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The Growth and Characterization of Copper Sulphide Thin Film Using CBD (Chemical Bath Deposition) Technique

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Abstract: Thin copper sulphide was deposited from a chemical bath onto clear glass slides using CBD (Chemical bath deposition). The bath contents comprise an aqueous solution composed of Copper acetate, Ammonia, Sodium citrate, Thiourea and distilled water at room temperature. Post deposition annealing was done for all slides except one at temperatures from 100 °C to 300 °C for duration of one hour. Optical characterization of the thin films showed transmittance of within 14%-86% in the wavelength of 200 nm-1,000 nm and allowed band gap of the range of 1.56 eV-2.00 eV. It also showed low reflectance of below 21%. The result showed that it has a good property which finds application in optoelectronics.

Key words: Deposition, annealing, transmittance, bandgap, reflectance, optoeletronics.

1. Introduction

The solar energy is by far the most abundant and accessible form of energy. The major problem facing the technologist is how to use solar energy in a useful form which is economically competitive, recognizing the added constraints that the materials used must also be readily available and abundant. Though not only the method, but also the direct conversion of solar energy to electricity by photovoltaic technology has a number of technological and social advantages over the energy technologies. For example, in addition to the positive aspects of using sunlight, photovoltaic systems are quite efficient, have no critical size and indeed size can be matched to load with little loss in efficiency, can be physically located near the load and are environmentally benign in operation. It is thus one of the most attractive future technologies.

Thin films posses unique properties which differ somewhat from the corresponding bulk materials. This is due to the fact that each atom in the film is very close to the surface and therefore may not have too many atoms surrounding it.

In this work, the CBD (Chemical bath deposition) technique of the CuS (Copper sulphides) films on a glass substrate was adopted. CuS are important materials for applications in p-type semiconductors and optoelectronics [1]. This finds use in photo thermal conversion applications [2], photovoltaic applications [3, 4], solar control coatings [5] and other electronic devices [6].

2. Materials and Methods

2.1 Thin Film Deposition Techniques

Thin film deposition is the process of placing the layers of thin film on a surface, usually a crystalline surface. Different deposition technique can be used amongst which are chemical bath deposition, vacuum evaporation, pulse laser, electrodeposition method [7], spray pyrolysis, SILAR method, electron beam evaporation and many more. Most of these techniques are expensive and require a high controlled formation conditions. The solution growth technique otherwise called CBD technique which was adopted in this project for thin film from aqueous solutions is highly

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accepted in recent time because of its low cost, advantage, stress free to the environment etc. So far, a number of thin films such as CdSe, ZnS, PbS, NiS, Bi_2S_3, $ZnLn_2Se_4$, $CdS_{1-x}Se_x$ and $ZnCd_{1-x}S$ prepared using CBD method have been reported by many researchers [8-15].

Solution growth technique is minimal because all materials are within reach. It can be scaled for large area production. It requires low temperature for film deposition and the film are uniformly deposited and above all can be compared to opto-electronic properties with solution from other techniques [16].

2.2 Experimental Technique

The CBD technique appears to be relatively simple, inexpensive method to prepare a homogeneous film with controlled composition. However, depending on the deposition conditions like pH of the solution, temperature, stirring and time of deposition, the quality as well as the stoichiometry of the film differ and hence their structural and optical properties [17].

For a compound to be precipitated from a reaction mixture, the ionic product has to exceed the solubility product. This condition is more easily achieved in a saturated solution of a weakly soluble compound. In order to form a thin film by a controlled ion-by-ion reaction, it is necessary to eliminate spontaneous precipitation. This can be achieved by the use of suitable complexing agents to form stable neutral complex ions, which then release the ion s slowly under a suitable medium.

2.3 Experimental Work

The experimental work was carried out at the crystal growth and characterization laboratory in University of Nigeria, Nsukka. The following apparatus were used for this work.

Glass beakers (50 ml and 100 ml);

Microscopic glass slide;

Stirring rod;

Measuring cylinders (50 ml and 100 ml);

Electronic weighing balance;

Temperature regulation oven.

The chemicals involve for the growth of copper sulphide thin film are; copper acetate $[(CH_3COO)_2\ Cu,\ H_2O]$, Ammonia $[NH_3]$, Thiourea $[(NH_2)_2\ CS]$ and water $[H_2O]$. In the process of the work, NH_3 is used as complexing agent, and the thiourea is functional for bringing out the sulphur or sulphide in the reaction.

2.4 Experimental Setup

The set-up for the experiment is as shown in Fig. 1. The glass slides used as substrates were dipped into a concentrated acid (HCl) for twenty-four hours. It is later brought out and scrubbed softly with synthetic foam in detergent water. It was afterwards rinsed with distilled water and clamped with a peg to drip dry in air. The glass slides were kept vertically and at the center of a beaker using synthetic foam such that they don't make contact with the bottom or walls of the bath containers (beakers). The reaction baths were thoroughly stirred before the substrates were inserted.

The deposition process was done at room temperature without stirring at about 27 $^{\circ}$C and the process was repeated for different dip times with various reaction baths. All of the solutions that were used in deposition were clear solutions without precipitation. After the deposition, the CuS films were rinsed with distilled water to remove the loosely adhered CuS particles on the film and finally dried in air.

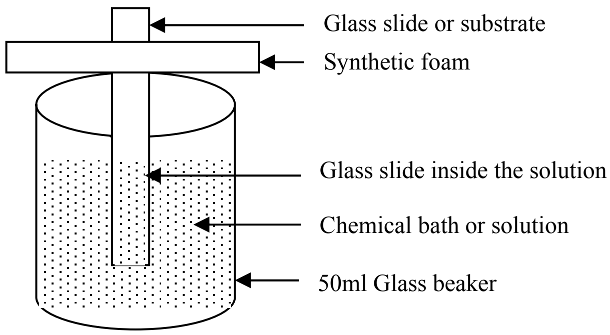

Fig. 1 Experimental set-up for the deposition of CuS thin film.

2.5 Experimental Observation

The dried samples were annealed at different temperatures. The details of various reaction bath and their dip times are displayed below in Table 1. Post deposition annealing at temperature greater than 100 °C for time duration of one hour lead to appreciable grain growth.

2.6 Reaction Mechanism

The deposition of CuS film is achieved from very dilute solutions. The chemical reaction that leads to the formation of CuS is as follows:

$$Cu(CH_3COO)_2 + 2NH_3 + (NH_2)_2\,CS + 2(OH)^- \leftrightarrow CuS + 2NH_4\,(CH_3\,COO) + CH_2N_2 + H_2O \quad (1)$$

Cu^{2+} ions are complexes with ammonia (NH_3) directly added as NH_3 (aq.) in the presence of sodium citrate. This ensures slow release of Cu^{2+} in the solution. Most of the copper ions will be presented as $[Cu\,(NH_3)_4]^{2+}$ and $[Cu\,(NH_4)\,OH]^+$.

$$Cu^{2+} + 4NH_3 \leftrightarrow [Cu\,(NH_3)_4]^{2+} \quad (2)$$

and

$$Cu^{2+} + 2NH4 + OH \leftrightarrow [Cu\,(NH_4)\,OH]^+ \quad (3)$$

The slow dissociation of these complexes i.e. the reverse direction, will produce free copper ion in the bath. Table 2 lists the complexing agents for different ions. Sulphide ions are released in the bath by the hydrolysis of thiourea in the presence of OH^- ions according to the equation.

$$(NH_2)_2\,CS + OH^- \rightarrow CH_2N_2 + H_2O + HS^- \quad (4)$$

$$HS^- + OH^- \rightarrow H_2O + S^{2-} \quad (5)$$

The copper II ions thus released can condense with sulfide ions to form thin films and precipitate of CuS.

$$Cu^{2+} + S^{2-} \leftrightarrow CuS \quad (6)$$

3. Results and Discussion

The aim of this study is to successfully deposit CuS on a glass slide and to study its optical properties so as to determine its application or usefulness. Thin film of CuS were successfully grown and characterized to obtain the optical and solid state properties. Their optical properties measured in the 200 nm-1,000 nm wavelength interval using a Unico-UV 2102 PC Spectrophotometer. The results showed that CuS thin film showed potential applications in the area of electronic device fabrication. The results so gotten agree with similar works done by other researchers [18, 19].

3.1 Physical Appearance of Films Deposited

The film deposited was grey in color. The films strongly adhere to the slides and its thickness was uniformly on the slides.

3.2 Study of Absorbance of the Films

The spectral absorbance variation with its wavelength for all samples is displayed in Fig. 2. The results were gotten for slides Cw_1, Cw_2, Cw_3 and Cw_4 which were re-labeled K, P, Q and R. The maximum value for sample K is 0.35 at 371 nm in the visible region which reduces gradually in the VIS-IR regions to a minimum value of 0.13 at 998 nm. The maximum value at the visible region for sample P is 0.15 at 371 nm and it reduced gradually in the VIS-IR region to a minimum of 0.07 at 998 nm. Sample Q has a maximum absorbance of 0.51 at 371 nm and reduces gradually to 0.44 at 542 nm still in the visible region. It then increases

Table 1 Six reaction baths and their dip times, weight and annealing temperatures.

Labeled slide	Duration in solution bath (h)	Weight before deposition m_1/g	Weight after deposition m_2/g	Difference on weight slide (m_2-m_1)/g	Annealing Temperature at 1h factor (°C)
Cw_1	16	2.45	2.46	0.01	100
Cw_2	18	2.55	2.56	0.01	150
Cw_3	20	3.42	3.43	0.01	200
Cw_4	22	2.19	2.20	0.01	250
Cw_5	24	2.27	2.28	0.01	300
Cw_6	26	2.90	2.91	0.01	control

Table 2 Ions and their common complexing agents.

Element	Complexing agents
Ag	CN^-, NH_3, Cl^-
Cd	CN^-, NH_3, Cl^-, EDTA, $C_6H_5O_7^{3-}$
Co	NH_3, CN^-, SCN^-, $C_4H_4O_6^{2-}$, $C_6H_5O_7^{3-}$
Cu	NH_3, Cl^-, CN^-, EDTA
Hg	NH_3, Cl^-, CN^-, EDTA
Mn	$C_2O_4^{2-}$, $C_6H_5O_7^{3-}$, $C_4H_6O_6^{2-}$, CN^-, EDTA
Ni	CN^-, SCN^-, EDTA, NH_3
Pb	EDTA, $C_6H_5O_7^{3-}$, $C_4H_6O_6^{2-}$, OH
Sn	$C_6H_5O_7^{3-}$, $C_4H_6O_6^{2-}$, $C_2O_4^{2-}$, OH
Zn	CN^-, NH_3, EDTA, $C_4H_6O_6^{2-}$, $C_6H_5O_7^{3-}$

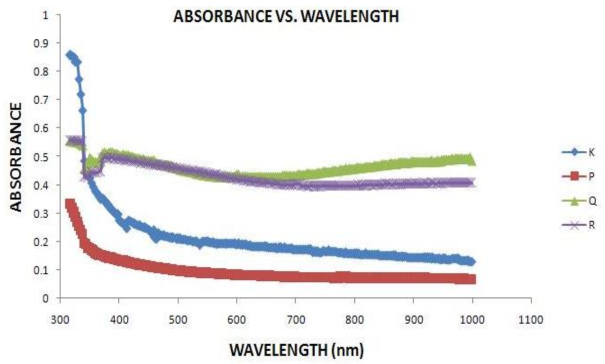

Fig. 2 Absorbance (A) as a function of wavelength (λ) for the different samples of CuS Thin Film.

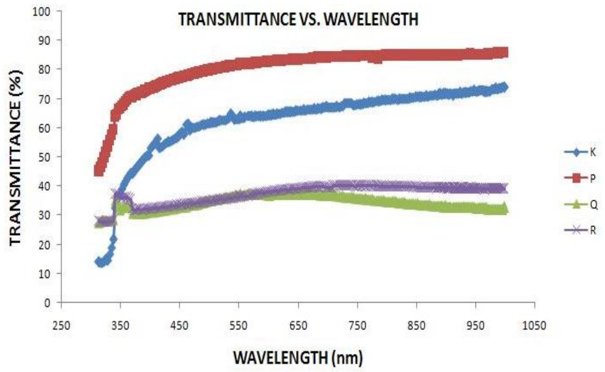

Fig. 3 Transmittance (T) as a function of wavelength (λ) for the different samples of CuS Thin Film.

at this point in the far VIS-IR regions to 0.49 at 998 nm. No absorbance was observed in the UV region for all the samples.

3.3 Study of Transmittance of the Films

The spectral transmittance as a function of wavelength for the CuS film is shown in Fig. 3. Sample K increases sharply from 13.95% at 314 nm to 44.34% at 371 nm in the near visible region. It then increases gradually from this point to 73.98% at 998 nm in the VIS-IR regions. That of film P increases sharply from 45.23% at 314 nm to 72.62% at 371 nm in the near visible region and then increases gradually in the VIS-IR regions to 85.75% at 998 nm. Sample film Q increases gradually from 27.90% at 320 nm in the near visible region to 37.25% at 656 nm in the far visible region and then reduces gradually to 32.69% at 998 nm. Sample R increases gradually from 28.05% at 314 nm in the near visible region to 40.16% at 716 nm in the near IR region. It then reduces moderately in the IR region to 39.21% at 998 nm. No transmittance was observed in the UV region for all samples.

3.4 Study of Reflectance of the Films

The reflectance as a function of wavelength for the CuS films is shown in Fig. 4. The graph reveals that the reflectance of the films is low below 25% throughout the VIS-IR region. No reflectance was observed in the UV region for all the films.

From the graph, film sample K reduces in reflectance from 20.34% at 371 nm in the visible region to 12.93% at 998 nm in the IR-region. That of film sample P reduces from 14.27% at 371 nm in the visible region to 7.57% at 998 nm in the IR-region. Sample Q increases gradually from 18.06% at 371 nm in the near visible region to 19.85% at 659 nm in the far visible region then reduces gradually to 18.75% at 998 nm in the IR-region. Sample R increases gradually from 18.47% at 374 nm in the visible region to 20.22% at 770 nm in the near IR-region then reduces moderately in the IR-region to 20.13% at 998 nm.

3.5 Study of Band Gap of the Films

Fig. 5 shows some curves of $(\alpha h\nu)^2$ against the photon energy from where the band gaps for the various samples were obtained. The result shows that:

Sample K has a band gap of 1.60 eV;

Sample P has a band gap of 2.00 eV;

Sample Q has a band gap of 1.56 eV;

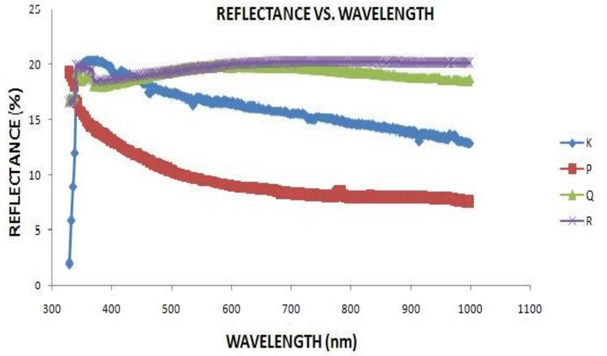

Fig. 4 Reflectance (T) as a function of wavelength (λ) for the different samples of CuS Thin Film.

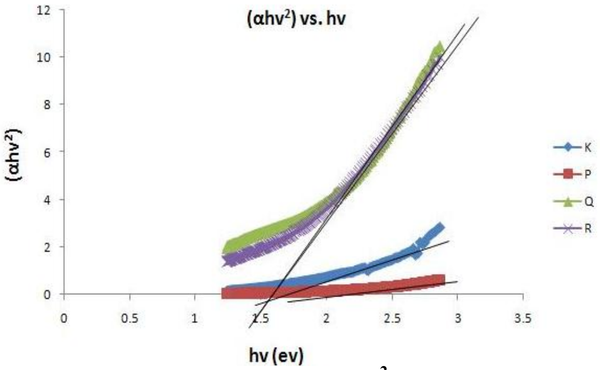

Fig. 5 Graph of photon energy $(\alpha hv)^2$ against energy band gap (hv) for the 4 sample substrates.

Sample R has a band gap of 1.56 eV;

The results show that the band gap of the samples falls in the range of 1.56 eV-2.00 eV.

4. Conclusions

CuS films which were grown on glass substrates by CBD at ambient temperature showed good optical properties and adhered well to the substrates. The optical properties deduced from the characterization include the transmittance, reflectance, and absorbance and energy band gap. Energy band gap values agree with the Shockley-Queisser limit for the theoretical maximum efficiency of solar cell semiconductors. The absorbance spectra clearly indicates that lower wavelengths correspond to maximum absorption compared to higher wavelengths. This absorbance thus produced in the visible region indicates the possibility of these materials to be used in the photo electrochemical cells .These properties was studied based on time intervals (16, 18, 20, 22 h) and post-deposition annealing temperatures (100, 150, 200, 250 °C) for a one hour period. The films also show an increase in transmission in the VIS-Near IR regions. The behavior of the optical properties of these films with wavelength shows that they are good solar transmittance.

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