

Electrosynthesis and Characterizations of Aluminum Silver Selenide (AlAgSe₂), Thin Films for Possible Device Applications

Chukwudi Benjamin MUOMELIRI^{1*}, Ngozi Agatha OKEREKE², Augustine Nwode NWORI²,
Uchechukwu Vincent OKPALA² and Nonso Livinus OKOLI^{3,4}

¹Department of Physics and Industrial Physics, Nnamdi Azikiwe University Awka, Anambra State, Nigeria

²Department of Industrial Physics, Faculty of Physical Science, Chukwuemeka Odumegwu Ojukwu University Uli, Anambra State, Nigeria.

³Department of Computer Education, Madonna University Okija, Anambra State, Nigeria.

⁴Nanoscience and Advanced Materials, Federal University of ABC, Santo Andre, Sao Paulo, Brazil

*Corresponding Author's

DOI: <https://doi.org/10.51244/IJRSI.2024.1109080>

Received: 25 September 2024; Accepted: 03 October 2024; Published: 14 October 2024

ABSTRACT

The semiconductor thin films of Aluminum Silver selenide (AlAgSe₂) have been successfully deposited onto FTO glass substrate using electrodeposition method. AgNO₃, AlCl₃.6H₂O and Selenium powder were the precursors used for sources of Ag, Al and Se ions respectively. Prototype of the films were again made and subjected to annealing at temperature of 150°C for 5 minutes to remove the element of moisture content in the as deposited films. The properties of the films such as optical, structural and compositional were investigated using UV-VIS Spectrophotometry, X-ray diffractometry and Rutherford Backscattering Spectroscopy (RBS) analysis respectively to determine the possible areas of applications of the films. Optical analysis revealed that the films have high absorbance in the UV region but decreased in the visible and near infrared regions. The increase in the concentration of selenide ions however decrease the absorbance of the films but annealing tends to increase the absorbance. The films also exhibited very high values of refractive index with minimum value in the order of 2.0 for both the annealed and as deposited samples. The bandgap energies of the films were found to be 1.7 eV, 1.8 eV, 2.2 eV, 2.8 eV and 2.9 eV for as deposited, but decreased to the values of 1.5 eV, 1.6 eV, 1.92 eV, 2.15 eV and 2.5 eV after annealing for the films deposited with 0.1 M, 0.2 M, 0.3 M, 0.4 M and 0.5 M Se ions respectively. The structural analysis indicates that AlAgSe₂ films are crystalline in nature with most preferential crystalline plane of (112). The RBS compositional analysis showed that the deposited thin films are rich in silver content. These properties exhibited by the deposited thin films of AlAgSe₂ are desirable for photovoltaic devices and for many other optical and optoelectronic applications.

Key Words: Photovoltaic cells, Bandgap, Silver-Selenide, Optoelectronics, Electrodeposition

INTRODUCTION

The interesting features and properties exhibited by most chalcogenides of selenium base semiconductor materials have positioned the materials for many applications including electronics, optoelectronics, microelectronics, communication, catalysis, coating, and energy generation applications, [1]. The high non-linear optics of the order 100 times compared to traditional non-linear material-silica for device applications has been reported for chalcogenide glasses of selenium-based compounds and in addition, they are known to have very good transmittance in mid IR region, high linear refractive index, low phonon energy and photosensitivity; hence, position them for device applications such as in optical recording, thermal imaging, night vision cameras, integrated optics, diffraction gratings and optical waveguides [2,3]. Other applications of these materials include

degradation of pollutants, photoreduction of pigments and dyes, wastewater treatment technologies, solar cells, photocatalysis, photochemical applications, opto-electronic materials for LEDs, thermoelectric materials application, etc. [4-6]. The selenium-based chalcogenides of group I-VI have been noted to possess highly unique properties and as such have been utilized in the fabrication of photovoltaic devices such as window material, super ionic conductor, electro-optical devices, optical filter, thermo electric converter and photo electrochemical cell, [7, 8]. The prominent group I-VI chalcogenides of interest that spur this research is silver selenide (Ag_2Se) semiconductors which have demonstrated quite amazing magnetic behavior despite their non-magnetic origin, [9]. This group of chalcogenides has also demonstrated higher carrier density irrespective of the preparation method and dual material states of displaying semiconducting properties and metal-like properties at low and higher temperatures respectively, [10, 11]. The low temperature phase below 400 K is known as $\beta\text{-Ag}_2\text{Se}$ with orthorhombic crystal structure and the high temperature is the $\alpha\text{-Ag}_2\text{Se}$ and has the body centered cubic (BCC)-structure, [12]. These two split phase states of silver selenide (Ag_2Se) have been viewed as the key factors propelling the material for diverse potential fields of technological applications such as thermo-chromic material for non-linear optical devices, multipurpose ion-selective electrodes, infrared sensors, electrochemical storage cells, electrochemical potential memory devices, biological imaging, photovoltaic cells, magnetic field sensing devices/magnetic resistive sensors etc. The $\alpha\text{-Ag}_2\text{Se}$ has been found to be rooting for super-ionic conductor used as solid electrolyte in photothermally chargeable batteries while the $\beta\text{-Ag}_2\text{Se}$ has been widely utilized for thermo-chromic material as photo sensitizer in photographic films, [13, 14]. Silver selenide is typically a very narrow bandgap material with the low-temperature phase having bandgap energy as low as the 0.07 to 0.15 eV. These energy range are in the infrared region of electromagnetic spectrum, hence Ag_2Se can be taken as a promising alternative for IR-detector device applications. In this scenario, report has it that the size-dependent quantum confinement in Ag_2Se QDs has been shown to tune optical response from mid-wave infrared (MWIR) into the near-infrared (NIR) region as a good alternative to Pb, mercury (Hg), and arsenic (As) based materials for various IR detectors as Ag_2Se is much safer to use in biomarkers than heavy metal containing compounds, [15]. The incorporation of group III element in the material structure of I-VI semiconductor materials in the case of AgSe have been viewed as the one the possible ways to advancing the wide applications of the material. The material structure obtainable from these groups of elemental combination such as $\text{A}_{\text{III}}\text{B}_{\text{I}}\text{C}_{2\text{VI}}$ or $\text{A}_{\text{III}}\text{B}_{\text{I}}\text{C}_{2\text{VI}}$ has been described as chalcopyrite and have proven to exhibit very good promising absorber for photovoltaic cell application due to their optimum direct energy gap and high optical absorption, [16]. The prominent element from group III that can be incorporated suitably into the structure of AgSe is Aluminum (Al). This is because Al has been known to have lower ionic radii $\text{Al}^{+3}(0.53 \text{ \AA})$ compared to $\text{Ag}^{+1}(1.29 \text{ \AA})$ and $\text{Se}^{-4}(0.56 \text{ \AA})$, [17]. These potential applications of the ternary chalcopyrite structure obtainable from the combination of these sets of elements are sought for in this report. However, to the best of our literature search, there are high level of limited works that have been done in these material combinations. Hence, in this work we report the properties of AlAgSe_2 prepared by electrodeposition technique for their possible device fabrications.

Experimental Detail

The AlAgSe_2 , (AAS) thin films were deposited on FTO glass substrate using electrodeposition technique. The films were synthesized from aluminum chloride (AlCl_3) and silver trioxonitrate (v) (AgNO_3) and selenium (Se) powder as sources of Al, Ag and Se. Saturated calomel electrode (SCE) and carbon electrode were used as reference electrode and counter electrode respectively, while the FTO glass substrates were used as the working electrodes. The FTO glass substrates were subjected to pre-treatment by degreasing with detergent, acetone, distilled water and dry in oven at 60 °C for 5 minutes and allowed to cool in air before use.

Preparation of Precursors

0.1 M of AgNO_3 solution was prepared by dissolving 1.7 g of AgNO_3 salt in 100 ml of distilled water. 0.1 M of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ solution was prepared by dissolving 2.41 g of the salt ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) in 100 ml of distilled water. These two solutions prepared (AgNO_3 and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ solutions) served as the cationic precursor for precipitation of Al^{3+} and Ag^{+} ions. Also, 0.1 M selenium solution was prepared by dissolving 0.79 g of selenium powder in 100 ml of distilled water. The (AlAgSe_2) films were deposited at room temperature at a constant voltage of 10 Volts for 5 minutes. The solutions of the three chemicals prepared were kept in three different beakers. 12 ml of each of the solutions was collected and transferred to the electrochemical deposition apparatus containing pure carbon (graphite) electrode, saturated calomel electrode (SCE) and FTO-working electrode.

Also, power supply and multimeter which is set to measure voltage and current were connected to the apparatus and the film were deposited.

Four more molar concentration of selenide source were obtained as from 0.2 M, 0.4 M and 0.5 M while the molar concentration of AgNO_3 and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ remain unchanged throughout the experiment to obtain a total of five sample of AlAgSe thin films at different selenium concentration variations as shown in Table 1. The process was repeated and another set of five samples of the films were obtained and annealed at temperature of 150°C . The deposited thin films of AlAgSe were then characterized for optical, structural and morphological properties for possible device applications.

Table 1: Variation of Molar Concentration of Selenide ion which was annealed at 150°C

Conc. $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (M)	Conc. AgNO_3 (M)	Conc. Selenium powder (M)	Working Voltage (volts)	Working Current (volts)
0.1	0.1	0.1	1.00	0.50
0.1	0.1	0.2	1.00	0.50
0.1	0.1	0.4	1.00	0.50
0.1	0.1	0.5	1.00	0.50

RESULTS AND DISCUSSION

Optical properties of the Films

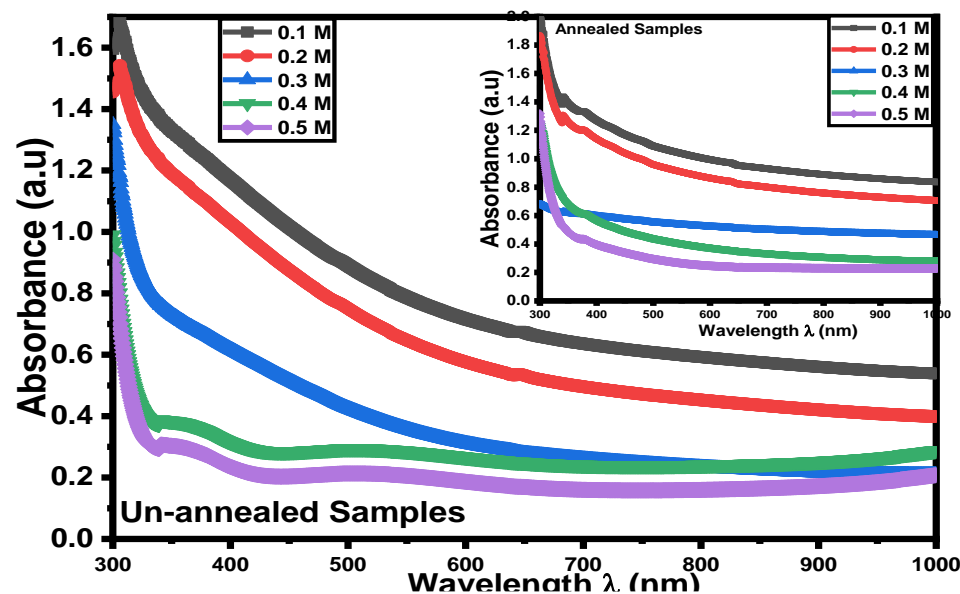


Figure 1: Graph of Absorbance against wavelength for the deposited AlAgSe thin films

Figure 1 represents the graph of absorbance against wavelength for the deposited thin films of AlAgSe . The figure contains the un-annealed film samples and the insert – annealed samples. The figure showed that the absorbance of the films is high in the UV region and decreased towards the VIS and NIR regions for the un-annealed and annealed samples. The figure also revealed that the absorbance decreased with an increase in the concentration of Se dopant. The films doped with 0.1 M of Se has the highest absorbance in the range of 0.5 to 1.8 for the un-annealed and 0.9 to 2.0 for the annealed samples, while the film doped 0.5 M has the lowest value in the range of 0.2 – 1.0 and 0.2 – 1.4 for the un-annealed and annealed samples within the UV, VIS and NIR regions. These results showed that annealing of the deposited thin films of AlAgSe has the effect of increasing the absorbance of the films. However, Se doping lead to decrease in the absorbance of the deposited thin films.

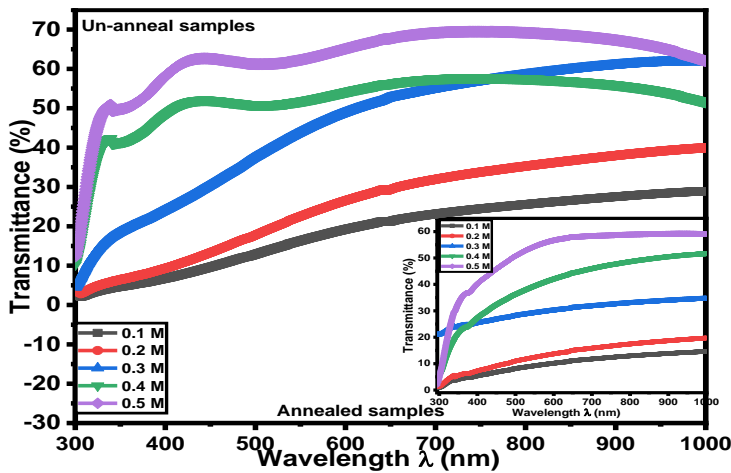


Figure 2: Graph of Transmittance (%) against wavelength for the deposited thin films

Figure 2 is the graph of percentage transmittance against wavelength for the deposited thin films of AlAgSe for both the un-annealed and annealed film samples. The transmittance of the films was evaluated using the formula as provided by [18, 19].

$$T = 10^{-A} \tag{1}$$

1

Where A is the measured absorbance of the films. The figure indicates that the transmittance of the films increased with an increase in the concentration of Se dopant with the film doped with 0.5 M having the highest value in the range 50-70% in the VIS/NIR region for the un-annealed film while the value for the annealed sample is in the range 40-80%. The film doped with 0.1 M Al source has the lowest transmittance in the range of 0-25% and 0-10% for the un-annealed and annealed samples respectively.

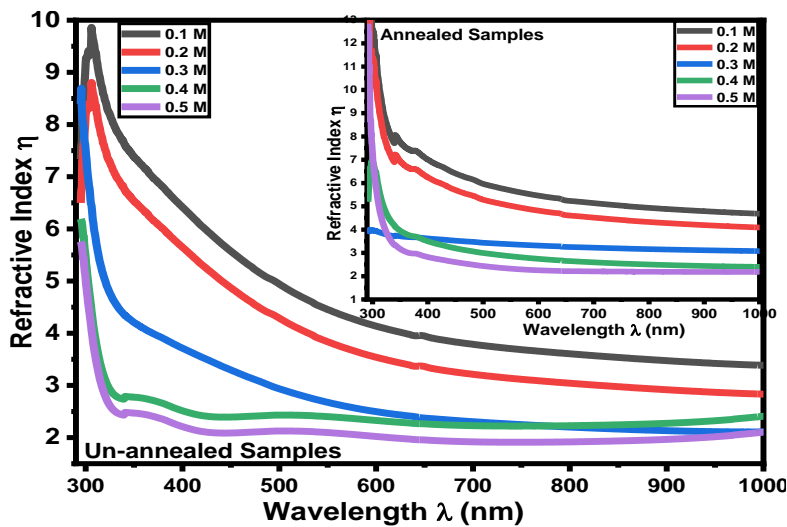


Figure 3: Graph of Refractive index against wavelength for the deposited AlAgSe thin films

The graph of refractive index of the films of AlAgSe as a function of wavelength is displayed in figure 3 to determine the refractive index of the films at different wavelength. The refractive index of the films was calculated using the relation as given by [20].

$$n = \frac{1+R^{1/2}}{1-R^{1/2}} \tag{2}$$

2

Where R is the reflectance of the films which was also computed using the relation given by.

$$R = \sqrt{\frac{e^A}{10^A}} \tag{3}$$

3

The figure showed that the refractive index of the films is very high but decreased with wavelength for both the un-annealed and annealed samples. The figure also showed that the refractive index of the films decreased with an increase in the concentration of Se doping with the film doped with 0.5 M Se having the lowest value in the range 2.0 to 2.5 for the un-annealed and 2.0 to 3.0 for the annealed samples.

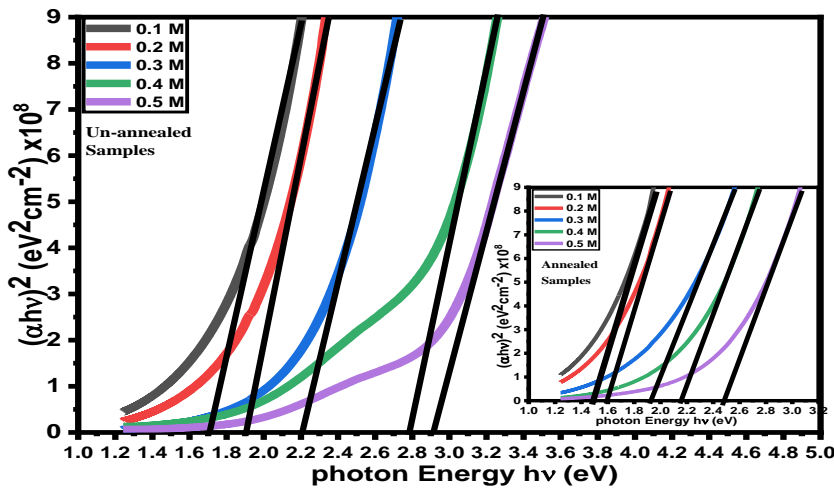


Figure 4: Graph of $(\alpha hv)^2$ against photon energy for the deposited AlAg Se thin films

The plots of $(\alpha hv)^2$ against photon energy are displayed in figure 4 to determine the bandgap energies of the deposited AlAgSe thin films for device application. The bandgap energies of the films were calculated using the relation as provided by [21].

$$(\alpha hv)^2 = A(hv - E_g) \tag{4}$$

4

Where α is the absorption coefficient of the films, h is the Planck's constant, ν is the frequency, E_g is the bandgap energy, A is energy constant. The figure showed that the bandgap energy of the films increased with an increase in the concentration of selenium source. The bandgap energies were estimated from the plots by extrapolating the straight-line portion of the curves to photon energy axes where $(\alpha hv)^2$ is equal to zero. The obtained values of the bandgap energies of the deposited films as shown in the plots for the un-annealed samples are; 1.7 eV, 1.8 eV, 2.2 eV, 2.8 eV and 2.9 eV for films doped with 0.1 M, 0.2 M, 0.3 M, 0.4 M and 0.5 M of Se ion source respectively. The values for the annealed sample as shown inserted in the figure are 1.5 eV, 1.6 eV, 1.92 eV, 2.15 eV and 2.5 eV for the films doped with 0.1 M, 0.2 M, 0.3 M, 0.4 M and 0.5 M of Se ion source respectively. These results indicate that increase in the concentration of Se ions in AlAgSe thin films increase its bandgap energy while annealing of the films lead to decreases in the bandgap energy. The obtained bandgap energies are in the range suitable for photovoltaic cell device fabrication and other devices like LEDs etc.

Structural properties of the Films

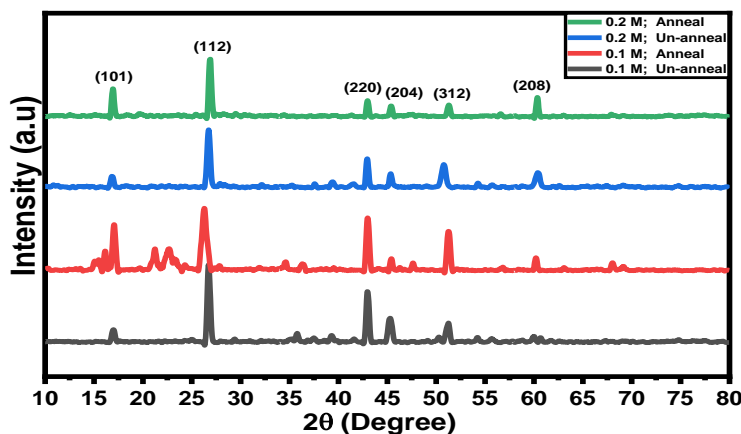


Figure 5: XRD patterns of the deposited thin films of AlAgSe with 0.1 M and 0.2 M

The XRD patterns of the deposited thin films of AlAgSe is shown in figure 5 for the films doped with 0.1 M and 0.2 M with their annealed samples. The films exhibit crystalline structures with preferential plane (112) at 2-theta angle position 26.28° . The XRD pattern matched well with the standard Crystallography open Database (COD) file number (96-150-9161) with tetragonal crystal structure for Silver Aluminum Selenide (AgAlSe_2). The average crystallite size, micro-strain and dislocation density of the films were calculated using the Dybcscherrer and Wilson relations as provided by [22-24].

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{5}$$

$$\varepsilon = \frac{\beta}{4 \cdot \tan\theta} \tag{6}$$

$$\delta = \frac{1}{D^2} \tag{7}$$

Where k is the shape factor with constant value 0.9, λ is the X-ray Cu-k- α wavelength, β is the full weight at half maximum (FWHM) and θ is the Bragg's angle. The average values of crystallite size, micro-strain and dislocation density of the films obtained are 22.65 nm, 2.0×10^{-3} and $5.6 \times 10^{-3} \text{ nm}^{-2}$ respectively.

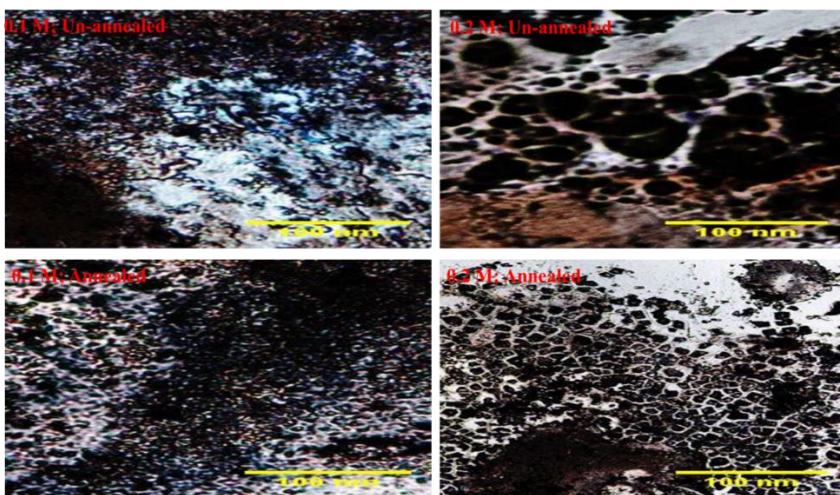


Figure 6: Micro-graph image of AlAgSe₂ thin films deposited with 0.1 M and 0.2 M Se.

The optical micrograph images of deposited thin films taken to visualize the microstructure of the films are displayed in figures 6. The micrograph done at 10000 magnification with the scale bar length of 100 nm revealed that the deposited films are brownish in color, well covered on the glass substrate. The annealing process modifies the morphology of the films. By annealing, the films acquired smooth and crystalline nature.

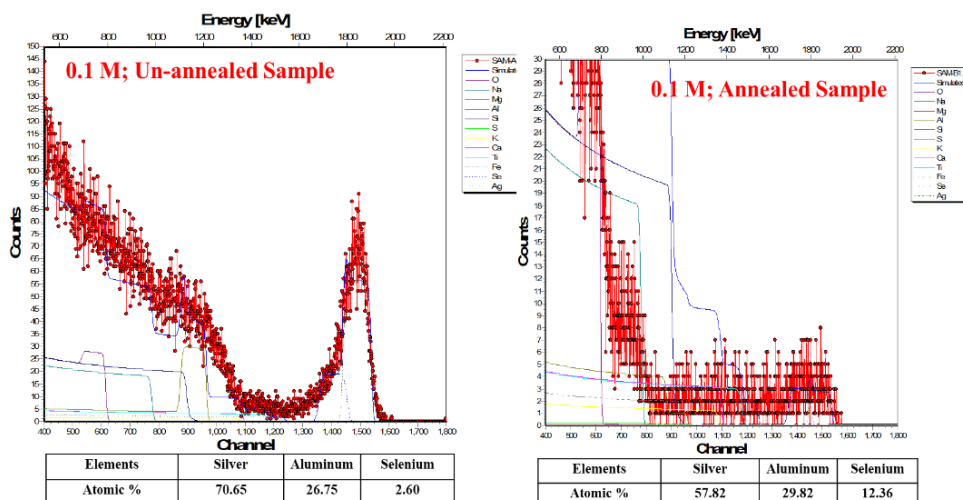


Figure 7: Compositional analysis of the AgAlSe₃ thin film deposited with 0.1M.

The Rutherford Backscattering Spectroscopy (RBS) spectra showing the elements in the grown AgAlSe₂ film were shown in figures 7. The composition ratio was found to be 27.2:10.3:1 of atomic mass percent for Ag, Al and Se respectively for the un-annealed film, while the composition ratio of 4.6:2.4:1 of atomic mass percent for Ag, Al and Se was found for the annealed film. This indicates that the grown films are rich in silver. Silicon, oxygen, calcium, iron, sodium, magnesium, tin, potassium and some other trace of elements with various atomic percentage were also detected and are believed to have come from the glass substrates used for the deposition

CONCLUSION

The properties of electrodeposited thin films of AlAgSe₂ at various Se ion variations were investigated for possible optimum device applications in this research work. The results of the sample analysis showed that the deposited thin films of AlAgSe₂ have high absorbance in the UV region but decreases towards VIS and NIR regions. The absorbance of the films was also found to decrease with an increase in the concentration of Se ion source within the electromagnetic spectrum. The thin films of AlAgSe₂ exhibit very high values of refractive index with minimum value in the order of 2.0 within the UV, VIS and NIR regions. The refractive index of the films is also influenced by variation of Se ion concentration as well as annealing of the films. The bandgap energies of the as deposited thin films of AlAgSe₂ were found to range from 1.7 eV to 2.9 eV, but decreased after annealing to the values in the range 1.5 eV to 2.15 eV and 2.5 eV for the films doped with 0.1 M, 0.2 M, 0.3 M, 0.4 M and 0.5 respectively. The results of the x-ray diffraction analysis showed that the deposited AlAgSe₂ have crystalline structure with average values of crystallite size, micro-strain and dislocation density of the films obtained are 22.65 nm, 2.0×10^{-3} and $5.6 \times 10^{-3} \text{ nm}^{-2}$ respectively. The results of the RBS analysis showed that the grown films are rich in silver. These results obtained for the deposited thin films of AlAgSe₂ make them desirable for photovoltaic devices, optical and opto-electronic application since such semiconductor materials allow power electronic components to be smaller, faster, more reliable and efficient.

ACKNOWLEDGEMENT

The authors appreciate the efforts of the team scientists and technologists at Nano Research Laboratory, University of Nigeria Nsukka, Enugu State Nigeria and the Scientists in the Electroscopy Unit, University Cape Town South Africa for their help in characterization of our samples.

Conflict of Interest

The authors declared that there is no conflict of interest that arose during the course of this research work.

REFERENCES

1. Hassanien, A. S., & Akl, A. A. (2016). Effect of Se addition on optical and electrical properties of chalcogenide CdSSe thin films. *Superlattices and Microstructures*, 89, 153-169.
2. Anshu, K., & Sharma, A. (2016). Study of Se based quaternary SePb (Bi, Te) chalcogenide thin films for their linear and nonlinear optical properties. *Optik*, 127(1), 48-54.
3. Frumar, M., & Wagner, T. (2003). Ag doped chalcogenide glasses and their applications. *Current opinion in solid state and materials science*, 7(2), 117-126.
4. Muslih, E. Y., Munir, B., & Khan, M. M. (2021). Advances in chalcogenides and chalcogenides-based nanomaterials such as sulfides, selenides, and tellurides. In *Chalcogenide-based nanomaterials as photocatalysts*, 7-31.
5. Thirugnanasambandan, T. (2021). Chalcogenides-based nanomaterials for artificial photosynthesis. In *Chalcogenide-Based Nanomaterials as Photocatalysts*, 219-242.
6. Ates, M., Yilmaz, E., & Tanaydin, M. K. (2021). Challenges, novel applications, and future prospects of chalcogenides and chalcogenide-based nanomaterials for photocatalysis. In *Chalcogenide-based nanomaterials as photocatalysts*, 307-337.
7. Perez-Taborda, J. A., Caballero-Calero, O., Vera-Londono, L., Briones, F., & Martin-Gonzalez, M. (2018). High thermoelectric zT in n-type silver selenide films at room temperature. *Advanced Energy Materials*, 8(8), 1702024.
8. Thirumavalavan, S., Mani, K., & Sagadevan, S. (2015). Investigation of the structural, optical and

- electrical properties of copper selenide thin films. *Materials Research*, 18, 1000-1007.
9. Mohanty, B. C., Murty, B. S., Vijayan, V., & Kasiviswanathan, S. (2006). Atomic force microscopy study of thermal stability of silver selenide thin films grown on silicon. *Applied surface science*, 252(22), 7975-7982.
 10. Pawar, S. J., Chikode, P. P., Fulari, V. J., & Dongare, M. B. (2007). Studies on electrodeposited silver selenide thin film by double exposure holographic interferometry. *Materials Science and Engineering: B*, 137(1-3), 232-236.
 11. Das, S., Priyadarshini, P., Alagarasan, D., Vardhrajperumal, S., Ganesan, R., & Naik, R. (2022). Role of tellurium addition on the linear and non-linear optical, structural, morphological properties of Ag₆₀-xSe₄₀Te_x thin films for nonlinear applications. *Journal of the American Ceramic Society*, 105(5), 3469-3484.
 12. Santhosh M. C.K and Pradeep B (2002). Electrical properties of silver selenide thin films prepared by reactive evaporation. *Bull. Mater. Sci.*, 25(5), 407-411.
 13. Chougale, U. M., Han, S. H., Rath, M. C., & Fulari, V. J. (2013). Synthesis, characterization and surface deformation study of nanocrystalline Ag₂Se thin films. *Materials Physics and Mechanics*, 17(1), 47-58.
 14. Chandrasekar, L. B., Vijayalakshmi, R., Rajeswari, B., Chandramohan, R., Arivazhagan, G., & Packiaseeli, S. A. (2014). Preparation and characterization of silver selenide thin film. *Brazilian journal of physics*, 44, 653-657.
 15. Mølneås, H., Paul, S. J., Scimeca, M. R., Mattu, N., Paredes, I. J., Röhr, J. A., ... & Sahu, A. (2023). Understanding the growth mechanisms of ultrasmall silver selenide quantum dots for short-wave infrared detectors. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 674, 131946.
 16. Sobhi S.N and Hussein B. H (2022). Influence of Al dopant on structural and optical parameters of AgInSe₂ thin film. *Chalcogenide Letters*, 19(6), 409 – 416.
 17. Shannon R.D (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A*, 32(5), 751-767.
 18. Emegha, J. O., Elete, E. D., Efe, F. O. O., & Adebisi, A. C. (2019). Optical and electrical properties of semiconducting ZnS thin film prepared by chemical bath deposition technique. *Journal of Materials Science Research and Reviews*, 2(3), 411-418.
 19. Nwori, A. N., Ezenwaka, L. N., Ottih, I. E., Okereke, N. A., Umeokwona, N. S., Okoli, N. L., & Obimma, I. O. (2021). Effect of deposition voltage variation on the optical properties of PbMnS thin films deposited by electrodeposition method. *Journal of Physics and Chemistry of Materials*, 8(3), 12-22.
 20. Muomeliri, C. B., Ekpunobi, A. J., Okoli, D. N., Okafor, C., Mimi, J. D., Odikpo, O. E., Anusiobi, O., Nwaodo, A., Azubogu, A., Ozobialu, L., E, O., Chiamaka, O., Chibuogwu, I., Nwori, A. N., & Okoli, N. L. (2024). Influence of Ti Doping on the Optical and Structural Properties of ZnTiO Thin Films Deposited by Electrodeposition Technique. *Journal of Materials Science Research and Reviews*, 7(4), 493-506.
 21. Pathak, T. K., Kumar, V., Purohit, L. P., Swart, H. C., & Kroon, R. E. (2016). Substrate dependent structural, optical and electrical properties of ZnS thin films grown by RF sputtering. *Physica E: low-dimensional systems and nanostructures*, 84, 530-536.
 22. Ali H.M and Khudayer I. H (2023). Influence Annealing on the Physical Properties of Silver Selenide Thin Film at Different Temperatures by Thermal Evaporation. *Ibn Al-Haitham Journal for Pure and Applied Sciences*, 36(2), 147-155.
 23. Pandiaraman M and Soundararajan N (2012). Micro-Raman studies on thermally evaporated Ag₂Se thin films, *Journal of Theoretical and Applied Physics*, 6(7), 1-5.
 24. Nwori, A. N., Ezenwaka, L. N., Ottih, I. E., Okereke, N. A and Okoli, N. L. (2022). Study of the Optical, Structural and Morphological Properties of Electrodeposited Copper Manganese Sulfide (CuMnS) Thin Films for Possible Device Applications. *Trends in Sciences*, 19(17): 1-11