Morphology and optical properties of CuAlS$_2$ crystals prepared using the solid-phase Al and S precursors

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Received: 05$^{th}$ March 2019, Revised: 25$^{th}$ May 2020, Accepted: 25$^{th}$ June 2020

Abstract Copper dithiocarbamate and aluminium dithiocarbamate were prepared and then characterized by infrared spectroscopy. The combination of the prepared precursors in different ratios was deposited on glass substrates using metal-organic chemical vapour deposition (MOCVD) technique at 450$^\circ$C through the pyrolysis of the precursors to yield Cu-Al-S thin films. Compositional, morphological, structural and optical characterizations were then carried out. The compositional analysis revealed that the ratio of Cu to Al in the precursor is not preserved in the films. Morphological study showed that the films are polycrystalline in nature whose homogeneity and grain size distribution decrease with a decrease in Al content of the films. The crystallinity of the films was further revealed from the PXRD results with the formation of the Cu-Al-S crystal structure as the Al content increases in the precursor. The energy gap obtained falls between 2.63 and 2.75 eV which decreases as the Al content in the films decreases. Optical constants such as refractive index and extinction coefficient exhibit a decreasing trend as the Al content in the film decreases.

Keywords: Energy gap, infrared spectroscopy, MOCVD, semiconductors, thin film.

1 Introduction

Copper aluminium sulphide has gained much attention due to its special properties such as high absorption coefficient of about 10$^5$ cm$^{-1}$ and wide direct energy gap of about 3.49 eV together with its constituent elements (Cu, Al and S) which are non-toxic and abundant in nature (Jaffe and Zunger 1983). These properties of Cu-Al-S have made it a potential material in many different optoelectronic applications such as oxygen gas sensor eyeglass industry, optical detectors, solar cells, light-emitting diodes (LED) and nonlinear optics (Abaab et al. 2000, Reshak and Auluck 2008). Several methods have been employed to synthesize Cu-Al-S semiconductors in the form of thin-films. These methods include chemical spray pyrolysis, atomic layer deposition (ALD), chemical vapour transport (CVT), thermal evaporation technique,
sulfurization, dip coating (Olejniček et al. 2011, Chaki et al. 2013, Duclaux et al. 2015, Kumar et al. 2015, Ahmad 2017). Other methods reported are metal decomposition (MD), chemical bath deposition technique (CBD), vacuum thermal evaporation, spray pyrolysis technique, thermal evaporation technique, and iodine transport (Miyake et al. 1995, Abaab et al. 2000, Brini et al. 2009, Mujdat et al. 2008, Alwan and Jabbar 2011). Most of these methods have their disadvantages which range from non-uniformity with different levels of impurities to lack of reproducibility.

In our previous study (Damisa et al. 2017), we established that the growth of CuAlS$_2$ from a single source precursor using the MOCVD technique is achievable. However, we observed from literature that the growth of CuAlS$_2$ in thin-film form proceeds via two or more precursors where a stable film of CuAlS$_2$ was not achieved (Miyake et al. 1995, Benchouck et al. 1999). This we believe due to the active aluminium in the matrix of CuAlS$_2$. Aluminium is highly sensitive to moisture, and it hydrolyses in air to form its oxide and hydroxide. This property of aluminium poses the difficulty in the growth of stable CuAlS$_2$. Duclaux et al. (2015) studied the effect of the number of Al-S cycles with respect to Cu-S cycles on the growth rate of Cu-Al-S but reported that none of the films grown represented a Cu-Al-S crystal structure. Therefore, the present study was designed to use solid source precursors of Cu and Al to grow Cu-Al-S thin films. These solid source precursors are novel to the best of our knowledge and are scarcely reported in the literature. The MOCVD technique used in this study had been previously used to synthesize binary and ternary oxides (Ajayi et al. 1994, Adedeji et al. 2002) and sulphide films (Osasona et al. 1997, Eleruja et al. 1998, Damisa et al. 2017).

2 Material and Methods

2.1 Preparation and characterization of precursor

Preparation of the intermediate complex had been reported previously by Damisa et al. (2017) by modifying the method of Ajayi et al. (1994). This was followed by coupling of the intermediate complex to prepare the various precursors. The preparation of copper dithiocarbamate followed the following procedure. Dried ammonium morpholino-dithiocarbamate (6.00 g, 0.03 M) was dissolved in 50:50 (v/v) of acetone – water solvent. Copper (II) chloride (3.00 g, 0.02 mol) was dissolved in 50 cm$^3$ of ethanol. Solution of copper (II) chloride in ethanol solvent was added gradually to the solution of ammonium morpholino-dithiocarbamate on a hot plate and stirred vigorously. Upon addition, there was a spontaneous formation of a brown precipitate which was heated for about 30 minutes at a temperature of 50 °C. The product was then filtered, allowed to dry in air for 24 h, and put in an oven maintained at a temperature of 60 °C for 96 h. The yield was found to be 58.40%. The same route was followed in the preparation of aluminium dithiocarbamate where 6.00 g (0.03 mol) of ammonium morpholino-dithiocarbamate was dissolved in 50:50 (v/v) of acetone – water solvent. Aluminium (III) chloride (2.00 g, 0.015 mol) was also dissolved in 30:10
(v/v) of ethanol-water solvent. Solution of aluminium (III) chloride in ethanol-water solvent was gradually added to the solution of ammonium morpholino-dithiocarbamate on a hot plate and stirred vigorously. Upon addition, spontaneous formation of a white solution was occurred which was then put in a freezer for 24 h to precipitate. The product formed was then filtered, allowed to dry in air for 24 h after which it was put in an oven maintained at a temperature of 60 °C for 96 h and the yield was found to be 44.33%.

The copper dithiocarbamate and aluminium dithiocarbamate were ground into smooth powder and characterized by infrared (IR) spectroscopy using a Shimadzu FTIR-8400 S spectrophotometer. The transmission spectrum was measured in KBr at normal incidence angle of \( \theta = 90^\circ \) over the range of 4000 and 500 cm\(^{-1}\) at ambient room temperature.

### 2.2 Film deposition and characterization

Combination of copper dithiocarbamate and aluminium dithiocarbamate in different proportions were deposited on the substrate (Table 1). These precursors were ground into smooth powder, poured into a receptacle and nitrogen gas was bubbled through at a pressure rate of 2.5 dm\(^3\)/min. The nitrogen-borne particle was then transported into the chamber which consists of a pyrex tube maintained at 450°C. To maintain good and uniform thermal contact, the substrate was supported on a steel block. The deposition process lasted for 2 h. During this process, the precursor sublimed before thermal decomposition on reaching the chamber, resulting in the formation of the films. The substrate, the steel block, and the pyrex tube were cleansed in distilled water, methanol, ethanol, acetone and distilled water before each deposition. To reduce some of the handling problems associated with sulphur, the deposition process was carried out in a fume cupboard. The MOCVD technique used in this work has the added advantage of not needing a machine-driven pump to expunge the byproduct as they are carried away by the nitrogen inert gas. After all the deposition, the films were designated as CAS1, CAS2, and CAS3 for easy identification.

| Thin Films | Precursor combination                                      |
|------------|-----------------------------------------------------------|
| CAS1       | 80% copper dithiocarbamate + 20% aluminium dithiocarbamate |
| CAS2       | 50% copper dithiocarbamate + 50% aluminium dithiocarbamate |
| CAS3       | 20% copper dithiocarbamate + 80% aluminium dithiocarbamate |

Compositional analysis was carried out using Phenom ProX energy dispersive X-ray (EDX) machine operated with acceleration voltages of 15 kV while the surface morphology was carried out by Zeiss Ultra plus 55 field emission scanning electron microscope (FE-SEM) operated at an accelerated voltage of 1.0 kV. The film was coated with gold in order to avoid charging effect and enhance the SEM micrograph.
The coating of the films was carried out using Coater Quorum (Q150R ES). The structural analysis was carried out by D8 Advance X-ray diffractometry (XRD) using CuKα radiation (\( \lambda = 1.5406 \, \text{Å} \)). The optical properties of the films were investigated at room temperature using Janway 6405 UV-visible spectrophotometer in the wavelength range of 300-1500 nm.

3 Results and Discussion

3.1 Infrared spectrophotometry of the precursor

![IR spectrum](image)

Fig. 1. IR spectrum of (a) aluminium dithiocarbamate complex and (b) copper dithiocarbamate complex.
The IR spectrum in Figure 1 shows that the two complexes exhibit the basic absorption bands between 4000 and 500 cm\(^{-1}\). The major peaks in Figure 1a are O-H vibration at 3421 cm\(^{-1}\), C-H vibration between 3037 and 2862 cm\(^{-1}\) and the three N-H bonds between 2476 and 2177 cm\(^{-1}\), the carbonyl stretching, C at 1631 cm\(^{-1}\), C-C stretching at 1419, 1219 and 1105 cm\(^{-1}\). Al-S bands are below 422 cm\(^{-1}\). In Figure 1b, the major peaks are O-H vibration at 3443 cm\(^{-1}\), C-H vibration between 2968 and 2854 cm\(^{-1}\), the carbonyl stretching, C at 1707 cm\(^{-1}\), C-C stretching at 1485, 1232, 1111 and 1026 cm\(^{-1}\), and Cu-S bands are below 420 cm\(^{-1}\). The peaks are real and plots above 420 and 422 cm\(^{-1}\) showed an insignificant result.

3.2 Compositional analysis

The spectra as shown in Figure 2 revealed the presence of Cu, Al, S and other elements that can be associated with the glass substrate without any carbon impurity.

![Fig. 2. EDX spectrum for Cu-Al-S thin films, (a) CAS1 (b) CAS2 and (c) CAS3.](image)

The Figure 2 shows that there is a complete pyrolysis of copper dithiocarbamate and aluminium dithiocarbamate to form Cu-Al-S thin films. The proportion of elements in the film Cu:Al:S was found to be 32.93: 35.03: 32.04 for CAS1, 42.40: 29.00: 28.60 for CAS2 and 42.64: 28.63: 28.73 for CAS3. These results are given within the limit of the equipment used. Furthermore, it is observed that the ratio of Cu to Al in the various combinations of copper dithiocarbamate and aluminium dithiocarbamate used as precursor is not preserved in the films. In fact, the aluminium content in the films decreases as the aluminium content in the precursor increases. Here, it is believed to be due to the reason that when the precursor first sublime in the hot zone of the MOCVD reactor, it results in the breakdown of the metal-metal bonds of the precursor in the vapour phase, and at the deposition temperature, there will be subsequent reconstitution of the bonds. This possible reconstitution of the bonds after the breaking of the metal-metal bonds then leads to the obtained stoichiometry in the various CAS films. This hypothesis has been observed by Adediji et al. (2002) and Eleruja et al. (1998).
3.3 Morphological analysis

Figure 3 shows the SEM micrograph of the deposited films. For 20% aluminium complex, the films (CAS1) are dense and the particle size distribution seems to be broad. It also shows the coalescence of small grains into big grains, which are well distributed over the surface. For the films deposited with 50% of aluminium complex (CAS2), the grains are seen to coalesce into short rods which are continuous with well-connected grains, dense, homogenous and without any visible cracks. As the aluminium complex increases to 80% (CAS3), the films show that the particle size distribution of the grains seems to be less broad, less dense and non-homogeneous with the formation of nano-rods. Furthermore, the micrographs revealed that all the deposited films are polycrystalline in nature. Overall, homogeneity and grain size distribution decrease with a decrease in aluminum content of the films.

3.4 Structural analysis

The X-ray diffraction of the film deposited at different aluminium content is shown in Figure 4. The film deposited with 20% aluminium complex (CAS1) shows that there is no Cu-Al-S crystal structure but a mixture of Cu$_{2}$S$_{x}$ polymorphs such as CuS$_{2}$ (chalcopyrite) with diffraction angle at 29.095° and Cu$_{38}$S$_{28}$ (spionkopite) with diffraction angle at 27.706°. Films deposited with 50% aluminium complex (CAS2) show the formation of Cu-Al-S crystal structure with intense peaks occurring at diffraction angle 29.329° with a preferred orientation at 112 planes and other peaks observed belong to the chalcopyrite Cu$_{2}$S polymorphs with diffraction angle at 35.631°, 32.028°, and 38.686° respectively. Also, films deposited with 80% aluminium complex show the formation of Cu-Al-S crystal structure with prominent peaks at diffraction angle 29.257° with a preferred orientation at 112 planes. Other peaks recorded belong to the Cu$_{2}$S (chalcopyrite) structure at diffraction angle 35.645°. Accordingly, the results showed that as the aluminium content in the precursor is increased, the films deposited...
become more crystalline. There is also an increase in the formation of the Cu-Al-S structure which is clearly in contrast to the result of Duclaux et al. (2015).

3.5 Optical properties

Figure 5 shows the transmission spectrum in the wavelength range of 300-1500 nm for all the CAS thin films deposited at 450 °C.
It was observed that all the films have high transmittance in the visible and near-infrared region. However, the transmittance decreases as the content of aluminium in the films decreases with CAS3 having the lowest. This is believed to be due to the non-homogeneous nature of CAS3 as observed by the SEM micrograph (Figure 3c) (Smaili 2011). Also, the high transparency in the visible region implies that the films absorb less photon of light imposed on it. This property of high transmittance in the VIS and IR makes the films suitable material for eyeglass industry as they are capable of transmitting the visible radiation needed for vision (Damisa et al. 2017).

The absorption co-efficient, $\alpha$ is evaluated using Equation (1) (Harbeke, 1972)

$$\alpha = \frac{1}{l} \ln \left( \frac{1}{T} \right),$$

where $t$ is the thickness of the films with values 319, 670 and 102 nm for CAS1, CAS2 and CAS3 films respectively. The optical energy gap can be estimated from the Tauc plot (Tauc, 1974)

$$\alpha = \frac{A}{h\nu} \left( h\nu - E_g \right)^r,$$

where $r$ is an index which can be assumed to have values, 1/2, 3/2, 2 and 3 depending on the nature of the electronic transition responsible for the absorption. Exponent $r = 1/2$ is for allowed direct transitions, $r = 2$ for allowed indirect transitions, $r = 3$ for forbidden indirect transitions and $r = 3/2$ for forbidden direct transitions. Figure 6 shows the plot of square of absorption against photon energy. The extrapolation of the linear portion of the plot to the energy axis gives the energy gap of the various CAS thin films. The energy gap obtained is 2.75 for CAS1, 2.68 for CAS2 and 2.63 eV for CAS3. This shows a slight decrease in the band-gap as the aluminium content in the films decreases.

**Fig. 6. Square of absorption coefficient against energy for Cu-Al-S thin films (CAS1, CAS2 and CAS3).**
However, our observed band gap is smaller than the expected value of 3.49 eV for CuAlS$_2$ but gives a better result when compared with 2.30 – 2.60 eV reported by Duclaux et al. (2015). Similarly, the observed result in this study is in good agreement with 2.88 – 3.28 eV band gap reported in our previous study (Damisa et al. 2017) and 2.40 – 2.81 eV obtained by Alwan and Jabbar (2011). Different factors may cause such a reduction in the energy gap as aluminium content in the films decreases. The decrease in energy gap tailing which is triggered by the disorder of the film, defects, residual strain, impurities, and disorders of grain boundaries can cause the reduction (Hossain et al. 2017).

Other important parameters usually considered for materials to be used in optical applications include the refractive index, $n$ and the extinction coefficient $k$. In the region of inter-band transition that has strong absorption, $n$ and $k$ can be determined by Equations (3) and (5) respectively (Swanepoel 1983), only when the illuminations of electromagnetic waves are perpendicular to the surface of the film

$$x = \frac{(n-1)^2(n+s^2)}{16n^2s}T,$$  \hspace{1cm} (3)

where $s$ is the refractive index of glass and $x$ the absorbance given by Equation (4) (Swanepoel, 1983)

$$x = e^{-\alpha t},$$  \hspace{1cm} (4)

$$k = \frac{\alpha \lambda}{4\pi},$$  \hspace{1cm} (5)

where $\alpha$ and $\lambda$ are the absorption coefficient and wavelength respectively.

Fig.7. Refractive index against energy for Cu-Al-S thin films (CAS1, CAS2 and CAS3)

Figures 7 and Figure 8 show the plots of refractive index, $n$ versus energy, $E$ and extinction coefficient, $k$ versus energy $E$, respectively. The refractive index and extinction coefficient first increase at lower energy, then decrease with energy, and finally increase again at higher energy. This fluctuation of $n$ and $k$ can be attributed to
successive internal reflections or as a result of trapped photon energy within the grain boundaries (Ongal et al. 2000). We conclude from our XRD results that the overall increase of $n$ and $k$ with $E$ can be attributed to the degree of crystallinity of the films as the aluminium content in the films decreases.

4. Conclusions

Cu-Al-S thin films were deposited on the glass substrate by MOCVD technique at 450°C and pressure rate of 2.5 dm$^3$/min using different proportions of copper dithiocarbamate and aluminium dithiocarbamate as the precursor. The elemental composition of the films as determined by EDX revealed that the expected element that is copper, aluminium and sulphur are present. We also observed that the ratio of Cu to Al in the various combinations of copper dithiocarbamate and aluminium dithiocarbamate was not preserved in the films. Morphological study shows that the films are polycrystalline in nature whose homogeneity and grain size distribution decreases with a decrease in aluminum content of the films. The crystallinity of the films where further revealed from the XRD results which shows the formation of the Cu-Al-S crystal structure as the aluminium content increases in the precursor. From the optical characterization, the Cu-Al-S thin film shows a high transmittance in the visible and near-infrared region which decreases as the aluminium content of the films decreases. The energy gap obtained falls between 2.63 and 2.75 eV which decreases as the aluminium content in the films decreases. Other optical constants such as refractive index and extinction coefficient also exhibit a decreasing trend as the aluminium content in the film decreases. The energy gap values together with other
optical properties exhibited by the material can find applications in areas like solar cells and other optoelectronic devices.

Acknowledgements

The authors are grateful to Dr. Remy and the entire staff of iThemba laboratory, South Africa for their assistance in the PXRD measurements. The deposition process was carried out at the Material Science/Solid State Laboratory of the Department of Physics and Engineering Physics, Obafemi Awolowo University Ile Ife, Nigeria, so we thank the entire staff of the department. We also wish to appreciate two anonymous reviewers for their comments and suggestions.

References

Abaab M, Bouazzi AS, Rezig B. 2000. Competitive CuAlS$_2$ oxygen gas sensor. *Microelectronic Engineering* 51: 343–348. https://doi.org/10.1016/S0167-9317(99)00495-5.

Adeideji AV, Egharevba GO, Jeynes C, Ajayi EOB. 2002. Preparation and characterization of pyrolytically deposited (Co-V-O and Cr-V-O). *Thin Solid Films* 402: 49-54. doi:10.1016/S0040-6090(01)01602-9.

Ahmad SM. 2017. Study of structural and optical properties of quaternary Cu$_x$Ag$_{1-x}$AlS$_2$ thin films. *International Journal for light and Electron optics* 127: 10004-100013. doi:10.1016/j.ijleo.2016.07.034.

Ajayi OB, Osuntola OK, Ojo IOA, Jeynes C. 1994. Preparation and characterization of MOCVD thin films of cadmium sulphide. *Thin Solid Films* 248:57-62. https://doi.org/10.1016/0040-6090(94)90211-9.

Alwan T, Jabbar M. 2011. Structure and optical properties of CuAlS$_2$ thin films prepared via chemical bath deposition. *Turkish Journal Physics* 34: 107-116. doi:10.3906/fiz-1007-14.

Benchouck K, El Moctar C, Marsillac S, Bernede JC, Pouzet J, Barreau N, Emziane M. 1999. Growth and physicochemical characterization of CuAlTe$_2$ films obtained by reaction, induced by annealing, between Cu/Al/Te/Cu/Al... Al/Cu/Al/Te layers sequentially deposited. *Journal of Materials Science* 34: 1847-1853. doi:10.1023/A:1004575612586.

Brini R, Schmerber G, Kanzari M, Werckmann J, Rezig B. 2009. Study of the growth of CuAlS$_2$ thin films on oriented silicon (111). *Thin Solid Films* 517: 2191–2194. doi:10.1016/j.tsf.2008.10.086.

Chaki SH, Deshpande MP, Mahato KS. 2013. Growth and microtopographic study of CuAlS$_2$ single crystals. *American Institute of Physics Conference Proceedings* 1536: 833–834. doi:10.1063/1.4810486.

Damisa J, Olotinjana B, Ebonwonyi O, Bakare F, Azi SO. 2017. Morphological and optical study of thin films of CuAlS$_2$: deposited by metal organic chemical vapour deposition technique. *Materials Research Express* 4: 086412 (1-10). https://doi.org/10.1088/2053-589X/aa851d.

Ducaux L, Donsanti F, Vidal J, Bouttemy M, Schneider N, Naghavi N. 2015. Simulation and growing study of Cu–Al–S thin films deposited by atomic layer deposition. *Thin Solid Films* 594: 232–237. https://doi.org/10.1016/j.tsf.2015.06.014.

Eleruja MA, Adeideji AV, Ojo IAO, Djebah A, Osasona O, Aladekomo JB, Ajayi EOB. 1998. Optical characterization of pyrolytically deposited ZnxCd$_{1-x}$S thin films. *Optical Materials* 10: 257-263. doi:10.1016/S0925-3467(97)00178-X.

Harbeke G. 1972. Optical properties of semiconductor. Amsterdam: North-Holland Pub.Con.

Hossain MS, Kabir H, Rahman MM, Hasan K, Bashar MS, Rahman M, Gafur MA, Islam S, Amri A, Jiang ZT, Altarawneh M, B.Z. Dlugogorski BZ. 2017. Understanding the shrinkage of optical absorption edges of nanostructured Cd–Zn sulphide films for photothermal applications. *Applied Surface Science* 392: 854-872. https://doi.org/10.1016/j.apsusc.2016.09.095.
Jaffe JE, Zunger A. 1983. Electronic struture of the theory chalcopyrite semiconductors CuAlS₂, CuGaS₂, CuInS₂, CuAlSe₂ and CuInSe₂. Physical Review B 28: 5822-5847. https://doi.org/10.1103/PhysRevB.28.5822.

Kumar K, Jariwala C, Pillai R, Chauhan N, Raole PM. 2015. Preparation & characterization of SiO₂ interface layer by dip coating technique on carbon fibre for Cu/SiC composites. American Institute of Physics Conference Proceedings 1675: 020046 (1-4). doi:10.1063/1.4929204.

Miyake H, Yamada M, Sugiyama K. 1995. Vapor phase epitaxy of CuAlS₂ on CuGaS₂ substrate by the iodine transport method. Journal of Crystal Growth 153: 180-183. doi:10.1016/0022-0248(95)00199-9.

Mujdat C, Salha I, Yasemin C. 2008. Structural, morphological and optical properties of CuAlS₂ films deposited by spray pyrolysis method. Optics Communications 281: 1615-1624. doi:10.1016/j.optcom.2007.11.031.

Olejniček J, Flannery LE, Darveau SA, Exstrom CL, Kment S, Ianno NJ, Soukup RJ. 2011. CuIn₁₋ₓAlₓS₂ thin films prepared by sulfurization of metallic precursors. Journal of Alloys and Compounds 509: 10020-10024. doi:10.1016/j.jallcom.2011.08.016.

Ongal HC, Dai JY, Hung KC, Chan YC, Ho ST. 2000. Electronic structure of polycrystalline ZnO thin films probed by electron energy loss spectroscopy. Applied Physics Letters 77: 1484-1486. doi:10003-6951/2000/77(10)/1484/3/$17.00.

Osasona O, Djebah A, Ojo IAO, Eleruja MA, Adedeji AV, Jeynes C, Ajayi EOB. 1997. Preparation and characterization of MOCVD thin films of zinc sulphide. Optical Materials 7: 109-115. doi:10.1016/S0925-3467(96)00065-1.

Reshak AH, Auluck S. 2008. Electronic properties of chalcopyrite CuAlX₂ (X = S, Se, Te) compounds. Solid State Communication 145: 571-6. doi:10.1016/j.ssc.2007.12.034.

Smaili F. 2011. Effect of annealing on the structural and optical properties of CuIn₁₋ₓAlₓS₂ thin films. Materials Sciences and Applications 2: 1212-1218. doi:10.4236/msa.2011.29164.

Swanepoel R. 1983. Determination of the thickness and optical constants of amorphous silicon. Journal of Physics E 16: 1214-1222. https://doi.org/10.1088/0022-3735/16/12/023.

Tauc J. 1974. Amorphous and liquid semiconductor, London: Plenum. 159.