Variation of Cathodic Voltages and their Effect on Optical Properties and Conductivity Type of Electrodeposited Aluminium Selenide Thin Films for Optoelectronic Applications

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Abstract- In this paper, Aluminium selenide (Al\textsubscript{2}Se\textsubscript{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 (SeO\textsubscript{2}), and Aluminum chloride (AlCl\textsubscript{3}). Aluminium 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\textsubscript{2}Se\textsubscript{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

A

luminium selenide (Al\textsubscript{2}Se\textsubscript{3}) is a promising material in the fabrication of optoelectronic devices due to its direct energy band gap, better charge transport, high 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 (Schneider & Gattow, 1954; Revaprasadu et al., 1999; Afzaal & Brien, 2006; Young & Kelley, 2005). Aluminium (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 (Adams et al., 2005; Shavel, Gaponik & Eychmüller, 2004). Since compound semiconductor has more functionalities than elemental semiconductor, compound semiconductors such as cadmium telluride, zinc oxide, zinc sulphide, lead sulphide etc, are therefore received scientific attention. We chose to form aluminium selenide because of the potential of selenium in compound semiconductors such as zinc selenide, copper selenide (Durdua et al., 2013), lead selenide (Ezenwa, 2012) etc. The band gap of Al\textsubscript{2}Se\textsubscript{3} has been reported as 3.1 eV at wavelength of 401 nm which make it possible to be potentially used in photoemitter (Mansoor & Yilbas, 2018; Beck & Funk, 2012).

Various deposition techniques have been employed in synthesis of compound semiconductor materials (Grecu et al., 2004; Norizam et al., 2012; Moutinho et al., 1998; Compaan et al., 2004; Chen, Sivananth & Faurie, 1993; Nuss et al., 1989). Since the primary aim of synthesizing material for device applications is to minimize cost, Electrodeposition (ED) technique 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 (Arya et al, 2013; Arya, Khan & Lehana, 2012; Khan et al, 2012; Lehana et al, 2012; Lehana, Khan & Arya, 2011; Hu et al, 2006; Li et al, 2010). In this study, Al\textsubscript{2}Se\textsubscript{3} was electrodeposited on a conducting substrate/FTO of 2.3 by 4 cm\textsuperscript{2} in dimension. Different samples of Al\textsubscript{2}Se\textsubscript{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.

2 MATERIAL AND METHOD

2.1 MATERIAL

Aluminium chloride (AlCl\textsubscript{3}, 99%) from strem chemical, selenium dioxide (SeO\textsubscript{2}, 99%) from strem chemical and ammonium solution were used without further purification.

2.2 METHOD

FTO of 2.3 by 4 cm\textsuperscript{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\textsubscript{2}Se\textsubscript{3} was prepared by dispensing 29 grams of aluminium chloride as a source of aluminium in 500 ml beaker containing 400 ml of deionized water to form 0.3 mol. 0.9 grams of SeO\textsubscript{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°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. Figures 1 and 2 shows the schematic diagram for both electrodeposition and photoelectrochemical cell measurement techniques. Equations 1 to 3 was adopted in the determination of film thickness, optical properties and electrical conductivity.

\[ T = \frac{J t M}{\rho n F} \]  

(1)

The film thickness is denoted as \( T \), \( J \) is the current density of the electrodeposited \( \text{Al}_2\text{Se}_3 \), \( t \) is the deposition time, \( \rho \) is the density of \( \text{Al}_2\text{Se}_3 \), \( n \) 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 \( \text{Al}_2\text{Se}_3 \).

\[ (a\nu)^2 = A(\nu - E_g) \]  

(2)

Where \( a \) is absorption coefficient, \( \nu \) 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.

\[ \text{PEC Signal} = V_L + V_D \]  

(3)

Where \( V_L \) is voltage under illumination and \( V_D \) is voltage under dark.

2.3 Morphology Characterization

The shape and the sizes of the deposited compound semiconductors were analysed using scanning electron microscopy (SEM) at University of Ibadan, Oyo State, Nigeria shown in Figure 3. SEM Jeol Tescan model taken at an accelerating voltage of 15kV was used to determine the shape and the size of the deposited \( \text{Al}_2\text{Se}_3 \) thin films with the help of an image analyser.

3 Results and Discussion

The optical properties of the electrodeposited aluminium selenide are revealed in Figures 4-8. The various optical characteristics of the film hold potentiality to \( \text{Al}_2\text{Se}_3 \).
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 confinement. 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 (Ojo & Dharmadasa, 2018).

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.

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

The extinction coefficient (Fig 9) of the films as a function of wavelength increases show relatively high extinction coefficient with the visible region. The current density reveals the quantity of electrical charges that passed through the electrolyte. The current decreases as voltage increase see Fig. 10. The increase in voltage can be attributed to Ohm’s law which means that deposition take place as resistance of conducting surface is built up.

In order to ascertain the conductivity type of electrodeposited aluminium selenide, a photo-electrochemical 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 AlS\textsubscript{2}Se\textsubscript{3}. From figure 11, it can be observed that at lower cathodic voltages the PEC signal falls within the positive region indicating p-type and intrinsic (i) AlS\textsubscript{2}Se\textsubscript{3} and as the cathodic voltages increased above 1100 mV, the PEC signal transited to negative region showing n-type AlS\textsubscript{2}Se\textsubscript{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 (Yang, Chou, & Ueng, 2010; Oluyamo, 2020).

Tauc plot is used to determine the optical bandgap or Tauc gap in semiconductors. It is also used to characterize practical optical properties of amorphous materials, represented by hv on the abscissa and (αhv)\textsuperscript{1/r} on the ordinate.
### Table 1. Potentiostat results

| Conducting substrate, $E_1$ | Conducting substrate, $E_2$ | Conducting substrate, $E_3$ | Conducting substrate, $E_4$ | Conducting substrate, $E_5$ |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Temperature = 70°C | Temperature = 70°C | Temperature = 70°C | Temperature = 70°C | Temperature = 70°C |
| Applied Voltage = 1000mV | Applied voltage = 1100mV | Applied voltage = 1200mV | Applied voltage = 1300mV | Applied voltage = 1400mV |
| 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 | 599.00 | 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 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 $V_{PEC} = (0.001 + 0.002 + 0.001)/3 = 0.001$ (which is a p-type material)

### Table 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 $V_{PEC} = (0 + 0 + 0)/3 = 0$ (which is an intrinsic material)

### Table 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 $V_{PEC} = (-0.001 + 0 + (-0.001))/3 = -0.007$ (which is a n-type material)

### Table 5. PEC results for electrodeposited substrate, $E_4$ Time = 20s

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

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

### Table 6. PEC results for electrodeposited substrate, $E_5$ Time = 20s

| $V_D$ | $V_L$ | $V_{PEC} = V_L - V_D$ |
|-------|-------|----------------------|
| -0.475 | -0.477 | -0.002 |
| -0.478 | -0.481 | -0.003 |
| -0.484 | -0.487 | -0.003 |

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

### 4 Conclusion

The achievement of aluminium selenide thin films from aluminium chloride as source of aluminium 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 aluminium selenide and this
showed that AlSe3 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.

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