Optical Properties of $CuAl_2S$ Alloyed Thin Films Prepared Using Enhanced Successive Ionic Layer Adsorption and Reaction Method

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***Abstract*: The synthesis of $CuAl_2S$ alloyed thin films, have been deposited using enhanced successive ionic layer adsorption and reaction (SILAR). The substrates were prepared by soaking them in aqua regia for 48hours, washed with detergent, rinsed in de-ionized water and were allowed to dry in air. The complexing agent used was 3M of aqueous solution of ammonia (NH_4OH), 1.0M solution of hydrated copper sulphate ($CuSO_4:5H_2O$) was used as cation source and 2.3M solution thiourea ($SC(NH_2)_2$)as anionic source and 0.5M of aluminum sulphate($Al_2(SO_4)_3$ as the alloying source material. The deposition of $CuAl_2S$ alloyed thin films were carried out at room temperature of 23^0C. The films were annealed at varying times of 1hour-2hours and varying temperatures of 100^0C-250^0C. The structural properties of the films were determined using XRD for crystal structures and SEM for morphological studies. The XRD patterns of $CuAl_2S$ of samples C and D grown under the same conditions but different annealing temperatures of 150^0C and 200^0C and annealing times of 1hr and 2hrs respectively, have one diffraction peak each at $2\theta = 24.94^0$ and $2\theta = 24.93^0$ with the grain sizes of the alloys of 3.5674nm and 3.5688nm respectively. The atomic concentrations were determined using EDX. The add-atoms of Cu, Al and S found on sample C are 3.33mol/dm^3, 2.14mol/dm^3 and 3.27mol/dm^3 respectively. EDX for sample D, the concentrations of the add-atoms of Cu, Al and S are 1.97 mol/dm^3, 2.09mol/dm^3 and 3.42mol/dm^3 respectively. The transmittance was measured by UV-double beam spectrophotometer in the wavelength range of 200nm to 1200nm.Other optical properties such as absorbance, reflectance, absorption coefficient, optical constants, optical conductivity, dielectric constants, and optical band gaps were determined, using relevant equations. The band gaps were determined from the graph of $(\alpha h\nu)^2$ against the photon energy, hv, by extrapolation of the straight portion of the curves where $(\alpha h\nu)=0$. The band gaps of samples A, B, C, D and E are 3.74±0.05eV, 3.69±0.05eV, 3.66±0.05eV, 3.62±0.05eV and 3.60±0.05eV respectively with p-type property. Due to the high transmittance exhibited in the visible and near infrared regions of electromagnetic spectrum by the films, it can be found useful as effective material for transparent conducting electrodes for photo-electronic applications, solar control coatings, tint on eyeglasses, poultry house warmer, sensors for gaseous substances and solar cell fabrications.**

***Keywords*: Thin Films, Adsorption, Absorbance, Band gap, Dielectric Constant, SILAR Technique**

I. INTRODUCTION

The chalcopyrite thin films have been in use as oxygen gas sensor at room temperature showing an enhanced sensitivity with the aging of the film(Chaki *et al*, 2017). Nanocrystals have been employed in targeted in-vitro imaging of cancer cells after nano-engineering their surface. The chalcopyrite micro- and nano-particles have been used as the catalyst in cellulose pyrolysis (Chaki *et al*, 2015). CuS nano-particles exhibit excellent physical, chemical, structural and surface properties which are very much different from bulk material. CuS has wide range applications in photo-catalysis, solar cells, sensors and as a cathode material in lithium chargeable batteries. (Salavati *et al.*, 2013 ; Eya and Eze, 2009; Offiah *et al*., 2012; Ajaya *et al*., 2013). CuS is an important semiconductor material because of its nonlinear optical properties (Chopra and Kaur, 1983), increased conductivity at high temperature (Umair *et al.*, 2016), excellent solar radiation absorbing properties (Buba and Adelabu.,2009) and high capacity cathode material in lithium secondary batteries (Chung *et al.*, 2002) and low energy band gap of 1.88eV with p-type property.

Thin film materials of nanometers and micrometers sizes can easily be prepared by successive ionic layer adsorption and reaction (SILAR) deposition technique. This method is suitable for industrial applications to develop synthetic materials of suitable properties for communication, information and solar energy conversion with decreased size of active electronic components, a higher packing density, higher seed performance and lower cost(Pathan and Lokhande, 2004).

Literature shows no report of deposition or study of chalcopyrite thin films of $CuAl_2S$ using enhanced SILAR deposition technique.

II. MATERIALS AND METHOD

$CuAl_2S$ thin films are deposited on glass substrates using enhanced successive ionic layer adsorption and reaction from aqueous solution of hydrated copper sulphate ($CuSO_4:5H_2O$) and solution of aluminum sulphate as cationic precursors and

the solution of thiourea and ammonia (NH_3) as anionic precursor and complexing agent respectively. The samples were grown at the pH value of 5.3. Enhanced SILAR deposition setup comprises of five containing vessels(beakers) instead of four traditional vessels as depicts in Figures 1: (a), (b), (c), (d) and (e), contain the cation, water, anion, water and the alloying material (Al^{3+}) respectively. Hydrated copper sulphate was made to react with ammonia, forming a deep blue solution of copper tetra-amine complex ion in excess ammonia. This is given in equation (1) and it provides the cationic base for the reaction process as shown in Figure (1a). The substrate was immersed in it for 5seconds and then removed and rinsed for 2 s in a beaker containing de-ionized water in Figure 1 (b) for weakly adsorbed atoms on the substrate to be removed by the water. The rinsed substrate was immersed in the third beaker for another 5s as depicts in Figure 1(c) for there to be a reaction between copper atoms impinged on substrate and sulphur atoms from the anionic precursor solution as shown in Figure 1(c). The reaction is given in equation (2). The deposit was rinsed in the forth beaker containing de-ionized water in order to remove un-adsorbed atoms that are loosely impinged on the substrate. The process of complete deposition was done for 20 cycles. In each dip, it took 5seconds in the cationic and anionic precursor solutions after which it was dipped in the fifth beaker containing aluminum tetra-amine complex ion solution shown in Figure 1(e) for 3seconds leading to the formation of chalcopyrite $CuAl_2S$, as given in equations (3) and (4). Four other samples were deposited under the same conditions as given above.

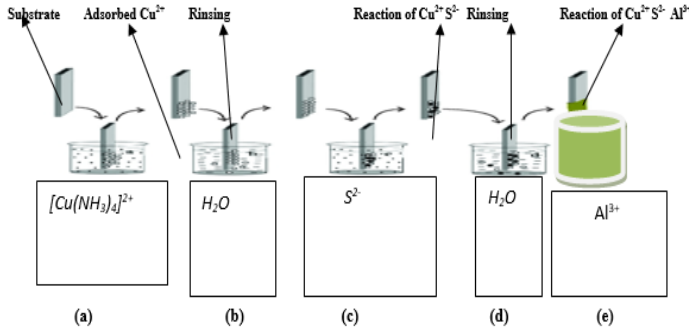

Figure 1 Set up of enhanced SILAR method(Pathan and Lokhande, 2004)

Reaction Mechanism

The reactions that led to the formationof $CuAl_2S$ alloye4d thin films as shown in Figure 1 are givenin equations (1),(2), (3), (4).

$$CuSO_4 :5H_2O + 4NH_{3(g)} \rightarrow [Cu(NH_3)_4]^{2+} + 5H_2O + SO_4^{2-} \quad (1)$$

$$[Cu(NH_3)_4]^{2+} + CS(NH_2)_2 \rightarrow CuS + C(NH_2)_2 + 4NH_3 \quad (2)$$

$$Al_2(SO_4)_3 + 4NH_3 \rightarrow 2[Al(NH_3)_2]^{3+} + 3SO^{2-}_4 \quad (3)$$

$$CuS + 2[Al(NH_3)_2]^{3+} \rightarrow CuAl_2S + 4NH_3 \quad (4)$$

III. RESULTS AND DISCUSSION

The results obtained from experimental procedure and characterizations are discussed below.

Table 1 The annealing time, temperature and thickness of samples A to E

Sample name	Time (hr)	Temperature (°C)	Thickness (nm)
A	1	100	135.87
B	1	150	128.56
C	1	150	129.65
D	2	200	108.08
E	2	250	100.43

The deposited samples were annealed between 100°C to 250°C at varying times of 1hour and 2 hours with the aim of removing water of crystallization and volatile atoms from them. The thicknesses of the samples decrease as the annealing temperature and annealing time increase as shown on Table 1.

Structural Properties of Samples C and D

X-ray diffraction of samples C and D are measured using Miniflex 600 by Rigaku Cooperation Japan. Figures 2 and 3, show that XRD patterns of $CuAl_2S$ has monoclinic crystal system of preferred orientations at (101). Samples C and D grown under the same conditions but different annealing temperatures of 150°C and 200°C and annealing times of 1hr and 2hrs respectively as given on Table 1, have one diffraction peak each at 2θ =24.94° and 2θ=24.93° with the grain sizes of 3.5674 nm and 3.5688 nm respectively.

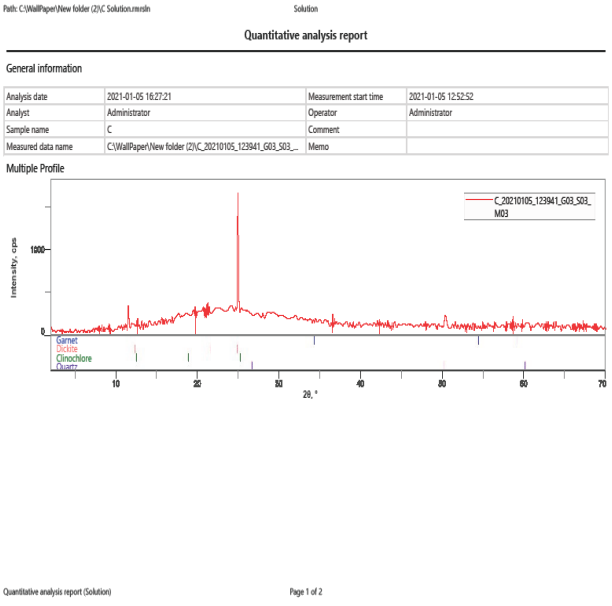

Figure 2 XRD of sample C

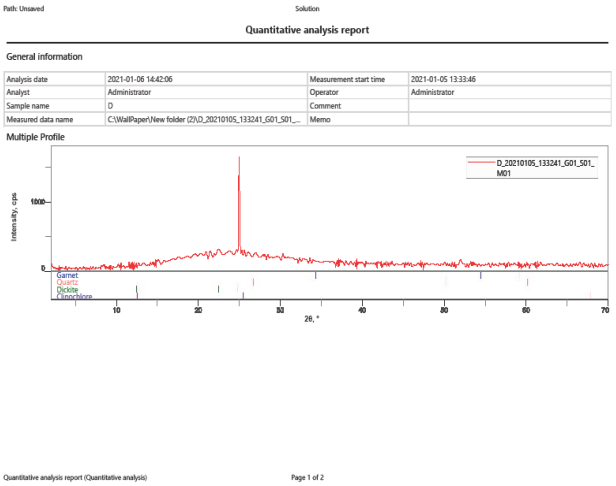

Figure 3 XRD of sample D

Table 2 Elemental concentration of sample C

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
14	Si	Silicon	55.57	45.89
82	Pb	Lead	2.03	12.37
20	Ca	Calcium	9.52	11.22
11	Na	Sodium	9.24	6.24
29	Cu	Copper	3.33	6.22
8	O	Oxygen	6.65	3.13
16	S	Sulfur	3.27	3.08
12	Mg	Magnesium	3.23	2.31
19	K	Potassium	1.59	1.83
47	Ag	Silver	0.56	1.78
13	Al	Aluminium	2.14	1.70
48	Cd	Cadmium	0.50	1.65
17	Cl	Chlorine	1.39	1.45
15	P	Phosphorus	0.74	0.67
30	Zn	Zinc	0.24	0.47

Table 3 Elemental concentration of sample D

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
14	Si	Silicon	58.21	52.53
20	Ca	Calcium	10.05	12.95
11	Na	Sodium	9.66	7.13
82	Pb	Lead	0.65	4.35
29	Cu	Copper	1.97	4.03
16	S	Sulfur	3.42	3.52
8	O	Oxygen	6.62	3.40
48	Cd	Cadmium	0.79	2.85
12	Mg	Magnesium	3.51	2.74
47	Ag	Silver	0.53	1.84
13	Al	Aluminium	2.09	1.81
19	K	Potassium	0.85	1.07
17	Cl	Chlorine	0.83	0.94
15	P	Phosphorus	0.83	0.82

Morphology of Samples C and D

The Phenom Proxy by Phenom World Eindhoven, Nethertland scanning electron microscope was used to scan samples C and D (representative samples). Sample C as revealed by scanning electron microscope (SEM) in Figure 4 shows that it has rough dark surface with white spots and a loop close to the center of the material which indicate the inter-atomic interactions between the constituent atoms that made up the emergent thin film compound which could be due to the presence of Al^{3+}. Figure 5 is the image of sample D as studied by scanning electron microscope, it shows that the deposited sample has a rough surface with very tiny white spots and a loop close to the center of the material, which could also be due to the presence of heavy Al^{3+}.

Elemental Compositions of Samples C and D

The EDX for Sample C as shown in Table 2 gives the various atomic concentrations of the deposited material. The add-atoms of Cu, Al and S are 3.33*mol/dm*^{3}, 2.14*mol/dm*^{3} and 3.27*mol/dm*^{3} respectively. The other atomic concentrations are associated with the substrate. EDX for Sample D as depicts in Table 3, the concentrations of the the add-atoms of Cu, Al and S are 1.97 *mol/dm*^{3}, 2.09 *mol/dm*^{3} and 3.42 *mol/dm*^{3} respectively. Also, other atomic concentrations are associated with the substrate.

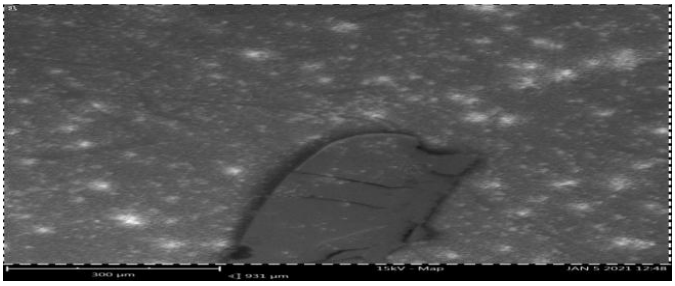

Figure 4 Scanned electron microscopy of sample C

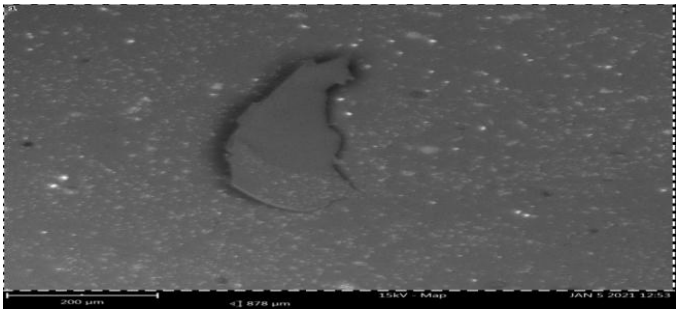

Figure 5 Scanned electron microscopy of sample D

IV. OPTICAL CHARACTERIZATION PROPERTIES

The optical properties of the thin films are transmittance, reflectance, absorbance, absorption coefficient, refractive index, extinction coefficient, optical conductivity and optical energy band gap. The transmittance was measured using UVI double beam spectrophotometer of the range of 200nm to 1200nm. Other optical properties of the films were obtained by using appropriate equations.

Transmittance

The high transmittance values were measured using UVI double beam spectrophotometer as shown in Figure 6. Samples A, C, D and E share similar characteristics of high transmittance as depicts in Figure 6 and this is as a result of the presence of the Al ion, while sample B and C have lowest transmittance, 20% at the UV and B has slightly high transmittance through the visible to near infrared regions. This means that samples A, C, D and E can be used as heat and cold windows in infrared optics, solar control coatings, eyeglasses, and warmer for poultry houses since it has high transmittance in the near infrared region of electromagnetic spectrum. Samples A, B, C, D and E can be used as UV filter because of their low transmittance at the UV. Most importantly, samples A, C,D and E can be effective materials for the fabrication of transparent electrodes for photo-electronics due to high transparency they exhibited in the visible and in the near infrared regions of electromagnetic spectrum.

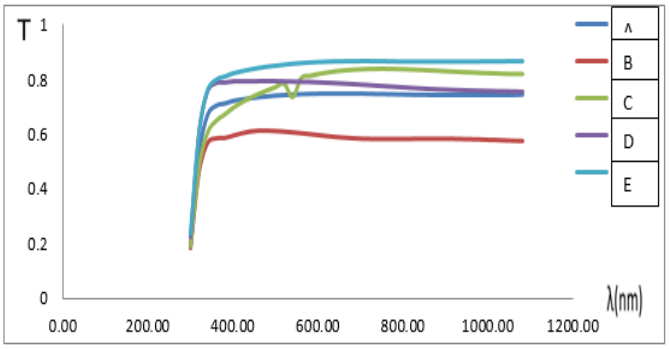

Figure 6 Graph of transmittance against wavelength

Absorbance

The absorbance is calculated using the equation.

$$A = \log_{10}(1/T) \qquad (4)$$

The graphs give sharp absorbance with increasing wavelength that indicates a shift from a region of high absorbance to a region of low absorbance as shown in Figure 7. Samples A, B, C, D share similar characteristics as indicated from the graph while sample E has the lowest absorbance of 0.06 and it can be used as UV sensors and UV spectroscopy because of its lower absorbance in the infrared region while sample A, B, C, D can be used as gas sensors.

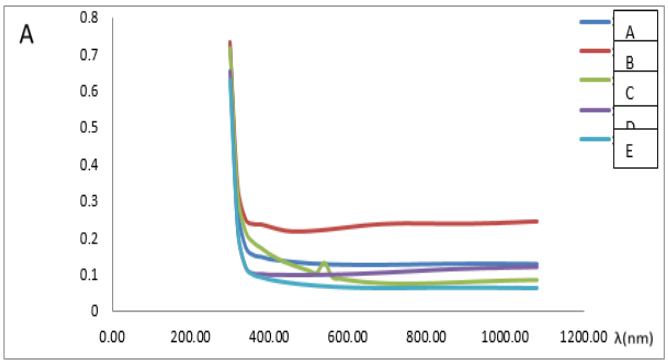

Figure 7 Graph of absorbance against wavelength

Reflectance

The ratio of the total amount of radiation of light reflected by a surface to the total amount of radiation incident on the surface. Reflectance is calculated as

$$R = 1 - (T + A)$$

Samples A, B, C, D and E decrease with increasing wavelength from the visible to near infrared regions of electromagnetic spectrum as shown in Figure 8. It means that since it shows almost linearly decrease in reflectance with increasing wavelength. It can therefore be used in multi-film layer technology to form antireflection coatings of almost zero reflectance in the visible spectrum and also, it can be found useful in solar energy conversion for opto-electronic applications.

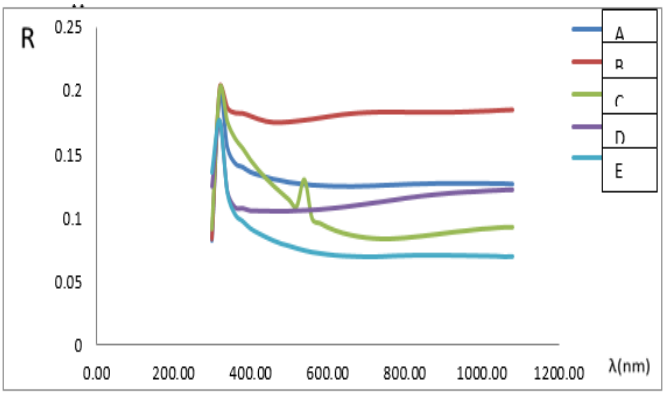

Figure 8 Graph of reflectance against wavelength

Energy Band Gap

The band gaps of the samples were determined from the graphs of $(\alpha hv)^2$ against photon energy hv, by extrapolation of the straight portion of the curve where $(\alpha hv)=0$, at the photon energy, hv. Samples A, B, C, D and E have band gaps of 3.74eV, 3.69eV, 3.66eV, 3.62eV and 3.60eV as shown in Figure 9. This material with wide energy band gap, can be found applicable in photo-electronics, photovoltaics, thin film electrodes, thin film transistors, liquid crystal displays etc.

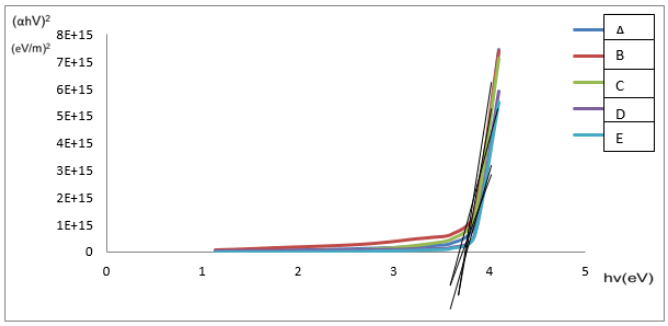

Figure 9 Graph of $(\alpha hv)^2$ against photon energy(hv)

V. CONCLUSION

The aim of this work was to successfully deposit chalcopyrite $CuAl_2S$ thin films. This was achieved using enhanced SILAR deposition method which was preferred over all other deposition methods, because of its easy process of deposition procedure. The substrates were prepared in aqua regia in order to degrease and create nucleation centers where captures take place. The complexing agents used was ammonia (NH_3) while hydrated copper sulphate ($CuSO_4.5H_2O$) solution was used as cation source and thiourea ($SC(NH_2)_2$) solution and aluminum Sulphate ($Al_2(SO_4)_3$ solution were employed as anion and dopant respectively. The pH value of the deposited samples is 5.3. The molarities of the ($CuSO_4.5H_2O$) solution, thiourea ($SC(NH_2)_2$) solution and aluminum sulphate ($Al_2(SO_4)_3$ solution are 1.0mol/dm^3, 2.3mol/dm^3 and 0.5mol/dm^3 respectively. The deposition of $CuAl_2S$ thin films was carried out at room temperature of 23°C. The films were annealed for varying times and varying temperatures. The structural properties of the films were determined using SEM and XRD. The atomic concentrations were determined using EDX. The transmittance was measured by UV1 double beam spectrophotometer in the wavelength range of 200nm to 1200nm. The values were used as default to calculate the values of other optical properties; absorbance, reflectance, absorption coefficient, optical constants, optical conductivity, dielectric constants etc. The graphs of optical properties were plotted against wavelength for all five samples. The band gap was determined from the graph of $(\alpha hv)^2$ against photon energy, hv by extrapolation of the straight portion of the curve where $(\alpha hv)=0$. The band gap for samples A, B, C, D and E are 3.74 eV, 3.69 eV, 3.66 eV, 3.62 eV and 3.60 eV respectively. From the properties of the films, it can be used effectively as coatings for solar control applications, tint on eyeglasses, warming of poultry houses, solar cell fabrications and most importantly as transparent electrode for photo-electronic applications.

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CONFLICT OF INTEREST

There is no conflict of interest between the authors.

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