Transactions of the Nigerian Association of Mathematical Physics
Volume 14, (January - March, 2021 Issue), pp173 –178

DUAL SOLUTION SYNTHESIS OF CUS: ZNS ALLOYED THIN FILMS FOR POSSIBLE APPLICATIONS

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Abstract

CuS:ZnS alloyed thin films were successfully deposited on glass substrates using two solutions based methods: electroless and SILAR. The deposited alloyed sulphides were annealed between (373-423) K using master chef annealing machine. The crystallographic studies were done using XRD and SEM which indicates that the samples are polycrystalline and have cubic crystal systems. Rutherford Back Scattering analysis confirmed the percentage of the elements of copper, zinc and sulphur alloyed sulphide thin films.

Keywords: Alloy, Thin films, Annealing

1. Introduction

The importance of energy in our lives and nation building is evident which cuts across the socio-economic and political lives of the citizenry both in rural and urban areas. In spite of the fact that energy lies around us in large quantities in different ways naturally-sun, wind, and biomass; there must be a way of harnessing them in order to achieve a desired purpose. Researches have shown that the year of oil production at its peak is past. Researchers have been challenged to search for the most economic and efficient technique for tapping the huge solar energy available on earth due to the problems and depletion caused by the existing source of energy-fossil fuel. The standard of living of a nation widely depends on the energy consumption and reduction in its supply may lead to change in lifestyle of the people and equally affect security of the nation.

Presently, researchers' interest in solar energy is in efficient, durable and low cost conversion systems as well as solar devices whose absorption of solar radiation in wavelength dependent. To achieve this goal, solar cells made of sulphide alloy thin films that are relatively inexpensive and readily available for use are employed. Sulphide alloys play important roles in many large and small scale applications

The films have been prepared from a wide variety of materials.

1.1 Alloys

An alloy is a mixture of metals or a mixture of a metal and another element. Alloys are defined by a metallic bonding character. An alloy may be solid solution of metal elements (a single phase) or a mixture of metallic phases (two or more solution). An alloy is distinct from an impure metal in that, with an alloy, the added elements are well controlled to produce desirable properties, while impure metals such as wrought iron, are less controlled but after often considered useful. Alloys are made by mixing two or more elements, at least one of which is a metal which is usually called the primary metal or the base metal, and the name of this method may also be the name of the alloy [1, 2]. The other constituents may or may not be metals but when mixed with the molten base, they will be soluble and dissolve into the mixture.

The primary metal is called the base, the matrix, or the solvent. The secondary constituents are often called solutes [3]. If there is a mixture of only two types of atoms (not counting impurities) such as a copper-nickel alloy, it is called a binary alloy [4]. If there are three types of atoms forming the mixture such as iron, nickel and chromium, then it is called a ternary alloy. An alloy with four constituents is a quaternary alloy [2], while a five-part alloy is termed a quinary alloy [5, 6].

In this present work, the synthesis of CuS: ZnS alloyed thin films for solar applications have been studied.

2.0 Reaction mechanism

The synthesis of the alloyed thin films using SILAR method constituted: 5ml of 3m solution of 99% ammonia used as complexing agent was measured with a syringe and added into separate beaker, containing 17.81g of 0.3m of $CuSO_45H_2O$ dissolved in 250cm^3 distilled water as given in Fig 1.

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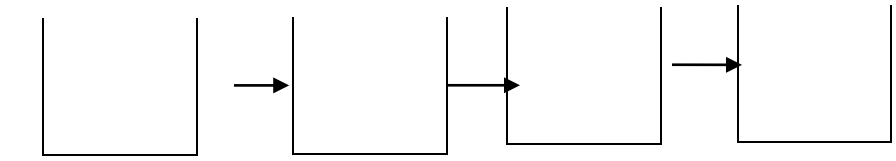
De-ionized water was added up to 50ml and the solution was stirred vigorously in order to achieve uniformity in the mixture. CuS thin films were deposited on substrates in cycles; one cycle is completed by dipping the substrate first into the beaker containing the cationic precursor shown in Fig. and then rinsed in a beaker of de-ionized water, shown in Fig 1b and immersed into the third beaker, containing the anionic precursor, shown in Fig.1c which is 20.53g of 0.5m solution of thiourea dissolved in 300 cm3 of distilled water, after which the substrates were rinsed in de-ionized water, Fig 1d and this is repeated based on the number of chosen cycles.



Cationic precursor (a) Water (b) Anionic precursor (c) Water (d)

Fig. 1 Stages of SILAR deposition

Table 1 below indicates the various samples of deposition, their dip time in Fig.1a and Fig.1c (the reactants), their number of SILAR cycles and their dip time in de-ionized water.

Table 1: The SILAR deposition of CuS thin films

Sample	Dip Time(s) in Each Reactant	No.of Cycle	Dip Time(s) in De-Ionized H_2O
P1	5	10	3
P2	5	10	3
P3	5	10	3
P4	5	10	3
P5	5	10	3

The parameters for SILAR deposition are depicted on table 1.

2.1 Depositions and reactions using electroless method

Fig 1 shows the constituent materials that make-up the deposited samples of CuS:ZnS on the substrates: 20.52g of 20ml of 0.5m of $ZnCl_2$ dissolved in 300cm3 of distilled water, 3ml of 3m solution of 99% NH_3 and 10ml of 0.5m solution of thiourea-ionized H_2O was added up to 50ml and the substrates containing the deposited samples of CuS prepared by SILAR method. Ammonia ($NH_{3(aq)}$) in this reaction is the complexing agent. It controls the rate of ion-ion interaction, thereby moderating the rate of formation of precipitate [7]. It also creates a basic medium for good formation of deposits.

Several bath compositions were employed, but the best result was achieved with the specification shown on table2. The depositions were in 50ml beakers and glass substrates as depicts in Fig 2

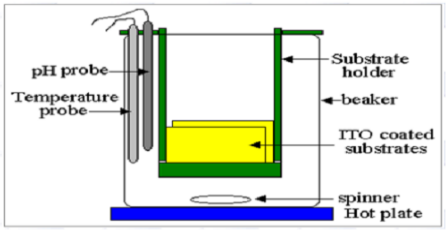


Fig. 2 Electroless deposition

The samples were annealed using master chef annealing machine of temperature change of 100°to 250 °C as depicted on Table 2.

Table 2a indicates the deposited samples, their annealing temperature, their concentration and quantity of rectants and complexing agents, quantity of distilled water and the number of SILAR cycles in SILAR deposition

Table 2b indicates the deposited samples, their annealing temperature, their concentration and quantity of rectants and complexing agents, quantity of distilled water and the dip time of the substrates in electroless method

Table 2: The different parameters for the deposition of CuS:ZnS alloyed thin films annealed at different temperatures

(a)

SAMPLES	ANNEALING TEMPERATURE(◦C)	CuSO4		Thiourea		NH3		Distilled water	No of SILAR cycles
		SILAR METHOD							
		M	Ml	M	Ml	M	Ml	ml	
P5	150	0.5	20	0.6	50	1.0	3	27	10
P6	200	0.5	20	0.6	50	1.0	3	27	10

(b)

SAMPLES	ANNEALING TEMPERATURE (◦c)	ZnCl2		NH3		Thiourea		Distilled water	Dip Time
		ELECTROLESS METHOD							
		M	Ml	M	ml	M	Ml	ml	
P5	150	0.6	20	1.0	3	0.6	10	17	5
P6	200	0.6	20	1.0	3	0.6	10	17	5

3.0 Characterization

3.1 Crystallographic studies of the deposited samples

The XRD analysis was carried out using X-ray diffractometer modeled GBC Enhanced Mini Material Analyzer (EMMA), XRD pattern gives information relative to the nature and structure of the alloyed thin films of CuS:ZnS. Fig 3 & 4 shows X-ray diffraction of the above listed alloyed thin films. The crystallite sizes given in table 5 are obtained using Debye-Scherer's equation [2,5,7,8].

$$D = \frac{K\lambda}{\beta\cos\theta} \quad (1)$$

Where k is the shape factor (k=0.9) , D is the grain size or average crystallite size, λ is the wavelength of Cukα radiation used (λ =1.54A≡0.154nm) , β is the experimentally observed diffraction peak with width at half maximum intensity (Full Width at Half Maximum FWHM) and θ is the Bragg's diffraction angle.

3.2 XRD pattern of CuS:ZnS alloyed thin films of P_5 and P_6

Fig 3 shows the XRD pattern of CuS:ZnS alloyed thin film of sample P_5 with more than one diffraction peaks with preferred orientation at 2θ = 29◦, The pattern indicates that the alloyed CuS:ZnS annealed at 150◦C thin film is polycrystalline in nature. The crystallite size for this alloy was calculated using equation 1 from the observed peak, the grain size of the sample was observed to be 6.060A◦. It has cubic crystal system.

From the data of the XRD peak the lattice parameters CuS:ZnS alloy thin film annealed at 150◦c of sample p_5 are a=b=c=10.37Aº. Fig 4 shows the XRD pattern of CuS:ZnS alloyed thin film of sample P6 with several diffraction peaks. Its preferred orientation is at 2θ = 30◦. The crystallite size for this alloy was calculated using equation 1 from the observed peak, the grain size of the sample was observed to be 5.153A◦. The pattern indicates that the alloyed CuS:ZnS annealed at 200◦C thin film is polycrystalline in nature. It has cubic crystal system.

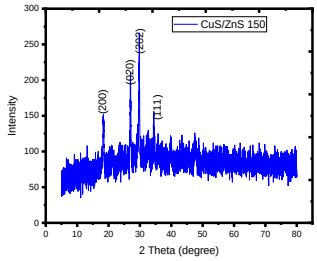


Fig. 3 XRD pattern of CuS:ZnS alloyed thin films of sample P5 annealed at 150◦C

Table 3: XRD results of CuS:ZnS alloyed thin film annealed at 150◦C

Sample	hkl	d-spacing(A◦)	FWHM(radian)	Grain size (nm)	Position(◦2theta)	Count(height)
P5	200	4.8228	0.1968	0.7126	18	234.34
	020	3.2961	0.2165	0.6584	27	219.98
	202	2.9959	0.2362	0.6060	29	277.95
	111	2.6029	0.1968	0.7365	34	88.59

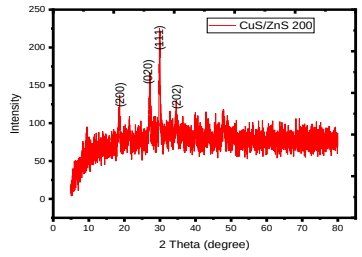


Fig. 4 XRD pattern of CuS:ZnS alloyed thin films of sample P6 annealed at 200◦C

Table 4: XRD results of CuS:ZnS alloyed thin film annealed at 200◦C

Sample	hkl	d-spacing(A◦)	FWHM(radian)	Grain size (nm)	Position(◦2theta)	Count(height)
P6	200	4.7582	0.2558	0.5493	17.5	143.37
	020	3.2860	0.2362	0.6034	27	187.45
	111	2.9829	0.2362	0.6074	30	270.86
	202	2.5951	0.3346	0.4343	34	58.58

3.3 Composition and thickness characterization

It is often necessary to determine the elements and the thickness of thin film sample. In this work, atomic compositions and the thicknesses of the samples were determined using RBS. Samples P1, P2 and P3 expected to be CuS:ZnS thin films annealed at 473k, 423k and 523k respectively have 1.55% of copper, 2.51% of Zinc, 1.55% of sulphur with thickness of 247.5nm, 1.09% of copper, 1.09% of Zinc, 1.32% of sulphur with thickness of 238nm and 1.55% of copper, 2.51% of zinc, 1.55% of sulphur with thickness of 247.5nm. These are shown in Figs 5, 6 and 7 respectively. Table 6, 7 and 8 depict the summary of the availability of the desired elements on the deposited samples.

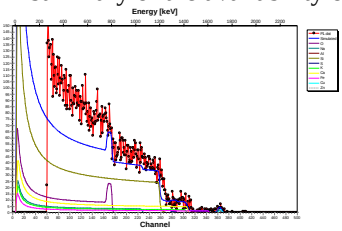


Fig. 5 The composition of sample P_1 with thickness 247.5nm, of CuS:ZnS measured by RBS

Table 5: The elements in sample P_1

Elements	Layer 1 % Composition	Layer 2 % Composition
Cu	0.89	
Si		23.74
Al		0.02
Zn	1.15	
O		63.42
K		0.69
S	1.24	
Na		8.91
Fe		0.59
Ca		2.63

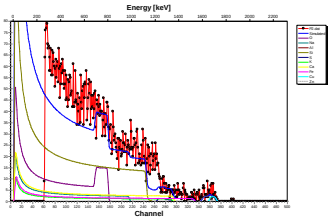


Fig. 6 The composition of sample P_2 with thickness 238nm as measured by RBS

Table 6: The elements in sample P_2

Elements	Layer 1 % Composition	Layer 2 % Composition
Cu	1.09	
Si		23.74
Al		0.02
Zn	1.09	
O		63.42
K		0.69
S	1.32	
Na		8.91
Fe		0.59
Ca		2.63

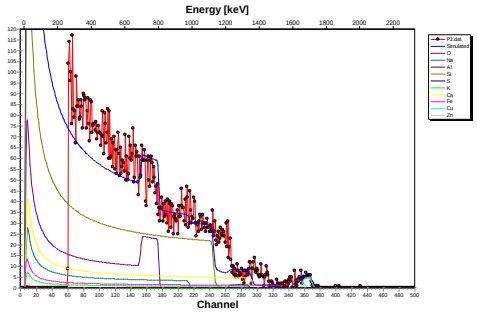


Fig. 7 The composition of sample P_3 with thickness 247.5nm as measured by RBS

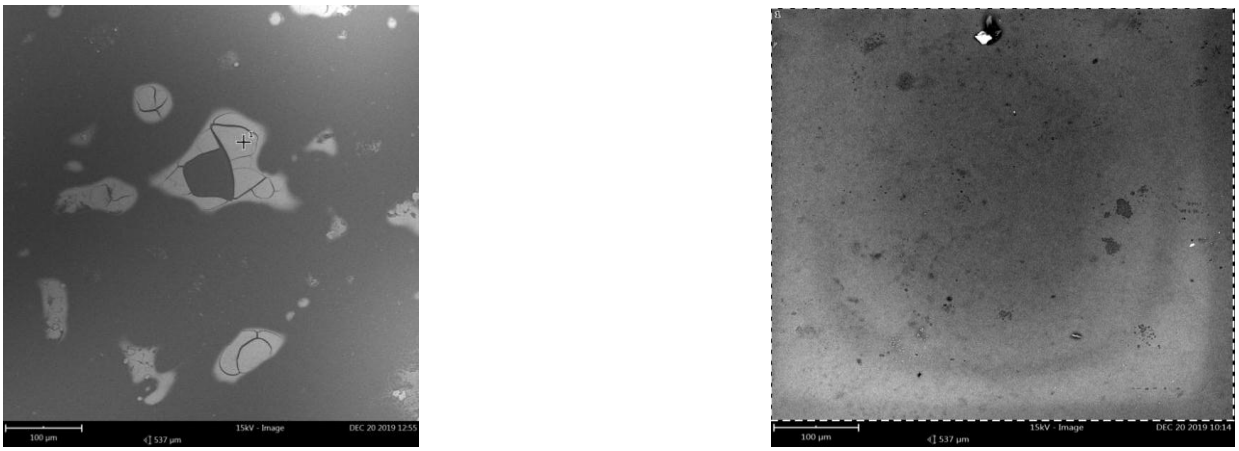
Table 7: The elements in sample P_3

Elements	Layer 1 % Composition	Layer 2 % Composition
Cu	1.55	
Si		23.74
Al		0.02
Zn	2.59	
O		63.42
K		0.69
S	1.55	
Na		8.91
Fe		0.59
Ca		2.63

3.4 Microstructure of the grown samples

Microstructure of the thin films CuS:ZnS were determined using SEM. The process of analysis is through imaging [9-11].

Sample P_5 has cracks. Its morphology is non-agglomerated and it has incoherent surfaces due to synthesis conditions. In sample P_6, a well crystallized grain is seen and the particles forming the films are in nano scale. This is shown in Fig 8



P5_150 P6_200

Fig. 8 Scanning electron microscopy of sample P5 and P6 of CuS:ZnS alloyed thin films

4 Conclusion

CuS:ZnS alloyed thin films were deposited on glass substrates using two solution based methods: SILAR and electroless method. NH_3 solution was used as complexing agent. The deposited samples were annealed between 100-250^{o}C, Using Master Chef Annealing Machine [9]. The alloyed thin films can be useful in active solar cell applications, semi conductor materials [12], etc. These alloyed thin films prepared under this condition, have the ability to sustain large electric field, higher breakdown voltage, low electronic noise, stable at higher temperature operation. Due to their thermal stability, they can be useful in the area of anti-corrosion coating in iron vulcanization, ceramics production, etc [5,13-15].

ACKNOWLEDGEMENTS

I am grateful to Dr Onwuemeka of Department of Physics of Imo State University, Professor Eya of Federal University of Technology Owerri, the Laboratory officials of Obafemi Awolowo University Ile-lfe in the person of Prof. E. I. Obioyunwa, the Director Centre for Energy Research and Development. Also I wish to give thanks to Isa Yakuba of Chemical Engineering Department of Ahmadu Bello University, Zaria for various roles in realizing this work.

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