



APPLICATIONS OF CHEMICALLY SYNTHESIZED CUS: PBO ALLOYED THIN FILMS IN MULTILAYER SOLAR CELLS AND OPTOELECTRONICS

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Abstract:

CuS: PbO, alloyed thin films were successfully deposited on glass substrates under the deposition condition of 40oC of NaOH solution, using two solution based methods: successive ionic layer adsorption and reaction (SILAR) and solution growth technique. The crystallographic studies were done using X-ray diffractometer (XRD) and scanning electron microscope (SEM). The deposited alloyed samples were annealed at 250oC and 1500C. using Master Chef Annealing Machine. Rutherford backscattering Spectroscopy (RBS) analysis confirmed the percentage of the elements of copper, lead, sulphur and oxygen in the alloyed thin films. The optical characterization was carried out using UV-1800 double beam spectrophotometer. Sample cp1 annealed at 250 oC has an optical transmittance of 27% -71% in the ultraviolet region, 71%-83% in the visible and 83%-88% in the near infrared regions of electromagnetic spectrum. The alloyed thin films of samples cp2 of CuS:PbO annealed at 150oC, show optical transmittance of 15%-61% in the ultraviolet region, 61%-59% in the visible, and becomes linear through the near-infrared regions of electromagnetic spectrum. The two samples, have equal direct wide band gap of $3.65 \pm 0.05\text{eV}$. From the spectral qualities, these compounds alloyed thin films may found useful in passive layer in heat and cold mirror application, vulcanization in tyre production due its thermal stability, active multilayer in various types of solar cells, liquid crystal displays, flat panel displays for optoelectronic applications and gas censor applications.

Keywords: Transmittance; Reflectance; Absorption Coefficient; Extinction Coefficient; Refractive Index; Optical Conductivity.

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1. Introduction

The increase in thin film researches is due to their extensive applications in the diverse fields of solar energy conversion, electronics, space science, optics, aircrafts and other industries. These investigations had led to numerous forms of active and passive components, piezoelectric devices, rectification and amplification, magnetic memories, superconducting films. Because of

compactness, better performance and reliability coupled with low cost production and low package weight, thin film components are preferred over the bulk counterparts [1].

Semiconductor thin films have been studied due to their potential application in solar energy conversion due its direct narrow gap with relatively large excitation Bohr radius [2]. The synthesis and characterization of semiconductor nanoparticles is an exciting field of research for future applications in optoelectronics.

Nanostructured materials and in particular semiconductor nanostructures and thin films may be exploited for their novel electronic and optical properties. These structures are of great interest since they have potential applications in future quantum and photonic devices. Chalcogenides of (PbS, CuS, PbO and CuO) have been the subject of considerable research due to their technological importance in crystalline and polycrystalline forms.

The sulphide and oxide are attractive semiconductor materials that exhibit strong size quantization effects due to the high dielectric constant and the small effective mass of electron and holes, suggesting that its band gap energy can be easily manipulated from the bulk value to a few electron volts by the changes in the material's size. Those materials have also been used in many fields such as infrared photography, diode laser, humidity and temperature sensors, and decorative and solar control coatings among other applications. Novel materials are needed for thin film solar energy conversion apart from the most extensively studied material [3]

Copper sulphides (CuS) are important materials for applications in p-type semiconductors and optoelectronics. This find use in photo thermal conversion applications, photovoltaic applications, solar control coatings and other electronic devices fabrication of microelectronic devices, optical filters as well as in low temperature gas sensor applications. Special attention is now given to the study of copper sulphide thin films probably due to the discovery of heterojunction solar cell [4][5]

Metal oxide nanoparticles have attracted considerable attentions in the last decades. Among them copper oxide (CuO) based materials have various technological applications in solar energy conversion, ceramics, sensors, catalysis, batteries, solar cells, magnetic storage media, semiconductors, capacitors, diodes, and so forth [6] because of their novel mechanical, electronic, magnetic, and optical properties compared with those of conventional bulk materials. Generally, these materials indicate high optical transmission, low electrical resistivity and high transparency in the visible region of the electromagnetic spectrum. Recently, these materials have been intensively investigated as a potential candidate material for solar energy conversion, smart window, gas sensors, IR detector, photodiode, conducting electrode, anti-reflection coatings and liquid crystal display [7][8].

Considering the factors of continued consumption for long run, it is possible to have sustainable energy by utilizing renewable energy sources particularly solar energy which is very available. Solar energy conversion is mainly classified as solar thermal energy and solar photovoltaic electricity.

The direct conversion of solar energy into electricity by photovoltaic (PV) solar cells was studied for the past 30years. Some countries are still far from making these sources cost effective.

Photovoltaic solar energy conversion offers one of the few ways of producing electricity in urban areas which is free of various emissions and noise. World energy demands are met from a variety of energy sources both conventional and non-conventional.

In spite of substantial increase during the last many decades in the supply of commercial sources of energy such as coal, oil and gas, and wood still meet about half of our energy needs, particularly in the rural areas. Besides being inefficient in terms of end use, loss of green wood for fuel also results in adverse impact on the environment and pollution control. There exists a substantial potential in non-conventional source such as solar, wind and tidal energy etc.

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 a solid solution of metal elements (a single phase) or a mixture of metallic phases (two or more solutions). 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 are often considered useful. Alloys are made by mixing two or more elements, at least one of which is a metal. This is usually called the primary metal or the base metal, and the name of this metal may also be the name of the alloy [9]. 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.

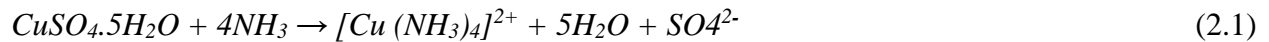
The mechanical properties of alloys will often be quite different from those of its individual constituents. Although the elements of an alloy usually must be soluble in the liquid state, they may not always be soluble in the solid state. If the metals remain soluble when solid, the alloy forms a solid solution, becoming a homogeneous structure consisting of identical crystals, called a phase. If as the mixture cools the constituents become insoluble, they may separate to form two or more different types of crystals, creating a heterogeneous microstructure of different phases, some with more of one constituent than the other phase has. However, in other alloys, the insoluble elements may not separate until after crystallization occurs. If cooled very quickly, they first crystallize as a homogeneous phase, but they are supersaturated with the secondary constituents. As time passes, the atoms of these supersaturated alloys can separate from the crystal lattice, becoming more stable, and form a second phase that serve to reinforce the crystals internally. Some alloys, such as electrum which is an alloy consisting of silver and gold, occur naturally [9].

The primary metal is called the base, the matrix, or the solvent. The secondary constituents are often called solutes. 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. 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, while a five-part alloy is termed a quinary alloy. In this respect, all the various forms of an alloy containing only two constituents, like iron and carbon, is called a binary system, while all of the alloy combinations possible with a ternary alloy, such as alloys of iron, carbon and chromium, and is called a ternary system [10] [12]

In this present work, the synthesis and characterization of CuS:PbO alloyed thin films have been studied.

2. Reaction Mechanism

The synthesis of the alloyed thin films using SILAR method constituted: 4ml of 3M solution of ammonia used as complexing agent was measured with a syringe and added into separate beaker containing 0.2M solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ by dissolving 10g in 150cm^3 of water. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ produced blue gelatinous precipitates when reacted with NH_3 , which dissolved in excess ammonia solution forming copper tetra-ammine complex ion, $[\text{Cu}(\text{NH}_3)_4]^{2+}$ as given in equation (2.1). as given in Figure 2.1a, represented in equation (2.1).



De-ionized water was added up to 50ml and the solution was stirred vigorously in order to achieve uniformity in the mixture. The suitable pH value for this work is 9 for the alloyed thin films of $\text{CuS}:\text{PbO}$ as detected by the piston pH meter.

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 and then rinsed in a beaker of de-ionize water, shown in Figure 2.1b and immersed into the third beaker, containing the anionic precursor, shown in Figure 2.1c which, is 0.8M solution of 17.51g of thiourea (C_2H_4)CS after which the substrates were rinsed in de-ionized water, **Figure 2.1d** and this is repeated based on the number of chosen cycles[11]. This is given in equations (2.2). The parameters for SILAR deposition are depicted on **Table 2.1**.

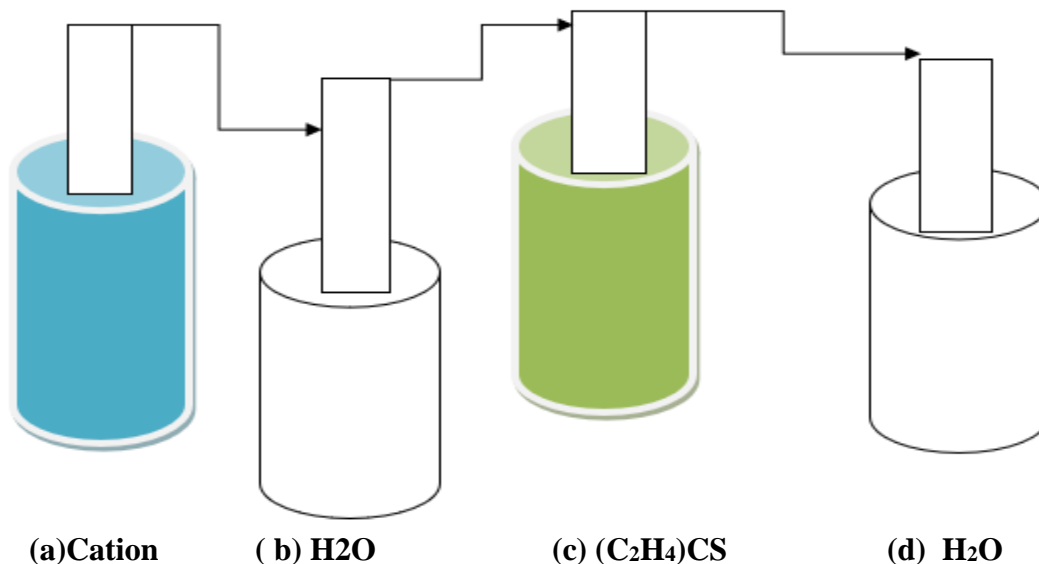
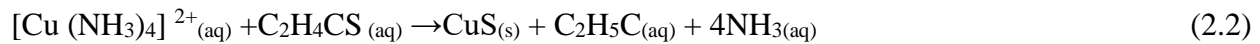


Figure 2.1: The stages of SILAR deposition process [12]

- a. Cationic precursor b. Ion exchange water c. Anionic precursor d. Ion exchange water

Table 2.1: The deposition of CuS thin films

Sample	Dip-time(s) in each reactant	No. of cycle	Dip-time (s) in each Beaker of H ₂ O
cp ₁	12	15	5
Cp ₂	12	15	5
cp ₃	12	15	5
cp ₄	12	15	5
Cp ₅	12	15	5

2.1. Depositions and Reactions Using Solution Growth Technique

Figure 2.2, shows the constituent materials that make-up the deposited samples of CuS; PbO on the substrates: 13.52g of 20ml of 0.2M of Pb (NO₃)₂ dissolved in 250cm³ of water, 4ml of 3M solution of NH₃, and 15ml of 2M solution of NaOH and the substrates containing the deposited samples of suspected sulphide CuS prepared by SILAR method. Ammonia (NH_{3(aq)}) in this reaction is the complexing agent. It controls the rate of ion – by – ion interaction, thereby moderating the rate of formation of precipitate. It also creates an alkaline medium for good formation of deposits. The reaction mechanisms that led to the deposition of the required samples are given in equation (2.3).

Several bath compositions were employed, but the optimum result was achieved with the specification shown on Table 2.2.

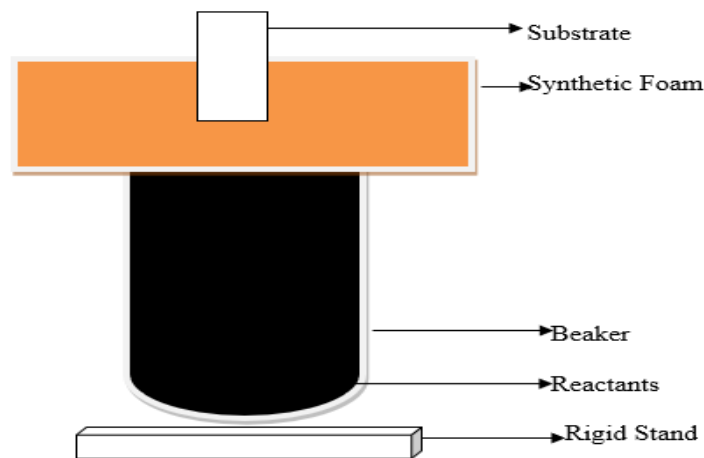


Figure 2.2: Set-up of Solution Growth Technique [12]



From equation 2.3, copper lead sulphate (IV) dihydrate (CuPbSO_{4(s)} · 2H₂O) is formed.

Two samples B₁ and B₂ are selected and are annealed using Master Chef annealing machine at 250⁰C and 150⁰C respectively for 1 hour to create quality and adherent films on the substrates with expulsion of water as given in equation (2.4).

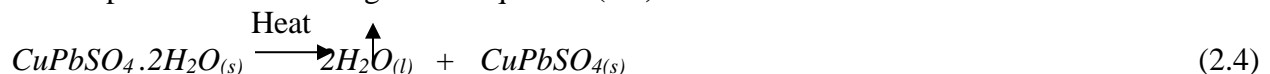


Table 2.2: The different parameters for the deposition of CuS:PbO thin films

Samp-les	Annealing Temp.(°C) (for1hour)	Pb (NO ₃) ₂ Conc. (mol)	NH ₃ Conc. (mol)	NaOH Conc. (mol)	Pb (NO ₃) ₂ Vol. (ml)	NH ₃ Vol. (ml)	NaOH Vol. (ml)	Dep. Temp (NaOH) (°C)	Dep. Time (hr)
cp ₁	250	0.20	3.00	2.00	15.00	4.00	10.00	40.00	8.00
cp ₂	150	0.20	3.00	2.00	15.00	4.00	10.00	40.00	8.00
cp ₃	250	0.20	3.00	2.00	15.00	4.00	10.00	40.00	8.00
cp ₄	150	0.20	3.00	2.00	15.00	4.00	10.00	40.00	8.00
cp ₅	250	0.20	3.00	2.00	15.00	4.00	10.00	40.00	8.00

3. Characterization

3.1. Composition and Thickness Characterization

It is often necessary to determine the elements and the thicknesses of the thin film samples. In this work, atomic compositions and the thicknesses of the samples were determined using 2.2MeV alpha beam, obtained from CERD Ion Beam Analysis (IBA) Facility With Model: NEC 5SDH 1.7 MV Pelletron Tandem Accelerator equipped with a Radio Frequency Charge Exchange Ion Source Alphasat. The Rutherford backscattering analysis shows the compositions samples of cp₁ and cp₂ of CuS: PbO alloyed thin films annealed at 250⁰ C and 150°C respectively have 0.64% of lead, 0.50% of copper, 3.50% of sulphur, 95.35% of oxygen with thickness of 386.03 nm and 6.42% of lead, 5.03% of copper , 3.50% of sulphur , 85.05% of oxygen 592.59nm. These results show oxygen rich films, which may be as a result of exposure to air and surface hydroxide [13] These are shown in **Figure3.1** and **Figure 3.2** respectively. **Tables 3.1** and **3.2** depict the summary of the availability of the desired elements on the deposited samples.

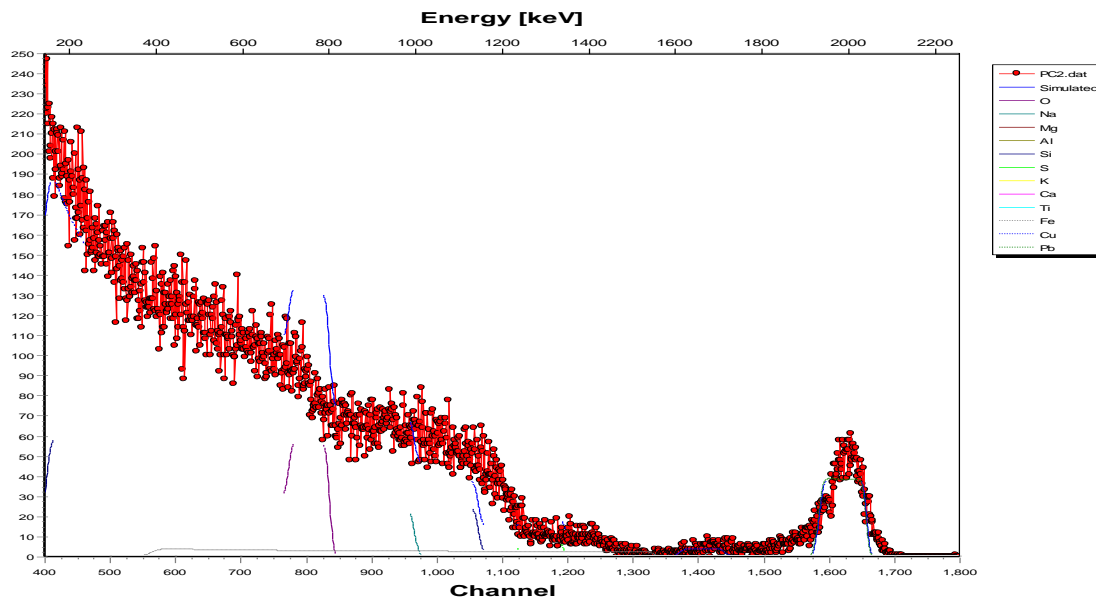


Figure 3.1: The composition of sample cp₁ with thickness, 386.03 nm as measured by Rutherford backscattering spectroscopy (RBS)

Table 3.1: The elements in sample cp₁

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	
Pb	0.64	
Cu	0.50	

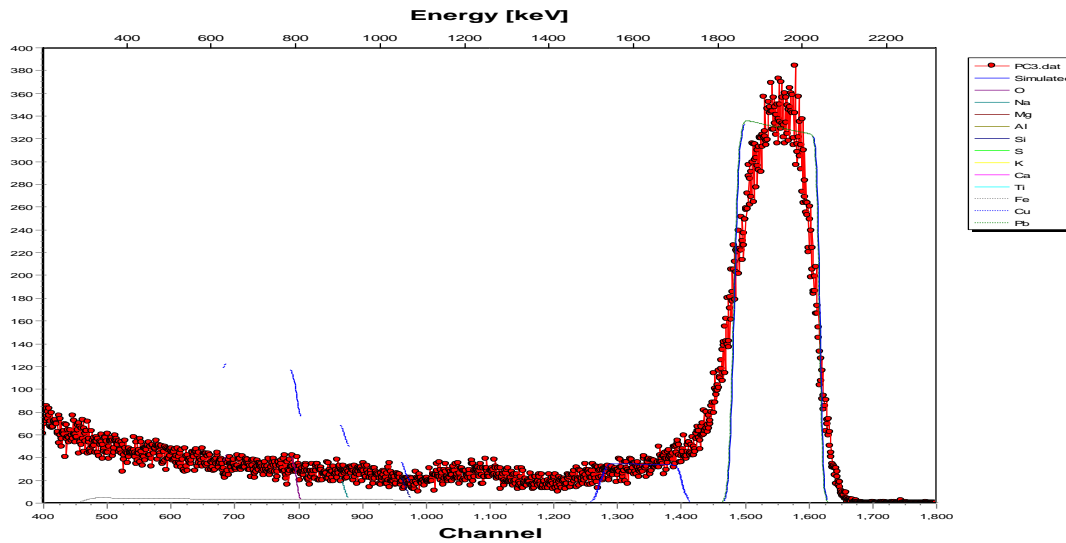


Figure 3.2: The composition of samples cp₂ with thickness, 592.59 nm as measured by Rutherford backscattering spectroscopy (RBS)

Table 3.2: The elements in sample cp₂

Elements	Layer (1) %Comp	Layer (2) %Comp
O	85.35	67.40
S	3.50	0.16
Pb	0.64	
Cu	5.03	
Si		18.53
Fe		0.48
Na		8.77
Al		2.18
Mg		0.11
Ti		0.87
Ca		1.06

3.2. 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: PbO, prepared at 40°C of sodium hydroxide solution. **Figure 3.3** show x-ray diffraction of the above listed alloyed thin films. The XRD patterns show sharp and well defined peaks which indicates the crystalline nature of alloys of CuS: PbO . The crystallite sizes given in **Table 3.3** are obtained using Debye-Scherer's equation [14].

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (3.1)$$

where k is the shape factor (k= 0.9), D is the grain size or average crystallite size, λ is the wavelength of CuK α radiation used ($\lambda = 1.54\text{\AA}$), β is the experimentally observed diffraction peak width at half maximum intensity (full width at half maximum FWHM) and θ is the Bragg's diffraction angle.

Table 3.3: X-ray Diffraction Results of CuS:PbO, Alloyed Thin Films

Sample	2 θ (degree)	d-spacing (\AA)	FWHM (radian)	Grain size (nm)	Count
CuS:PbO (cp1)	19.752	4.539	0.354	41.28	47
	22.911	3.899	0.156	93.47	132

XRD Pattern of CuS:PbO Alloyed Thin Films of B₁

Figure 3.3, shows the XRD pattern of CuS:PbO alloyed thin film of sample cp₁ with two diffraction peaks at $2\theta = 19.40^\circ$ and at $2\theta = 22.911^\circ$. The pattern shows well defined peaks, which indicates the crystalline nature of the alloyed of CuS:PbO at 40°C of NaOH solution. The crystallite size for this alloy, is calculated using **equation 3.1**. From the observed peaks the grain sizes of the sample are 41.28nm and 93.47nm. XRD results shows that a new compound alloyed thin films known as copper lead sulphate (IV) was formed. It has monoclinic crystal system with chemical formula; CuPbSO₄. From the data of the XRD peak the lattice parameters of CuS:PbO alloy thin film of sample B₁ are $a = 9.682\text{\AA}$, $b = 5.646\text{\AA}$, $c = 4.683\text{\AA}$

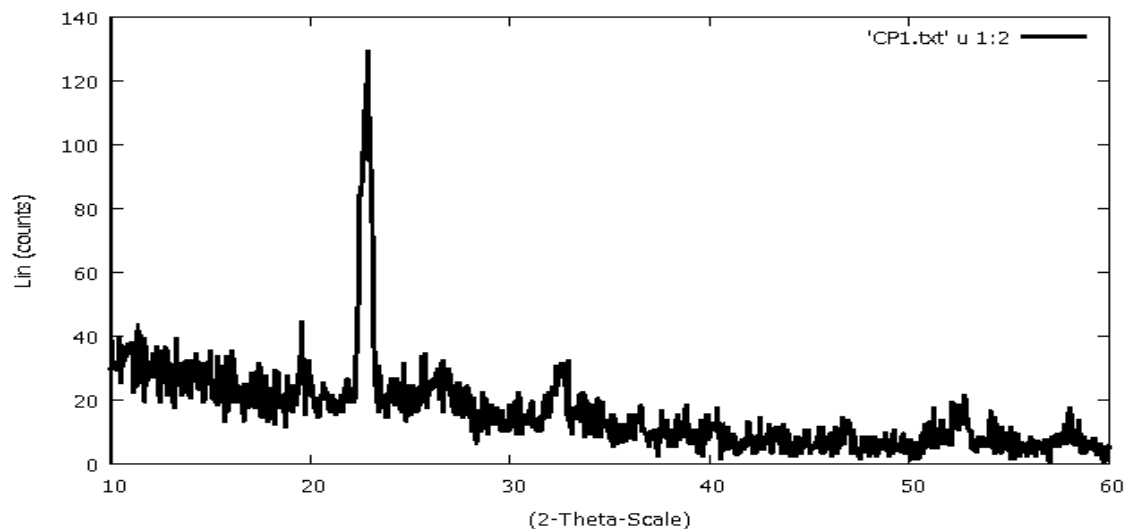


Figure 3.3: XRD pattern of CuS:PbO alloyed thin films of sample cp₁.

3.3. Microstructure of the Grown Samples

Microstructure of the thin films of CuS:PbO was determined using electron microscope Phenom Prox, Model number MVEO16477830 manufactured by Phenom World Eindhoven Netherland. The process of analysis is through back scattering electron imaging method.

Sample **cp₁**, of CuS:PbO has minor cracks. It has incoherent surfaces which is due to synthesis conditions. It contains non-agglomerated morphology. The sample has rough texture and granular microstructures. This is shown in **Figure 3.4**.

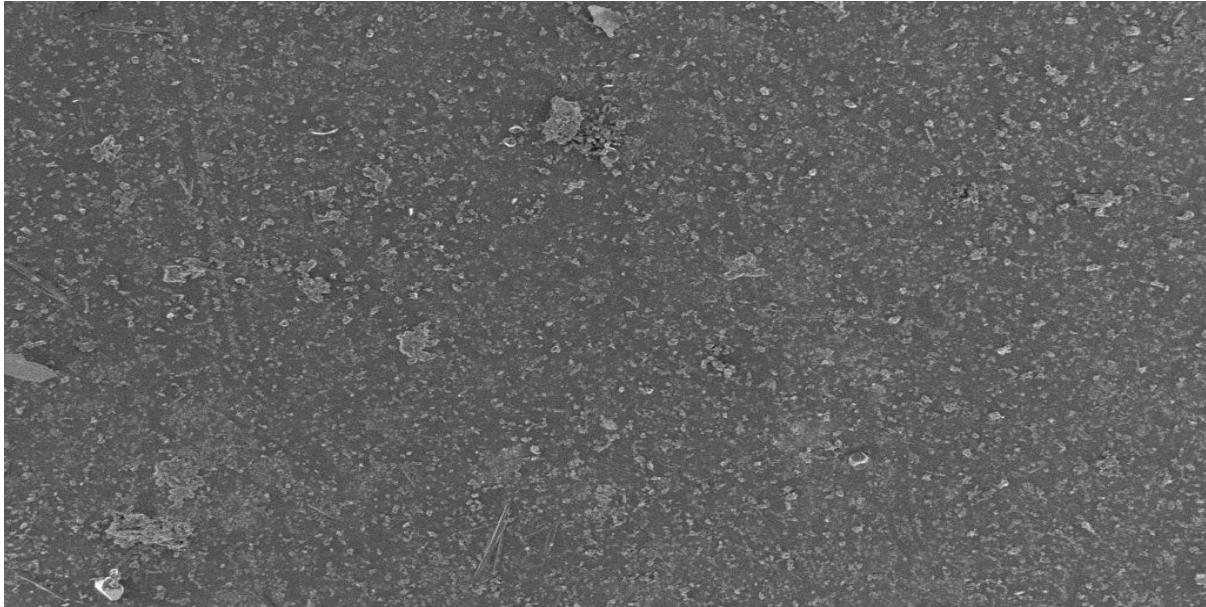


Figure 3.4: Scanning electron microscopy of sample cp₁ of CuS:PbO alloyed thin films

3.4. Optical Characterization

UV1-1800 series double beam spectrophotometer was used to study the optical properties of the deposited samples. The transmittance spectra of the two samples, have good transparency in the UV (15%-61%) for sample cp₂ annealed at 150⁰C and good transmittance (27%-71%) for sample cp₁ annealed at 250⁰C in the wavelength range (320nm-400nm). The high transmittance (60%-58%) for sample cp₂ in the visible region (400nm-700nm), becomes almost linear through the near infrared region of electromagnetic spectrum. The transmittance of sample cp₁ increases as wavelength increases up to the near infrared region of electromagnetic spectrum. In the near-infrared region, sample cp₁ has high transmittance (83%-88%) within the wavelength of 700nm-1080nm of the region of electromagnetic spectrum as shown in **Fig.3.5**. This makes these alloyed films good materials for UV filter [15]. It can also be used as optoelectronic material, It can also be a good material for cold and heat windows, dazzling coatings, solar thermal-energy conversion.

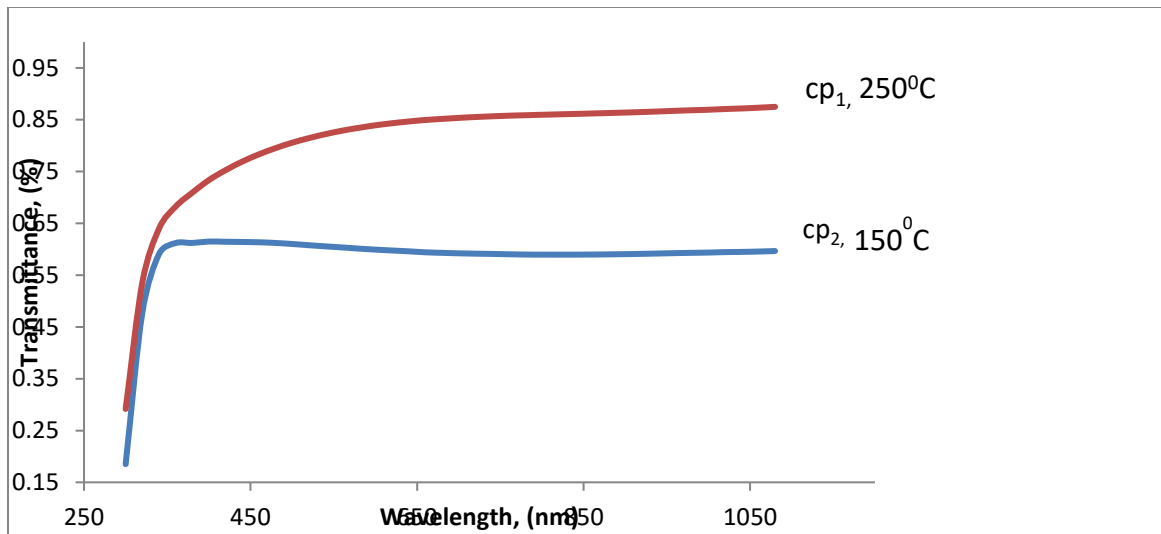


Figure 3.5: The Graph of transmittance against wavelength for CuS:PbO alloyed thin films of samples cp₁ and cp₂

The optical energy band gap is obtained in k space using **equation (3.2)** given as

$$(\alpha h\nu)^2 = A(h\nu - E_g) \tag{3.2}$$

where α is the absorption coefficient, h is the Planck's constant, ν is the frequency, E_g is the energy band gap and A is the constant which depends on the materials. The energy band gaps of samples B₁ and B₂ are obtained by extrapolating the linear portion of the plot $(\alpha h\nu)^2$ against $h\nu$ at $(\alpha h\nu)^2 = 0$ as shown in **Figure 3.6**. A direct band gap value of $3.65 \pm 0.05\text{eV}$ is obtained for both samples cp₁ and cp₂. The wide band gap obtained in this work makes the CuS:PbO a good material for the production of laser diodes and light emitting diodes (LEDs) [16]. It will also be useful in solar energy conversion, liquid crystal displays and flat panel displays for optoelectronic applications.

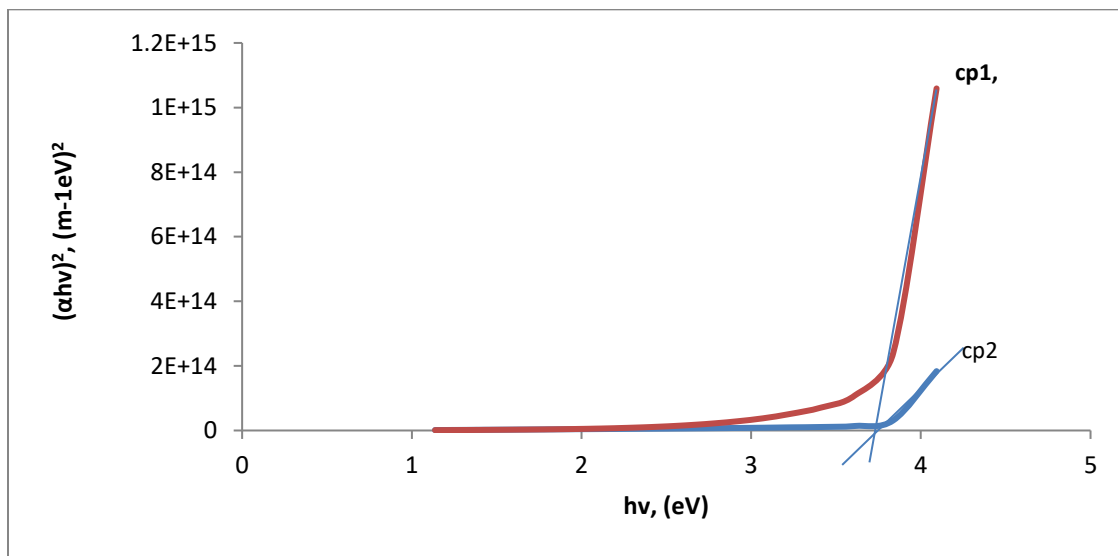


Figure 3.6: The Graph of $(\alpha h\nu)^2$ against photon energy $h\nu$ for CuS:PbO alloyed thin films of samples cp₁ and cp₂

4. Conclusion

CuS:PbO, alloyed thin films were deposited on glass substrates using two solution based methods: successive ionic layer adsorption and reaction and solution growth technique at constant temperature of 40°C of NaOH solution while other reactants were kept at room temperature of 20°C. NH₃ solution was used as complexing agent. The deposited samples were annealed between 250°C and 150°C, using Master Chef Annealing Machine. The alloyed thin films exhibited appreciable good transmittance from the ultraviolet region, through the visible to near infrared regions of electromagnetic spectrum. Other optical properties of the samples were determined using appropriate equations. Direct average energy band gap of 3.65±0.05eV was obtained for CuS:PbO alloyed thin films. The other properties investigated are absorbance, reflectance, optical conductivity, optical constants and absorption coefficient using their appropriate equations. These material alloy thin films prepared under this condition with wide energy band gap and high transparency in the visible region can be found useful in passive applications as dazzling coating, cold and heat windows, solar thermal-energy collector, selective absorbing layer and active solar cell applications, semiconductor materials, for optoelectronic applications, UV light emitting devices, laser diodes, sensors, and optical communications etc. Also, this material, has higher breakdown voltage, ability to sustain large electric field, low electronic noise, stable at higher temperature and high-power operation due to the simultaneous combination of the two separate binary compounds. Due to its thermal stability, it can be found useful in the area of tyre production(vulcanization).

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