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# Electrical Conductivity of CU$_X$S Thin Film Deposited by Chemical Bath Deposition (CBD) Technique

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**ABSTRACT:** Thin films of Cu$_x$S have successfully been deposited on glass substrates using the Chemical Bath Deposition (CBD) technique. The films were then investigated for their electrical properties. The results showed that the electrical conductivities of the Cu$_x$S films with different molarities (n) of thiourea (Tu), determined using the two-point probe technique, decreased with increase in the molarities of Thiourea . Thus, the conductivity ranged from 1.23 x $10^{-7}$ – 1.3 x $10^{-1}$ S/cm.

**KEYWORDS:** CBD; Electical conductivity; Molarity; Two-point probe; Thiourea

## INTRODUCTION

The term "thin film" generally refers to layer of material with one dimension much smaller than the other two (Thiyaharajan *et al*, 2009). Thin film materials have become technologically important in recent years (Thiyagarajan *et al*, 2009). This is because the importance of coatings and the synthesis of new materials for industry have resulted in a tremendous increase of innovative thin film-processed technology. Some examples are Microelectronic Integrated Circuits, Magnetic Storage Systems, Optical, Solar Coatings, Solar Cells, Photoconductors, Sensors, Anti-reflection Coatings, Interference items, Polarisers, Narrow and Band Filters, Infrared (IR) Detectors Waveguide Coatings, Temperature Control of Satellite, Photo-thermal Coatings, etc.

Copper Sulphide (CuS) belongs to group I – VI compound semiconductor materials (Pathan and Lokande, 2004). At room temperature, copper sulphide (CuS) form five stable phases: (i) Covellite (CuS), (ii) anilite (Cu$_{1.7}$S) (iii) digenite (Cu1$_{1.8}$S), (iv) djurtite (Cu$_{1.95}$S) and (v) chalcocite (Cu$_2$S). Copper Sulphide (Cu$_x$S) has different crustal structures depending on the value of X such as hexagonal, orthorhombic pseudo-cubic and tetragonal (pathan and Lokhande, 2004). For example, Cu$_x$S has hexagonal structure and Cu$_2$S may be present in both the crystal structures, i.e. orthorhombic and hexagonal (Pathan and Lokhande, 2004; Buba, 2004).

The Chemical Bath Deposition (CBD) technique has become very popular in recent decades, especially for thin film deposition due to its low cost since no expensive and sophisticated vacuum equipments isrequired, ease of handling and ease of application to many compounds such as sulphides, oxides and selenides which includes ZnS, CdS, PbS, CuS, ZnO, CdO, BaBrO CdSe, PbSe, CuSe, etc. (Ezema and Okeke, 2003;Buba, 2007).

The Chemical Bath Deposition (CBD) techniques has been used extensively (Sharma *et al*, 1979; Inderjeet *et al*, 1980; Chopra *et al*, 1982; Nair *et al*, 1991; 1993; Ndukwe, 1993; 1995; Eze and Okeke, 1997; Fajinmi, 2000; 2001; Gurku *et al*, 2002; Adelabu and Buba, 2005; Nnabuchi, 2006; Buba, 2007) for the deposition of group II – VI and group IV – VI compound semiconductors. It has also been exploited successfully for the deposition of oxide films.

The chemical bath deposition (CBD) technique offers some advantages among which are: (1) films can be deposited on all kinds of hydrophilic substrates; (2) it is very simple and inexpensive technique suitable for large area deposition; (3) impurities in the initial chemicals can be made ineffective by suitably complexing them.; and (4) in contrast to the difficulty of obtaining stoichiometric such techniques are reactive as co-evaporation, reactive sputtering, and electro deposition for deposition of compound films. Deposits formed by homogenous precipitation are always nearly \stoichiometric. This is because the basic building blocks are ions instead of atoms, so that the condition of charge neutrality maintains the stoichiometry. However, the deviations from stoichiometry may arise if the metal ion is multivalent (Chopra and Kaur, 1983).

In this paper, we report the synthesis and electrical properties of CuS thin film deposited by chemical bath depiosition (CBD) technique.

## THEORETICAL CONSIDERATION AND CALCULATIONS

The resistance (R) of rectangular shape of length ($\ell$), of thin film (measured in direction parallel to the film surface), width (b) and thickness (d), at constant temperature (Maissel and Glang, 1970):

$$R = \frac{\rho}{d}\frac{\ell}{b} \text{ .......................... (1)}$$

Where ρ is the resistivity.

The same sample could be used for mobility measurements.

If $\ell$ = b, equation (1) become

$$R = \frac{p}{d} = R_s \text{ .......................... (2)}$$

Hence resistance $R_s$ of square film is independent of the size of square, depends on resistivity and thickness. The quantity $R_s$ is called sheet resistance of the film and is expressed in ohms per square. It is very useful quantity that is widely used for comparing films, particularly those of the same materials deposited under similar conditions. If the thick ness is known, the resistivity is readily obtained from $\rho = R_s d$. So the most direct method of measuring ρ or $R_s$ is to prepare a rectangular sample of film and measure its resistance. It is very necessary to ensure that the contacts are ohmic or as close to ohmic as possible, so that the bulk resistivity, not the contact resistance, is measured (Schroder, 1998).

The most commonly used method for measuring the resistivity of arbitrary shaped sample is Vandre Pauw Method (Schroder, 1998). The specific resistivity of a flat sample of arbitrary shape can be measured without knowing the current pattern, if the following conditions are met: (1) the contacts are at the circumference of the sample, (2) the contacts are sufficiently small, (3) the sample is uniformly thick and the surface of the sample is singly connected i.e. the sample does not contain any isolated holes. Considering a flat sample of a conducting material of arbitrary shape, with contacts 1, 2, 3 and 4 along the periphery to satisfy the above conditions.

The resistance $R_{1234}$ is defined (Schroder, 1998) as:

$$R_{1234} = \frac{V_{34}}{I_{12}} \text{ .......................... (3)}$$

Where the current $I_{12}$ enters the sample through the contact 1 and leaves through contact 2 and $V_{34} = V_3 - V_4$ is the voltage difference between contact 3 and 4; $R_{23,41}$ is defined similarly. The resistivity is given (Schroder, 1998) by:

$$p = \frac{\pi t}{In(2)} \bullet \frac{(R_{12,34} + R_{23,41})}{2} F \text{ ... (4)}$$

and

$$\frac{Rr-1}{Rr+1} = \frac{F}{In(2)} arcchosh\left(\frac{\exp[In(2)/F[}{2}\right) \text{ ......... (5)}$$

For symmetrical sample such as circular or square Rr = 1 and F = 1.

However, materials of very high resistivity, (p ~ $10^7$ – $10^9$Ω-cm) are difficult to measure by Conventional Vander Pauw Method.

Different energy band models for amorphous semiconductors have been proposed (Chopra and Das, 1983). In order to explain the conduct process in these materials, and all the models invoke the concept of localised states in band tails.

On the Basis of Davi-Mott model (Eckertova, 1977; Mott and Davis, 1979; Chopra and Das, 1983) which is widely used for amorphous thin films of chalcogenide semiconductors (Mott and Davis, 1979; Chopra and Das, 1983), three distinct mechanisms for conduction are possible.

The first mechanism is excitation of carriers from localised states at or near the Fermi level to non-localised or extended states in the valence band beyond Ev (for p-type condition). The conductivity in this region can be represented (Chopra and Das, 1983) by

$$\sigma_1 = \sigma_1 (o) \exp [-(E_f - E_v)/K_B T) \text{................ (6)}$$

Where $E_v$ represents the critical energy at which de-localisation of states in the valence band occurs, $\sigma_1(o)$ is the conductivity at 1/T = 0 and other symbols have their usual meaning.

The second region results from the excitation of carriers at or near the Fermi level to the localised states in the valence band. Conduction in this case is by hopping and is given (Chopra and Das, 1983) by

$$\sigma_2 = \sigma_2(o) \exp [-E_f - E_B + E_{hop})/KBT] \text{ ......... (7)}$$

Where $E_{hop}$ is the activation energy for hopping conduction, $E_B$ is the energy at valence band edge and $\sigma_2(o)$ is the extrapolated conductivity, at 1/T= $\sigma_2(o)$, it is expected to be lower than

$\sigma_1(o)$ as a result of reduced effective density of the states and reduction in the mobility.

The third mechanism arises from hopping between the localised states near the Fermi level. If this is between nearest neighbours only, the conductivity can be represented (Chopra and Das, 1983) by

$$\sigma_3 = \sigma_3(o)\ \mathrm{Exp}\ (-E_3/K_BT) \ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

Where $E_3$ is the activation energy for hopping conduction in the defect band and $\sigma_3(o)$ is the extrapolated conductivity at $1/T = 0$. As the temperature is lowered, hopping may occur to more distant site in the defect band and the log of conductivity will then follow a $T^{-1/4}$ dependence.

For low and medium resistive samples, Vander Pauw may be used for resistivity measurements at room temperature. The resistance of the film is calculated from the following relation (Chopra and Das, 1983)

$$R = \frac{V}{I} - R_i \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

Where R is the film resistance, V is the applied voltage, I is the measure current and $R_i$ is the internal resistance of the current meter. The resistivity could then be calculated as:

$$\rho = \frac{Rtw}{\ell} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

Where R is the resistance of the film, t is the film thickness, $\ell$ is the length and w is the width of the film.

Hence, the electrical conductivity, $\sigma$ is from:

$$\rho = \frac{RA}{L} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (11)$$

$$\text{Since } \sigma = \frac{1}{\rho} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12)$$

Where R is the resistance of the sample A is the surface area and L is the thickness of the sample.

## EXPERIMENTAL DETAILS

Copper Sulphide ($Cu_xS$) thin films were deposited by chemical bath deposition (CBD) techniques. Glass slides were used as substrates. The bath was composed of the following (i) 5ml of 1M $CuCl_2$; (ii) 1M NaOH; (iii) nM Thiourea (where n=1, 2, 3, 4, 5, 6); (iv) 7.4M TEA; (v) 30% $NH_3$ and (v) The rest distilled water.

The substrates were cleaned using commercial detergent, and distilled water, and afterwards dried in open air.

The deposition was carried out in three different baths, consisting of all the reagents listed above with the same compositions, but the drip times were varied and the molarity of thiourea being the source of sulphur was varied for the purpose of standardizing the baths and optimising the growth of the films. The films were removed from the baths after 2 hour, 4 hour and 6 hour dip times, and were washed in distilled water before air drying.

The electrical conductivity of the samples used in this study was measured using the Two-point probe techniques. In this technique, copper wires were attached to both ends of the film sample. Silver paste was applied to the surfaces of the sample to serve as electrodes. The current I, which flowed through the film samples was measured by Keithley System consisting of voltage source and current detector. The resistivity ($\rho$) of the material was obtained by measuring the resistance and physical dimensions of the film samples, based on the expression given in equation (11), and the electrical conductivity ($\sigma$), was calculated from equation (12).

## RESULTS AND DISCUSSION

Fig. 1 shows the I–V characteristics for the $Cu_xS$ samples deposited for 2 hours, 4 hours and 6 hours dip time. The I– V characteristics of these samples indicate linear behaviour for both forward and reverse bias conditions. The shape of the graphs provides the conductance value which can be used to calculate the electrical conductivity of the sample.

Fig. 2 shows the electrical conductivity $\sigma$ as a function of molarity (n) of the thiourea (source of sulphur) in the samples. The conductivity decreased with increased molarity of the thiourea. The bulk electrical conductivity values of the $Cu_xS$ were in the range of $1.23 \times 10^{-7}$ to $1.38 \times 10^{-1}$ S/cm.

From the figure, larger values of electrical conductivities were observed at regions where the thiourea concentration is low, and that, this could probably be due to the fact that at lower thiourea concentration, the $Cu_xS$ could be Copper rich and Sulfur poor. In other words, samples with low thiourea concentration showed a remarkably larger electrical conductivity as compared to the samples with high thiourea concentration.

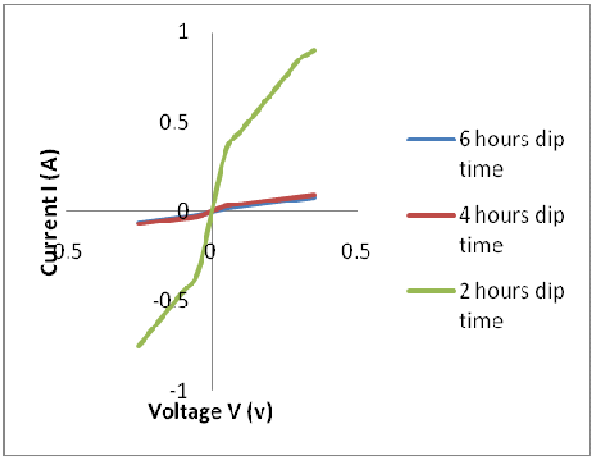

**Fig.1:** I-V characteristics of $Cu_xS$ thin films at different times

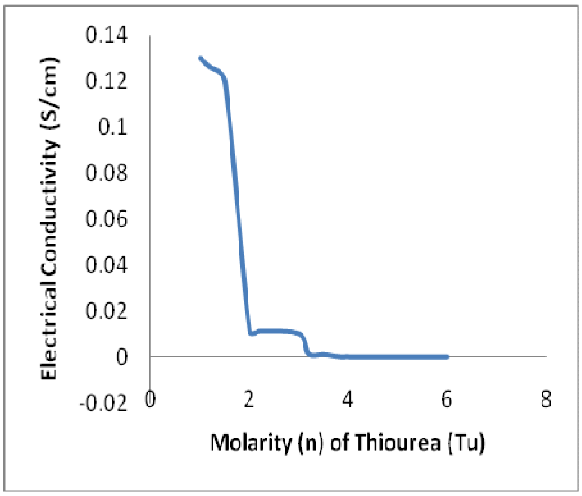

**Fig.2:** The electrical conductivity of CuxS films at different molarities (n)

The deposition of $Cu_xS$ films from the chemical bath requires that $Cu^+/Cu^{2+}$ and $S^{2-}$ ions are provided through the hydrolysis of thiourea in an alkali bath (Nair and Nair, 1989). The presence of $Cu^+/Cu^{2+}$ was considered, since the interest in $Cu_xS$ films is with the composition X closer 2 (typically 1.75 – 2.0) as suggested by Nair and Nair (1989) giving room for wide range of applications to be possible, since the availability of $Cu^+$ is a requirement. However, $CuCl_2$ is highly insoluble in water and the acidic medium (Ph ~ 3.5) is incompatible with chemical bath deposition. However, it is known that, the equilibrium

$$2Cu+ \rightleftharpoons Cu + C_u^{2+}$$

Can be displaced in either direction through complexation, depending on the complexing agent.

Therefore, here the Copper II salt has been used to generate $Cu^{2+}$ ions. These salts dissolve readily in water to give the aqueous $[Cu\ (H_2O)_6]^{2+}$ and the complexation proceeds by successive displacement of water molecules by the complexing molecules (Nair and Nair, 1989). Thus, in the present case, where TEA, Thiourea and Ammonia are simultaneously existing in the bath it was suggested that the complexions of $[Cu(TEA)_n]^{27}$, $[Cu(NH_3)_m]^{2+}$ and even $[Cu_4(Tu)6]^{4+}$ may be simultaneously present and the relative concentrations of these species will change with time as the deposition proceeds (Nair and Nair, 1989). Following the above suggestions, the release of $Cu^{2+}$, $Cu^+$ and $Cu^o$ (elemental) may all be possible. However, in chemical bath deposition (CBD) the substrates with the already formed nucleation centres acts as catalytic surfaces promoting the adherence of particular atom/ions. Thus the resultant effect as to which ionic form of copper is inducted into films requires detailed study (Nair and Nair, 1989).

## CONCLUSION

Chemical bath deposition (CBD) techniques had been used successfully to deposit $Cu_xS$ thin films on glass substrates. The electrical conductivity of $Cu_xS$ compound films with different molarities (n) of thiourea were investigated using Two-point probe technique. The electrical conductivity of the film decreased with increase in the molarity of thiourea (Tu).

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