**Time (min.)**	**Current (μA) x10**	**Time (min.)**	**Current (μA) x10**
0.00	448.00	0.00	540.00	0.00	697.00	0.00	728.00	0.00	773.00
1.00	290.00	1.00	330.00	1.00	475.00	1.00	554.00	1.00	550.00
2.00	218.00	2.00	250.00	2.00	406.00	2.00	509.00	2.00	505.00
3.00	177.00	3.00	225.00	3.00	368.00	3.00	485.00	3.00	495.00
4.00	152.00	4.00	211.00	4.00	349.00	4.00	475.00	4.00	487.00
5.00	137.00	5.00	204.00	5.00	333.00	5.00	465.00	5.00	486.00
6.00	126.00	6.00	199.00	6.00	322.00	6.00	459.00	6.00	490.00
7.00	119.00	7.00	196.00	7.00	314.00	7.00	455.00	7.00	492.00
8.00	113.00	8.00	193.00	8.00	306.00	8.00	450.00	8.00	496.00
9.00	108.00	9.00	191.00	9.00	300.00	9.00	445.00	9.00	498.00
10.00	106.00	10.00	190.00	10.00	294.00	10.00	440.00	10.00	492.00
11.00	103.00	11.00	189.00	11.00	289.00	11.00	439.00	11.00	490.00
12.00	101.00	12.00	187.00	12.00	285.00	12.00	430.00	12.00	490.00
13.00	99.00	13.00	187.00	13.00	280.00	13.00	425.00	13.00	495.00
14.00	97.00	14.00	186.00	14.00	275.00	14.00	422.00	14.00	496.00
15.00	96.00	15.00	184.00	15.00	257.00	15.00	420.00	15.00	496.00

Table 3.2: PEC results for electrodeposited substrate, E_1
Time = 20s

V_D	V_L	$V_{PEC} = V_L - V_D$
-0.421	-0.420	0.001
-0.418	-0.416	0.002
-0.416	-0.415	0.001

Average of V_{PEC} = $\frac{0.001 + 0.002 + 0.001}{3}$ = 0.001 (which is a p-type material)

Table 3.3: PEC results for electrodeposited substrate, E_2
Time = 20s

V_D	V_L	$V_{PEC} = V_L - V_D$
-0.417	-0.417	0.000
-0.416	-0.416	0.000
-0.416	-0.416	0.000

Average of V_{PEC} = $\frac{0 + 0 + 0}{3}$ = 0 (which is an intrinsic material)

Table 3.4: PEC results for electrodeposited substrate, E_3
Time = 20s

V_D	V_L	$V_{PEC} = V_L - V_D$
-0.470	-0.471	-0.001
-0.471	-0.471	-0.000
-0.471	-0.472	-0.001

Average of V_{PEC} = $\frac{-0.001 + 0 + (-0.001)}{3}$ = -0.007 (which is a n-type material)

Table 3.5: PEC results for electrodeposited substrate, E_4
Time = 20s

V_D	V_L	$V_{PEC} = V_L - V_D$
-0.417	-0.418	-0.001
-0.419	-0.420	-0.001
-0.421	-0.422	-0.001

Average of $V_{PEC} = \frac{-0.001 + (-0.001) + (-0.001)}{3} = -0.001$ (which is a n-type material)

Table 3.6: PEC results for electrodeposited substrate, E_5
Time = 20s

V_D	V_L	$V_{PEC} = V_L - V_D$
-0.473	-0.475	-0.002
-0.478	-0.481	-0.003
-0.484	-0.487	-0.003

Average of $V_{PEC} = \frac{-0.002 + (-0.003) + (0.003)}{3} = -0.0027$ (which is a n-type material)

4.0 Conclusion

The electrodeposition of nanocrystalline metals and alloys is probably the only mature nanotechnology, producing a broad range of materials which find extensive practical application in many fields of the industry, spanning both high- and low-technology areas. Still, there is much scope for knowledge-driven innovation in this field. 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 cathodic potential on the band gap of the films. It can be concluded that material can exhibit various energy band gaps and conductivity types by the variation of deposition parameters. The optical properties of the films at varied voltages showed that the films are interesting material in the formation of optoelectronic devices such emitters and collectors. In the work, we have successfully achieved p-type, i-type and n-type aluminum selenide and this showed that Al_2Se_3 can form heterojunction with any compound material as the film conductivity changes with the deposition potential variation. 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 EDS analysis were shown in figures 12 to 14.

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