

# Composition and Optical Properties of Quaternary Alloy of $\text{PbCuSO}_4$ Thin Films Prepared by Advanced SILAR Deposition Technique

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**Abstract:**  $\text{PbCuSO}_4$  thin films were prepared by SILAR method on glass substrates using  $\text{Pb}(\text{NO}_3)_2$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  as the cationic precursors, hydrogen peroxide and thiourea as the anionic precursors and Triethanolamine (TEA) ( $\text{C}_6\text{H}_{15}\text{NO}_3$ ) as the complexing agent. The samples were subjected to heat treatments at  $100^\circ\text{C}$ ,  $150^\circ\text{C}$ ,  $200^\circ\text{C}$ , and  $250^\circ\text{C}$  for 1hour. The samples were transparent and adherent to the substrates. The transmittance increases from 0.13 to 0.64 as the wavelength increases from 300nm to 1100nm for the samples as measured by UV 1800 series double beam spectrophotometer. The band gaps obtained under various thermal treatments are between  $3.5 \pm 0.05\text{eV}$  to  $3.75 \pm 0.05\text{eV}$ . The thickness for  $\text{PC}_1$  is 386nm,  $\text{PC}_2$  is 592nm,  $\text{PC}_3$  is 403.29nm and  $\text{PC}_4$  is 399nm. These properties of the material makes it suitable for applications in solar cells, gas sensor, thin absorber, aesthetic window, smart window antireflection coating.

**Keywords:** Absorbance, Band Gap, Transmittance, Quaternary, Alloy.

## I. INTRODUCTION

The metal elements are capable of forming a variety of oxide compounds which can adopt a vast number of structural geometries with some electronic structures that can exhibit various interesting properties (Fernández-Garcia and Rodriguez, 2007). Oxides have long been used in a variety of technological applications, for example, almost all catalysts involve an oxide as active phase, promoter (or support) which allows the active components to disperse on. In the chemical and petrochemical industries, products worth billions of dollars are generated every year through processes that use metal oxide catalysts. For the control of environmental pollution, catalysts or solvents that contain oxides are employed to remove the CO, NO<sub>x</sub>, and SO<sub>x</sub> species formed during the combustion of fossil-derived fuels. Furthermore, the most active areas of the semiconductor industry involve the use of oxides. Thus, most of the chips used in computers contain oxide components.

The oxides of transition metals are an important class of semiconductors, which have applications in magnetic storage media, solar energy transformation, electronics and catalysis (Lanje, *et al.*, 2010; Debbarma, *et al.*, 2015). Among various transition metal oxides CuO has attracted much attention due to its fascinating properties (Srinivasan, *et al.*, 2002). It is the basis of high T<sub>c</sub> superconductors. Copper oxide is also

referred to as Copper (I) oxide (cuprous oxide,  $\text{Cu}_2\text{O}$ ), Copper (II) oxide (cupric oxide,  $\text{CuO}$ ), Copper peroxide ( $\text{CuO}_2$ ),

$\text{CuO}$  is a semiconducting compound with a narrow band gap and used for photoconductive and photothermal applications. It also possesses an incommensurate antiferromagnetic structure below the Neel temperature of 230 K, which is quite unusual (Eliseev, *et al.*, 2000). In some recent reports,  $\text{CuO}$  has shown high temperature superconductivity as well, where the specific coordination between Cu and O atoms plays a crucial role (Ray, 2001). Due to the existence of copper vacancies in the structure,  $\text{CuO}$  exhibits native p-type conductivity (Figueiredo, *et al.*, 2008). Its band gap is reported to be between 1.3 and 1.9 eV with a black colour and a partial transparency in the visible range (Horaka, *et al.*, 2016).

Lead sulphide, also known as galena or plumbous sulfide is a black crystalline solid or a silver powder. Its density is  $7.5 \text{ g mL}^{-1}$ . Its melting point is  $1114^\circ\text{C}$  and its boiling point is  $1281^\circ\text{C}$ . Its molar mass is  $239.26 \text{ g mol}^{-1}$ . Lead sulfide is formed by the cation  $\text{Pb}^{+2}$  (the lesser oxidized ion of Pb) and the anion  $\text{S}^{-2}$  (the lesser oxidizer ion of S). Lead (II) sulfide has a cubic crystal structure with a unit cells forms by one anion surrounded by 6 cations (it can also be considered one cation surrounded by 6 anions) (NCIB, 2017).

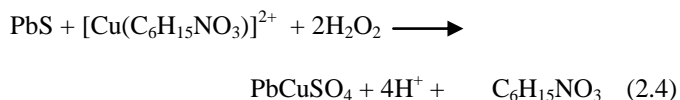
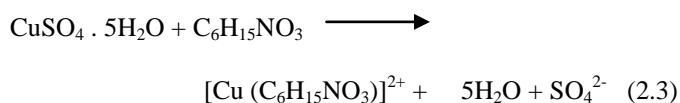
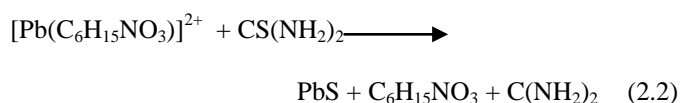
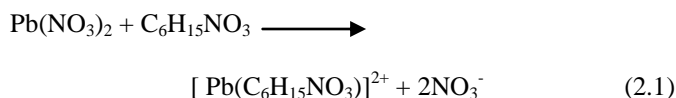
Lead sulfide ( $\text{PbS}$ ) has a direct narrow bandgap value of  $0.41\text{eV}$  at 300K, with excitation Bohr radius of 18nm (Ratanatawanate, *et al.*, 2008; Zheng, *et al.*, 2016)  $\text{PbS}$  is a very suitable IV–VI semiconductive material for infrared detection, solar cell,  $\text{Pb}^{2+}$  ion selective sensor, photo-thermal, and optoelectronic applications. The optical and electrical properties of this semiconductive material are highly related to some factors e.g. crystallinity, particle size, film thickness and surface properties (Üst, *et al.*, 2016; Hernández-Borja, *et al.*, 2011; Jing, *et al.*, 2008). The physical and chemical properties of  $\text{PbS}$  can be modified through doping with various elements for practical applications (Jana, *et al.*, 2012).

## II. EXPERIMENT

$\text{PbCuSO}_4$  thin films, were deposited by immersing the substrates in complex lead solution as given in (2.1) in presence of TEA as complexing agent for 5s where lead ion

were adsorbed on the surface of the substrates. Subsequently, the substrates were immersed for 5s in de-ionized water to remove loose and unadsorbed  $Pb^{2+}$  from its surface. The substrates were immersed in thiourea solution for 5s, where the  $S^{2-}$  react with adsorbed  $Pb^{2+}$  ions on the substrates to form PbS layer as given in (2.2). The substrates were again immersed in de-ionized water to remove loose and unadsorbed materials from its surface. Afterwards, the substrates were immersed in complex copper solution with TEA as a complexing agent for 5s to adsorb  $Cu^{2+}$  ions on the pre-adsorbed PbS layer (2.3). The Unadsorbed  $Cu^{2+}$  ions were removed from the substrates by rinsing it in deionized water for 5s. The substrates were then immersed in hydrogen peroxide for 5s where  $O^{2-}$  ions react with  $Cu^{2+}$  to form a layer of CuO, which finally combined with the existing PbS on the substrate to form  $PbCuSO_4$  thin films (2.4).

#### Reaction Mechanism



The pH of the solution was recorded as 10.5. The samples after were annealed machine with the aim of removing water of crystallization. The heating is done at temperatures of 100°C, 150°C, 200°C, and 250°C. And constant time of 1 hour.

### III. RESULTS AND DISCUSSION

#### Composition and thickness characterization

It is often necessary to determine the elements that make up the thin film samples. In this work, atomic compositions and thicknesses of the samples were determined, by Rutherford backscattering spectroscopy (RBS) analysis as shown in Figs., 3.1 and 3.2 respectively. The Rutherford backscattering analysis shows the compositions of the samples: PC<sub>1</sub>, of annealed at 250<sup>0</sup> C has 0.72% of lead, 0.60% of copper, 4.50% of sulphur, 95.35% of oxygen and PC<sub>2</sub> 150<sup>0</sup> C has 6.42% of lead, 5.03% of copper, 3.50% of sulphur, 85.05% of oxygen as depicts in Tables 3.1 and 3.2 respectively (Onwumeka and Nwulu, 2017).

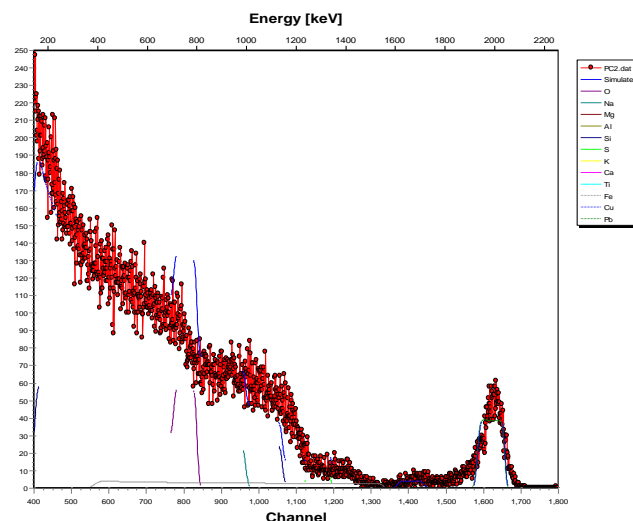


Fig 3.1 the composition of sample PC<sub>1</sub> with thickness, 386 nm as measured by RBS

Table 3.1: The elements in sample PC<sub>1</sub>

Elements	Layer (1)% Comp	Layer(2)% Comp
O	95.35	67.40
Ca	-	1.06
Si	-	18.53
Fe	-	0.48
Na	-	8.77
Al	-	0.49
Mg		0.11
Ti		0.87
S	0.12	0.12
Pb	0.64	
Cu	0.50	

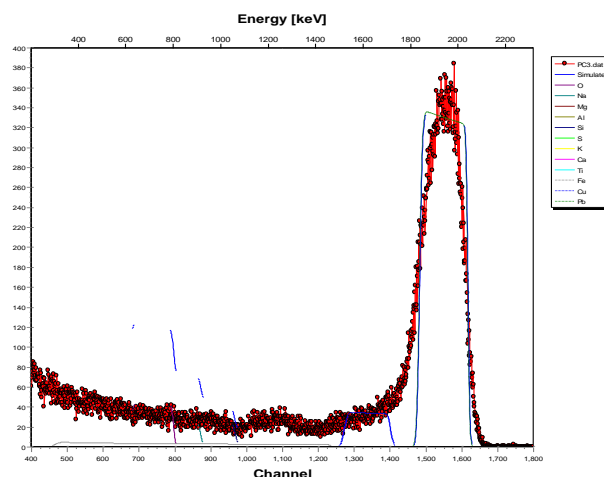


Fig. 3.2 The composition of samples PC<sub>2</sub> with thickness, 592 nm as measured by RBS

Table 3.2: The elements in sample PC<sub>2</sub>

Elements	Layer(1)% Comp	Layer(2)% Comp
O	85.35	67.40
Ca		1.06
Pb	0.64	
Cu	5.03	
Si		18.53
Fe		0.48
Na		8.77
Al		2.18
Mg		0.11
Ti		0.87
S	3.50	0.12

**Transmittance (T)**

The transmittance increases from 0.13 to 0.64 as the wavelength increased from 300nm to 1100nm. Sample PC<sub>1</sub>, PC<sub>2</sub>, PC<sub>3</sub>, PC<sub>4</sub> share similar characteristics as indicated by the graph in Fig 3.3, while PC<sub>4</sub> have a higher transmittance, this means that they can be window in infrared optics, since it has high transmittance in the near infrared regions.

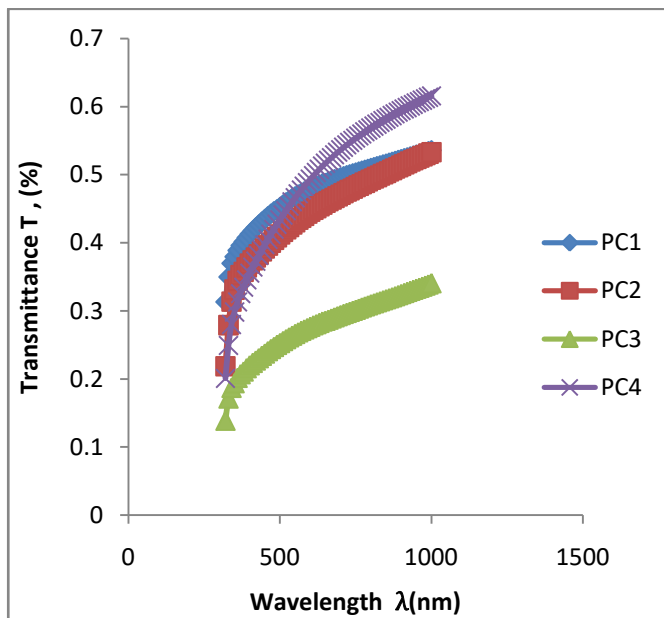


Fig 3.3 Graph of transmittance against wavelength

**Absorbance**

The graphs show sharp falls of absorbance with increase in wavelength which indicated a shift from a region of more absorbance to a region of less absorbance as shown in Fig. 3.4. Samples PC<sub>2</sub>, PC<sub>3</sub>, PC<sub>4</sub> have similar characteristics as indicated from the graph while sample PC<sub>1</sub> has the lowest absorbance, the range was from 0.24 to 0.59. Samples PC<sub>1</sub>, PC<sub>2</sub>, PC<sub>3</sub>, PC<sub>4</sub> can be used in heat and cold windows

applications, solar cells, gas sensor, thin absorber, aesthetic window and antireflection coatings.

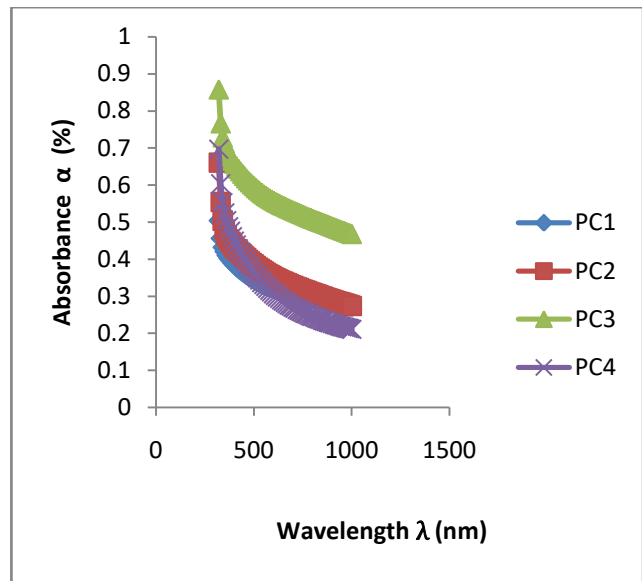


Fig. 3 4 Graph of absorbance against wavelength

**Energy Band Gap**

The band gap is determined from the graph of  $(\alpha h\nu)^2$  against  $h\nu$ , by extrapolating the straight portion of the curve where  $\alpha h\nu = 0$  as plotted in Fig. 3.5. The band gaps of PC<sub>1</sub>  $3.2 \pm 0.05\text{eV}$ ,  $3.40 \pm 0.05\text{eV}$ ,  $3.5 \pm 0.05\text{eV}$  and  $3.10 \pm 0.05\text{eV}$  respectively. The samples have wide energy band gaps and can be suitable for applications in solar cells, gas sensor; thin absolute is suitable for application in solar cells, gas sensor, thin absorber, aesthetic windows, antireflection coatings and other uses.

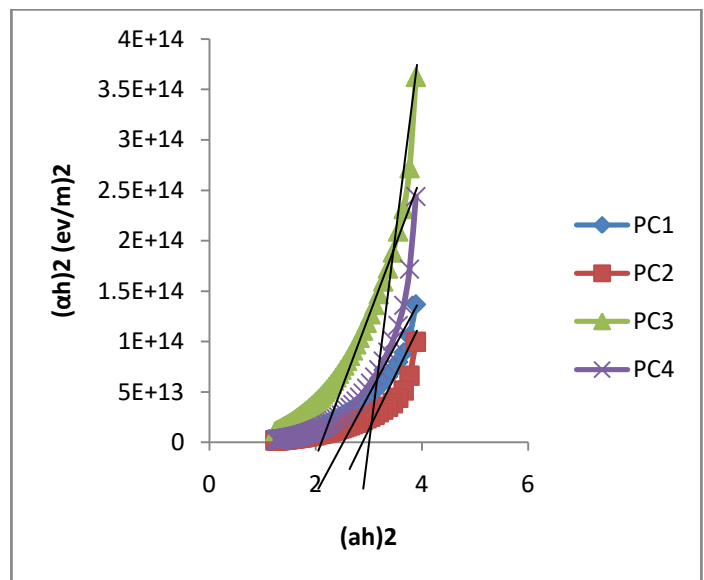


Figure 3.5: The graph of  $(\alpha h\nu)^2$  (ev/m)<sup>2</sup> against  $h\nu$ (ev) for the four samples

## IV. CONCLUSION

Layers of  $\text{PbCuSO}_4$  were deposited using SILAR deposition technique. Lead nitrate and Copper sulphate were cationic precursors, hydrogen peroxide and thiourea were the anionic precursors. Triethanolamine (TEA) was used as the complexing agent. 20ml of lead nitrate and 20ml of copper were used for cation, for the whole mixture, 20ml of hydrogen peroxide and 20ml of thiourea were used for the anionic precursors for the entire process. 4ml of TEA was used as the complexing agent.

Rutherford back scattering was used in determining the atomic composition of the samples. The thicknesses of the films were measured using gravitational method. The optical properties were measured using UV1800 series double beam spectrophotometer.

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