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Opto-Electrical Properties of Chemical bath Deposited Cu4SnS4 Thin Films

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Abstract: Thin films could be explained as a very thin layer of a substance deposited onto various substrates. Nowadays, a variety of binary, ternary, quaternary and pent nary films have been produced by using different deposition techniques. A comprehensive study of the effects of deposition temperature on the optical and electrical properties of chemical bath deposited copper tin sulphide (Cu_4SnS_4) thin films is reported. The Cu_4SnS_4 thin films were prepared, characterized, and optimized for solar light trapping. Optical properties of the films namely, reflectance and transmittance were measured using UV-VIS NIR 3700 spectrophotometer. Transmittance and band gap of the optimized Cu_4SnS_4 thin films were found to be below 25 % and 1.46 eV respectively (films deposited at 70 °C). Further, these films showed a peak average absorbance of 62.95 %. The films were characterized using a four-point probe to determine their surface sheet resistivity. The resistivity decreases from 19.28 Ω-cm to 8.38 Ω-cm with an increase in the deposition temperature (40°C to 70°C). The obtained optical and electrical results showed the optimum deposition temperature (70°C) for the formation of Cu_4SnS_4 thin films, could be used as an absorber layer for solar cell applications. The optimized Cu_4SnS_4 films had the lowest transmittance and reflectance, highest absorbance, minimum band gap, and lowest resistivity, all positive qualities of potential material for use as an absorber layer for photovoltaic applications.
Keywords: Thin film, Electrical behaviours, Chemical bath deposition, Cu_4SnS_4 films, Solar cell, Semiconductor.

1 Introduction

There has been a steady increase in demand for clean and renewable energy globally [1]. As a result, more effort has been put into research to harness solar energy from the sun to generate electricity using solar cells [2]. Solar cells are optoelectronic devices that convert light energy into useful electrical power. They are produced from light-absorbing materials which on illumination produce carriers that generate electric current [3]. A variety of optical and electrical measurements are necessary to determine the potential of the material for solar cells [4] and its characteristics when the load is connected. The ternary compound such as Cu_4SnS_4 is a promising solar cell absorber material [5] because of its high absorption coefficient of approximately 10^4-10^5cm^{-1}.

Solar energy is the principal source of energy due to its abundance [6]. However, in most cases, it goes to waste. The solar energy can be harnessed using a photovoltaic cell to produce reliable power for domestic use [7]. Thin films are used in the fabrication of a photovoltaic cell that acts as a transducer to converts light energy into electric energy [8]. Researchers have dedicated time and effort to study thin-film technology for the sole aim of reducing the cost of production [9], maximizing efficiency [10], and production of durable and reliable solar cell [11]. Recent research findings indicate that the properties of thin-film solar cells strongly depend on the various deposition techniques, chemical bath deposition (CBD) being one of them [12]. This technique yields stable [13], adherent, uniform [14], and hard films with good reproducibility by a relatively simple process [15].

The solar cell performance is influenced by the film layers' thickness which ranges up to tens of micrometers [16]. However, a major challenge is to harness this solar energy and convert it into electrical energy using a material with good optoelectrical properties [17]. Materials with desirable properties such as direct band gap, high absorbance, and low electrical resistivity, perfect crystalline structure, and high transparency are needed to efficiently convert photovoltaic energy into electrical energy. For example,s Cu_4SnS_4 thin film is composed of II-VI group of compounds and is shown to exist in a few stoichiometric and

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crystallographic structures which have a primary preferred standpoint for making cheap, reliable, and efficient photovoltaic cells [18]. Moreover, it is easily deposited using the CBD technique and generates a great quality thin film especially when deposition conditions like temperature and concentrations are well selected.

The investigation of the behaviors of nanostructured thin films has received great attention all over the world. These binary [19,20], ternary [21, 22], quaternary [23] and pent nary materials [24] have been employed gas sensing, biomedical, laser devices, photonic devices, electro luminescence devices, anti-microbial activity, optical devices, electronic devices, and field emission devices. Characterization of thin films is an important step to study the properties of samples [25]. Several tools have been selected to study the structure, optical, morphology, electrical and composition of obtained films.

Synthesis of metal sulfide, selenide, telluride materials has been reported by many researchers [26-30]. Generally, physical and chemical deposition technique were used to produce films [31-36]. These deposition techniques such as electro deposition, chemical bath deposition, evaporation method, sol gel method, pulsed laser deposition, successive ionic layer adsorption and reaction, spray pyrolysis, molecular beam epitaxy and RF Sputtering.

The chemical bath deposition (CBD) method has been used for the deposition of thin films for photovoltaic cell application [37]. This method is preferred because it is a non – expensive technique for thin film preparation and is suitable for the deposition of group II and VI metal chalcogenides elements. Different elemental dopants like Cu (copper), Sn (tin), and S (sulfur) can be used to dope group II and VI metal chalcogenides elements using the CBD method [38]. Other elements like arsenide, nickel [39,40], and indium [41] have also been used as dopants to improve cell efficiency by addressing the problem of high spectral reflectivity and high resistivity.

The world's sulfur production (as of 2020) was highlighted in Table 1. The biggest producer countries are China [42], United States and Russia, produced 17000, 8100 and 7500 (in 1000 metric tons), respectively. In 2020, Chile, contributed about 28.5%, which makes Chile [43] the global leading copper producer (Table 2). In 2019, China accounted for about 38% of the global tin [44] resources (Table 3).

Great interest in the optoelectronic research field has led to the development of new ternary derivatives of Cu4SnS4 that are applied in the fabrication devices such as solar cells. They offer great flexibility for optimization towards higher efficiency [45]. Copper tin sulphide is becoming popular for high carrier mobility material [46] and a wide band gap for photo-conducting and photovoltaic devices [47]. It has a band gap that can be manipulated to range from 1.40 eV to 2.40 eV using the elemental dopants [48] or by changing deposition conditions like temperature. Increasing deposition temperature helps in enhancing short circuit current (Isc) and open-circuit voltage (Voc) in devices with hetero-junction the rate of absorption increases [49] Cu4SnS4 compound has a tremendous heat capacity. This enables the solar cell fabricated from such a material to behave as a heat sink. Furthermore, Cu4SnS4 has almost a perfect lattice match, and it can be grown on a transparent substance like glass. Additionally, Cu4SnS4 has been found to be a good absorber material with low transmittance and low band gap [50]. Other researchers [5] prepared Cu4SnS4 thin films by CBD technique in aqueous solutions containing CuSO4, SnCl2, Na2S2O3, and Na2EDTA. They had good photo-response activity indicating a semiconductor of the p-type and a band-gap value of 2.4 eV with a direct transition that is required for photovoltaic activities. In addition, other scientists [51] observed that the deposition of thin films onto the indium tin oxide (ITO) coated glass substrate was showing uniformity that was good with a large surface coverage of Cu4SnS4.

The main aim of this research was to study a ternary semiconductor material of Cu_4SnS_4 and to optimize it for photovoltaic applications. The study involved synthesis, optical and electrical characterization of the material.

Table 1: Sulfur production worldwide in 2020, by country.

Country	Production (in 1000 metric tons)
China	17000
United States	8100
Russia	7500
Saudi Arabia	6500
Canada	6300
India	3600
Kazakhstan	3500
Japan	3400
United Arab Emirates	3300
South Korea	3100
Iran	2200
Qatar	1800
Chile	1500

Table 2: World's copper production by country (as of 2020).

Country	(%) Percentage
Chile	28.5
Other	16.5
Peru	11
China	8.5
Congo	6.5
United States	6
Australia	4.35
Russia	4.25
Zambia	4.15
Mexico	3.45

Kazakhstan	2.9
Canada	2.85
Poland	2

Table 3: 2019 Global tin resources.

Country	(%) Percentage
China	38
Other	32
Russia	11
Indonesia	7
Australia	7
Bolivia	5

2 Experimental Details

2.1 Preparation of Thin Films

Glass slides were used as a substrate for the deposition of the thin films. Before deposition, the slides were cleaned by a liquid detergent before being dipped in ethanol for 10 minutes to remove grease. Afterward, the glass slides were soaked in 100 ºC hydrochloric acid (HCl) for nucleation centers to be created. Finally, the substrates were cleaned with distilled water for around 15 minutes and then dried at a temperature of 200 °C. The chemicals used were copper (II) sulfate ($CuSO_4$), tin (II) chloride ($SnCl_2$), sodium thiosulfate ($Na_2S_2O_3$), disodium ethylenediaminetetra acetic acid (Na_2EDTA), and hydrochloric acid (HCl). A mixture of 10 ml of $CuSO_4$ (0.05 M), 10 ml of $SnCl_2$ (0.05 M), and 10 ml of Na_2EDTA (0.1 M) were mixed for a few minutes to get a clear and homogeneous solution. At that point, 10 ml of $Na_2S_2O_3$ (0.05 M) was added under these stirring conditions. Finally, HCl acid was added till the solution was acidic with a pH of 1.5. These concentrations were maintained for all the films to be deposited. A clean glass substrate was then placed perpendicularly inside the beaker and the beaker was left for 120 min without disturbance at 40 °C. (This was repeated for 50°, 60°, 70°, and 80°C). The glass substrates were removed cleaned and dried in a desiccator.

2.2. Characterization of Thin Films

Once the thin films were prepared, the transmittance and reflectance of the films within the 300nm-1200nm wavelength range were measured using UV-NIR VIS spectrophotometer 3700 DUV. The band gap value was calculated from the allowed direct transition given by Eq. (1).

$$\alpha h\nu = \left(h\nu - E_g\right)^{\frac{1}{2}} \qquad (1)$$

where is the absorption coefficient, *h* the Planck's constant, ν the photon frequency and **Eg** the band gap energy. In this study, FESEM images were obtained using JEOL (JSM 7800F) Field emission scanning electron microscope. The morphological study of Cu_4SnS_4 was undertaken at an accelerating voltage of 20 kV and a beam current of 1-3 nA. The accelerating voltage was set constant at 20 k*eV* and the resolution was adjusted to 10 eV. The highest accelerating voltage (20 k*eV*) was set to obtain clear images and to maximize the X-ray count rate to avoid damaging the beam-sensitive samples like our Cu_4SnS_4. Finally, the electrical resistance of the Cu_4SnS_4 films deposited at various temperatures (40 °C to 80 °C) was analyzed. The sheet resistivity was experimentally determined by using a four-point probe (Fig.1). The current was set through the external probes 1 and 4 and instigates a voltage in the internal voltage probes 2 and 3.Using the current and voltage readings from the probe, sheet resistivity (ρ) was calculated using Eq. (2).

$$\rho = \frac{\pi}{\ln(2)}\left(\frac{V}{I}\right) t \qquad (2)$$

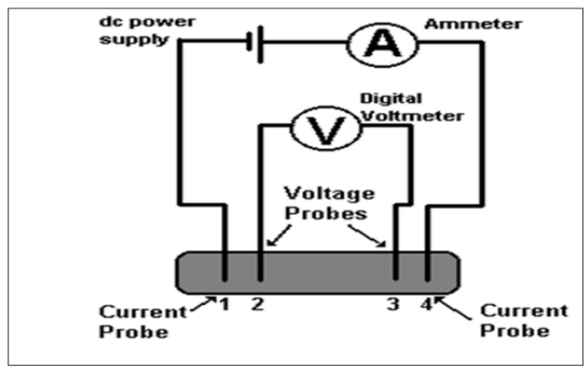

Fig.1: Four-point probe sheet resistivity measurement apparatus.

3 Results and Discussions

Chemical bath deposition was used for the preparation of thin films. Figure 2 shows transmittance curves against wavelength in the range of 300-1200 nm for Cu_4SnS_4 thin films deposited at different temperatures. It is observed that all the samples have transmittance below 50 % in the entire wavelength range. To note also is that there is no clear trend exhibited by the transmittance curves with an increase in the deposition temperature. The film deposited at 70 ºC exhibits the lowest transmittance which is less than 25 % in the entire wavelength range. Thus, an optimum deposition temperature of 70 ˚C was found to be appropriate for the deposition of the Cu_4SnS_4 thin films for photovoltaic applications as an absorber layer.

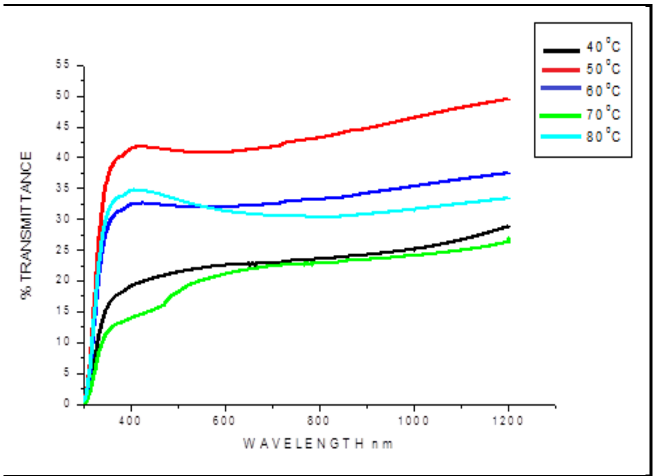

Fig.2: Transmittance against wavelength for *Cu4SnS 4*films deposited at different temperature.

Figure 3 illustrates reflectance spectra as a function of wavelength for Cu_4SnS_4 thin films deposited at different deposition temperatures. It is observed that all the samples have a maximum reflectance which is below 24 % in the given wavelength range. Further, there is no observed trend in the reflectance spectra as the deposition temperature is increased. The observed low reflectance could be attributed to the transmittance losses and absorption of the film in homogeneities. The values of reflectance below 20 % lower than the one obtained in this study were reported by Guddeti and co-workers in the wavelength range 300-1500 nm [17]. Further, another value (30 %) higher than 24 % observed in this work, was observed in the work of Chalapathi and co-workers on Cu_4SnS_4 films annealed at 500-580 °C [47], indicating that the values obtained in this study are within the acceptable range. The low reflectance exhibited by the Cu_4SnS_4 thin films showed that these films are poor reflectors of light and hence they are appropriate for photovoltaic cell applications.

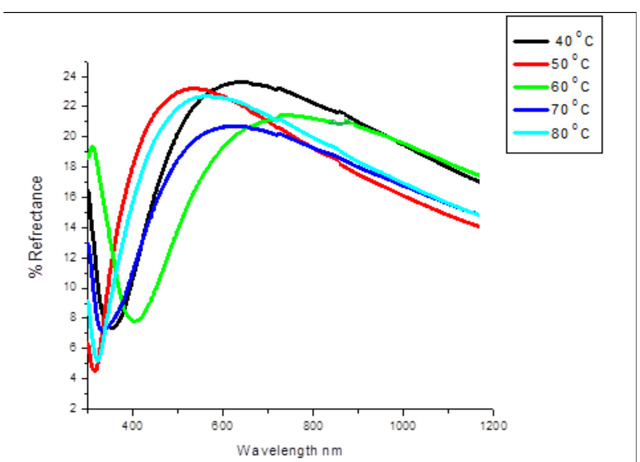

Fig.3: Reflectance against wavelength for *Cu4SnS 4*films deposited at different temperatures.

The figure 4 shows the absorbance of Cu_4SnS_4 thin films that were deposited at different deposition temperatures. The absorbance (A) was obtained from recorded values of transmittance (T) and reflectance (R) as shown in equation (3). The trends in figure 4 showed that absorbance increases gradually with deposition temperature. Comparative results have been obtained for Cu_4SnS_4 synthesized by loading stoichiometric mixture of the elements in a fused quartz ampoule inside N_2-filled glove box [51] as having films with absorbance above 50 %. Fan and co-workers also recorded absorbance above 50 % for copper zinc tin sulfide (CZTS) films [52] prepared by non-vacuum compacting process. Further, it is observed that at higher wavelengths above 750 nm, absorbance tends to remain constant indicating that it is quasi-dependent on temperature. The absorbance of thin film deposited at 70 °C exhibited the highest absorbance value. The films deposited at the lowest temperature of 40 °C showed the lowest absorption. Therefore, the deposition temperature is an essential factor in the preparation of Cu_4SnS_4 thin films for the fabrication of a photovoltaic cell.

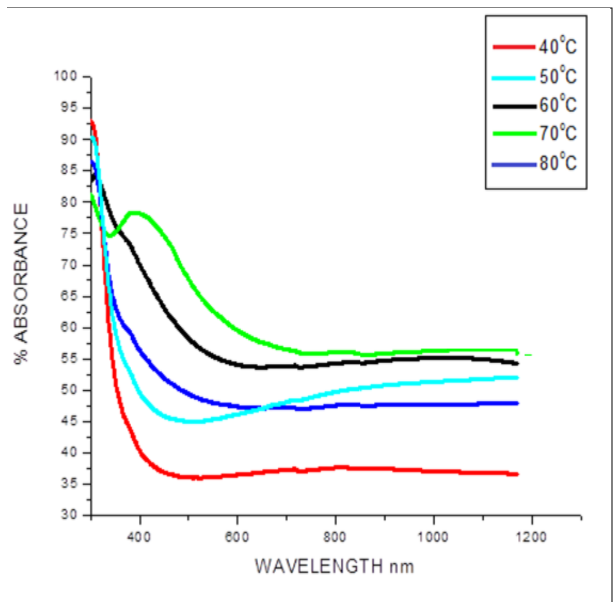

Fig. 4 : Absorbance as a function of wavelength for *Cu4SnS 4* thin films deposited at different temperatures.

The Figure 5 shows an average absorbance graph as a function of temperature for Cu_4SnS_4 thin films. The curve was plotted using data tabulated in Table 4. Average absorbance was calculated by taking the total sum of percentage absorbance divided by the wavelength range. The trends in figure 5 shows that the average absorbance increases with deposition temperature to a maximum value before starts to decrease. At a temperature above 60 ºC, the value of average absorbance was observed to be above 50 %. The absorbance of above 50 % makes Cu_4SnS_4 reliable material for use as an absorber layer in the fabrication of a photovoltaic cell. A similar trend of increase in absorbance with temperature was reported in the wavelength range 350-800 nm with a maximum absorbance of 60 % recorded for Cu_4SnS_4 thin films [5] deposited by the CBD technique. Table 4 shows the deposition temperature (ºC) and the average absorbance for the Cu_4SnS_4 thin films. The highest average absorbance of 62.95 % was obtained at 70 ºC. The high value of average absorbance reported in this work indicates that Cu_4SnS_4 thin films are a potential candidate for the absorber layer in the fabrication of photovoltaic cells.

Table 4 :Average absorbance for Cu_4SnS_4thin films deposited at different temperatures.

Deposition Temperature (C°)	Average Absorbance (%)	Error Bars (%)
40	37.03	0.18±
50	47.00	0.24±
60	57.62	0.29±
70	62.95	0.31±
80	49.23	0.24±

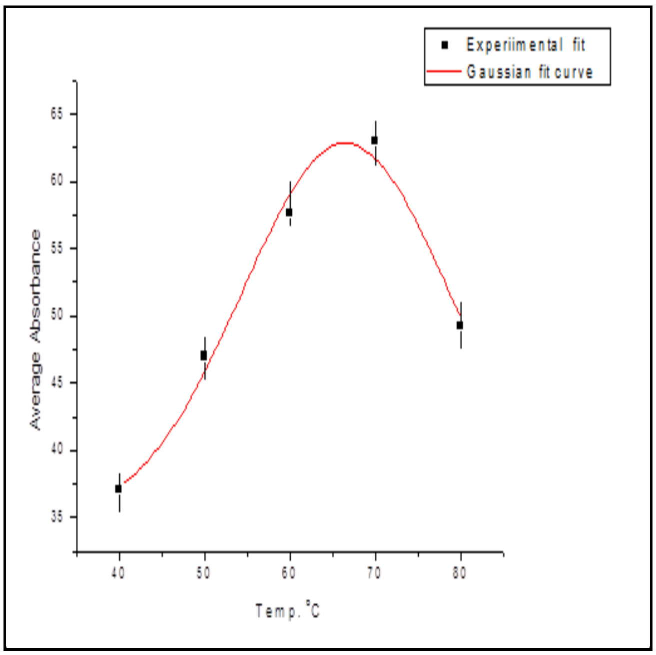

Fig.5 : Average absorbance against temperature for Cu_4SnS_4 thin films deposited at different temperatures, plotted using the values tabulated in Table 4.

The Table 5 shows the deposition temperatures (ºC) and the determined band gap energies for the resulting Cu_4SnS_4 thin films. The band gap energies were obtained by extrapolating the linear region of αhν12 versus hν plots. The band gap energy values are observed to decrease from 1.78 eV to 1.46 eV with an increase in deposition temperature from 40 °C to 70 °C before a slight increase to 1.50 eV as the temperature is increased to 80 ºC. The minimum band gap obtained was 1.46±0.06 eV. The decrease of band gap from 1.78 eV to 1.46 eV with deposition temperature could be due to an increase in thin film thickness [50] with an increase in deposition temperature. Similar research obtained optical band gap [17] in the range of 1.34 eV to 1.49 eV indicating that the values obtained in this work are within the acceptable range. The minimum band gap of 1.46 *eV* at 70°C reported in this study indicates that Cu_4SnS_4 thin films is suitable for use as an absorber layer in the fabrication of photovoltaic cell [53].

Table 5 :Energy band gap values for *Cu_4SnS_4*thin films deposited at different temperatures.

(ºC) Deposition Temperature	(eV) E_g	Error in E_g %
40	1.78	0.09±
50	1.68	0.08±
60	1.51	0.07±
70	1.46	0.06±
80	1.50	0.07±

The figure 6 shows a FESEM image of Cu_4SnS_4 thin films on a glass substrate deposited at 70 °C. The image shows an irregular morphology and irregular dimension of particles with plate-like shape. Different types of morphology have been reported with similar plate-like shaped particles [16]. It is noticeable that the surface of the film is homogeneous on large scale with no cracks or pinholes, which makes it suitable for photovoltaic applications.

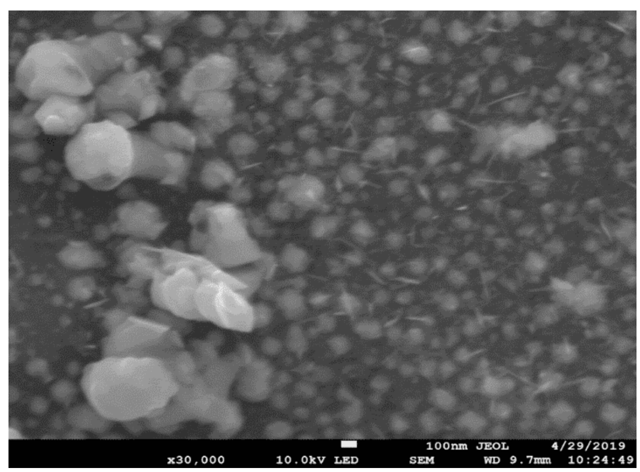

Fig.6 : FESEM image of Cu_4SnS_4thin film on a glass substrate deposited at 70 ºC.

The table 6 shows electrical resistivity values for the Cu_4SnS_4 films deposited at different deposition temperatures. The values were used to plot figure 7. The electrical measurements were carried out at room temperature and in the dark using a four-point probe. Throughout the experiments, the time between measurements was maintained for 1s to allow the films to stabilize. From the Table 3, it is observed that conductivity and film thickness increase with an increase in deposition temperature. The resistivity, on the other hand, decreases with an increase in the deposition temperature. An increase in film thickness and conductivity is due to an increase in kinetic energy of the reactants with the rise in deposition temperature. The increase in kinetic energy causes an increase in the nucleation on the surface of the substrate; consequently, increases the film thickness and conductivity of the material [17]. The decrease in resistivity with temperature is attributed to the improvement of film homogeneity [53]. Further, it was found that the electrical conductivity of the films increased with deposition temperature, showing a typical semiconductor behavior of the material.

Table 6 : Conductivity and resistivity of Cu_4SnS_4thin films deposited at different temperatures.

Deposition Temperature (ºC)	Resistivity(ρ) ±0.005 [Ω-cm]	Conductivity(σ) ±0.0005 $^{1-}$[Ω-cm]	Thickness ±0.05 (nm)
40	19.28	0.0519	200
50	12.39	0.0807	205
60	10.76	0.0929	207
70	8.38	0.1193	210
80	8.43	0.1186	226

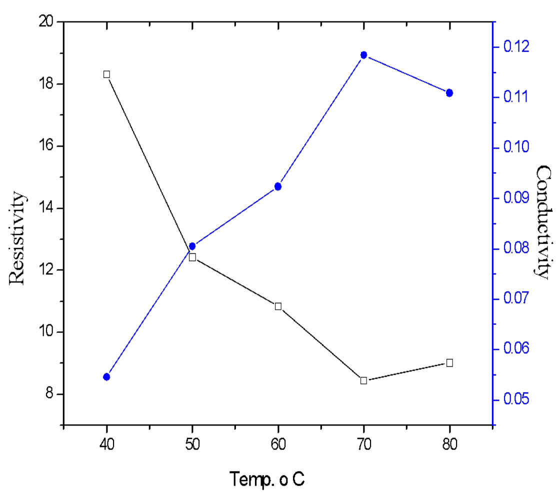

Fig.7 : Plot of conductivity and resistivity of Cu_4SnS_4thin films against deposition temperature applying the values tabulated in Table 6**.**

4 Conclusions

The chemical bath deposition method was successfully used to deposit Cu_4SnS_4 thin films on a glass substrate. The investigation was done on the effect of substrate deposition temperature on the optical and electrical properties of the Cu_4SnS_4 thin films. Solid spectrophotometer, FESEM, and four-point probe were used to measure optical transmittance and reflectance, surface morphology, and sheet resistance of the thin films, respectively. The optical, morphological, and electrical properties of the deposited thin films were discussed in regard to the absorber layer for the fabrication of photovoltaic cells. Within the visible range, the average absorbance of Cu_4SnS_4 was found to be between 37% - 62.95 % and was highest for the film deposited at 70 ºC. The band gap energy values were found to be between 1.46-1.78 eV for films deposited between 40 ºC and 80 ºC. Resistivity values decreased with an increase in deposition temperature and they ranged from 8.38 Ω-cm to 19.28 Ω-cm. It was observed that a further increase in temperature beyond 70 °C lead to an increase in resistivity of the thin films. An optimum deposition temperature of 70 °C was established as the film deposited at this temperature had the lowest transmittance, highest absorbance, and minimum band gap of 1.46 eV.

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