Published by The College of Science & Information Technology (COSIT), TASUED, Vol. 18, No. 1, pp. 177-184.

COSIT, TASUED
Journal of Science and Information Technology (JOSIT)

Opto-electrical Investigation of Thallium Cuprate (Tl_2Cu) Binary Chalcogenide Thin Films via Chemical Bath Deposition Technique

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Abstract

Thallium Cuprate (Tl_2Cu) thin films were grown on microscope glass slide in order to investigate its opto-electrical properties and examine the effects of annealing on the deposited films and suitability for solar applications. Thallium was chosen to serve as alternative and relief stress on the availability of germanium. Chemical bath deposition (CBD) technique was used and the chemical bath was developed from aqueous solution of Thallium Chloride ($TlCl_2$) and copper(II)chloride dihydrate ($CuCl_2.2H_2O$) as precursors with trisodiumcitrate (TSC) and triethanolamine (TEA) as the complexing agents. The bath was conditioned at $80^{\circ}C$ for about 5 hours to deposit the films. A four-point probe machine and an Avantes Electrophotometer operating in the 200-1000 *nm* wavelength range were used to characterize the deposited thin films. The optical properties such as reflectance, transmittance, absorbance and bandgap energy and the electrical properties of the grown films were reported in this article. This study revealed that annealing temperature has a linear proportion effect on the reflectance of Tl_2Cu deposited. The absorption spectra exhibited a relatively high direct bandgap. Materials of this nature are good for window layers where the film is not to capture any photon but serve as passage to the absorber layer where charge carriers are produced.

Keywords: Thallium cuprate (Tl_2Cu), chemical bath deposition (CBD), thin films, Opto-electrical, annealing.

INTRODUCTION

The strategy to replace some indium and gallium in solar cell technology with thallium should ease the pressure on these two elements' supply, which are crucial for optoelectronic device technologies. These elements are found in the earth's crust at 0.6 ppm, 0.049 ppm, and 18 ppm of thallium, respectively (Estrella *et al.*, 2001). Chalcogenide compounds have attracted increased attention in recent years due to their many uses in a variety of fields, such as microelectronics, solar cells, photoconductors, interference filters, polarizers, waveguide coatings, magnetic and superconducting films, and solar cells (Mane *et al*., 2000; Janickis *et al*., 2004). Because of their numerous uses in window layer solar cells and opto-electronic devices,

Cite as:
Fowodu, T.O., Adeniji, Q.A., Adelaja, A.D., Odunaike, K., Okusanya, A.A., Falayi, E.O., Akinsipo, O.B., Bamidele, K.J., Ogunneye, A.L., Olayiwola, O.G., Saheed, R.A., Leshi, D.A. and Fagbohun, M.A. (2024). Opto-electrical Investigation of Thallium Cuprate (Tl_2Cu) Binary Chalcogenide Thin Films via Chemical Bath Deposition Technique. *Journal of Science and Information Technology (JOSIT)*, Vol. 18 No. 1, pp. 177-184.

binary and ternary thin films are the subject of intensive research (Olayiwola, *et al*., 2024; Odunaike *et al*., 2021; Adeniji *et al*., 2020; Obasi *et al*., 2016). Thallium sulfide's electrical conductivity varies when it is exposed to infrared light, which makes it a valuable compound for photocells. Thallium sulfide layers are typically created by the deposition technique using solutions (Estrella *et al*., 2001).

Although there are few reports on the production of thallium cuprate (Tl_2Cu) thin films via Chemical bath deposition (CBD) technique for the fabrication of solar cells, this study was motivated by the fact that some researchers have successfully deposited and studied thin films of thalium chalcogenide compounds using various methods, such as electrodeposition (ED) (Olusola et al., 2016), thermal evaporation (Adeleke, 2017), and CBD (Estrella *et al*., 2001; Ezema *et al*., 2009).

MATERIALS AND METHODS

Materials

For the investigation, stoichiometric and analytical grade thallium chloride ($TlCl_2$), and copper(II)chloride dihydrate ($CuCl_2.2H_2O$), were utilized as reagents. Here, the complexing agents were trisodiumcitrate (TSC) and triethanolamine (TEA) with deionized water and ammonia solution (NH_4OH), while the precursors were ($TlCl_2$) and $CuCl_2.2H_2O$.

Methods

Preparation of Glass Substrate

This study used chemical bath deposition (CBD) technique. The glass substrates (with dimension 76.2 *mm* x 2.5 *mm* x 1.2 *mm*) were extensively cleaned and degreased for 24 hours by soaking in HCl, in order to eliminate both organic and inorganic contaminants from the surface. After being cleaned and dried in air, the slides were rinsed in distilled water, which provided them with the benefit of acting as nucleation sites for the development of thin films that were uniformly deposited and extremely sticky.

Preparation of Tl_2Cu Deposition Bath

In a 100 *ml* beaker, 10 *ml* of 1.0 M $TlCl_2$ solution, 20 *ml* of 0.3 M $CuCl_2.2H_2O$ solution, and 1.5 *ml* TEA complexing agent were used to create the bath for Tl_2Cu. To create a uniform mixture, 40 *ml* of distilled water were added to the mixture and gently swirled at room temperature. Drop by drop, 2 *ml* of 0.3 M NH_4OH was added until the pH reached 8.0. The Mettler Toledo AG 8603 pH meter was used to determine the solution's bath pH.

Deposition of the Thin Films

In order to avoid the substrates leaning against the bath walls and each other, they were positioned vertically and in the middle of the beaker. It took five hours at 80ºC to complete the deposition. Glass slides were withdrawn from the deposition, cleaned with distilled water, and left to dry naturally. Since the sample was exposed to the environment during preparation, it is typical for chemically deposited samples to contain environmental contamination from oxygen. The procedure of annealing eliminated oxygen pollution. Two of the film samples, labeled *TlCu at 300C* and *TlCu at 350C*, were annealed at 300ºC and 350ºC, respectively. The remaining sample, labeled *TlCu Deposited* for As-deposited for comparison, was utilized as a control. Three samples were obtained. The setup for the chemical bath deposition procedure is depicted in Figure 1.

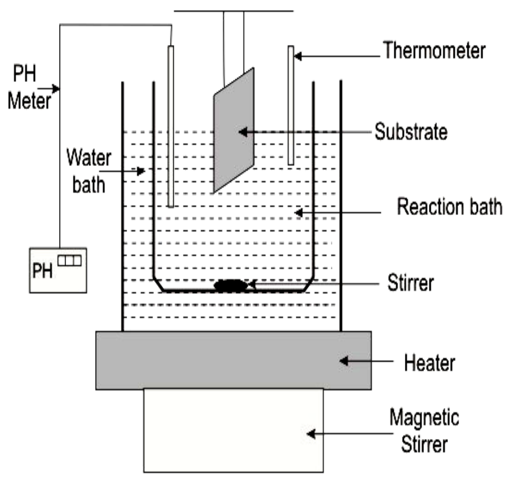

Figure. Schematic experimental set-up for chemical bath deposition of Tl_2Cu (Adapted from Adeniji, 2018).

Annealing

In thin film technology, annealing modifies surface morphology by varying temperature and time. This relieves stress, improves structure, and regulates roughness. The temperature-controlled furnace was used to anneal samples *TlCu at 300C* and *TlCu at 350C*. Using a thermometric multimeter, the temperature was recorded at 300ºC and 350ºC in 2.5 and 3 hours, respectively. This is to investigate how annealing affects the samples' optical characteristics, such as reflectance.

Characterization

The films synthesized were characterized for optical reflectance (R) and transmittance (T) using Avantes UV-VIS-NIR Electrophotometer. Other properties such as film absorbance (A), absorption coefficient (α), thickness (t) and band gap energy (E_g) were obtained theoretically from the values of reflectance and transmittance obtained. The wavelength range in which these optical properties were acquired was 200 – 1000 *nm*.

The absorbance (A) was obtained using the relation as given by Odunaike *et al*. (2021);

$$A = 2 - \log_{10} T(\%) \quad (1)$$

where, T is the percentage transmittance.

Osanyinlusi and Aregbesola (2021) gives the full details of the relationship of how to obtain A, α, t, E_g and k.

The absorption coefficient (α) was determined using Lambert equation adopted from Osanyinlusi and Aregbesola (2021):

$$\alpha = 2.303 \frac{A}{t} \quad (2)$$

where A = absorbance, t = estimated film thickness ($t = 0.1\, mm$) obtained from gravimetric (weight gain) method:

$$t = \frac{M}{\rho S_a} \quad (3)$$

where M = mass of the thin films deposited on the surface of the microscopic glass slide, obtained from the expression ($M = m_2 - m_1$) where m_1 = mass of the glass slide before film deposition and m_2 = mass weighted by the glass slide after film deposition, ρ is the average of the bulk densities (gcm^{-3}) of CuS and Fe and S_a = surface area of the thin films on the substrate.

The photon energy E, is given by:

$$E = h\text{v} \quad (4)$$

$$\text{v} = \frac{c}{\lambda} \quad (5)$$

where $h = 6.626\, x\, 10^{-34} Js^{-1}$ (Planck's constant), v is the frequency of the photon, $c = 3\, x\, 10^{8}\, ms^{-1}$ (velocity of light) and λ is the wavelength of the photon.

The energy band gaps (E_g) of the obtained films were extrapolated from the Tauc plot relation given by Ivanauskas (2021):

$$\alpha = \frac{A}{hv}(h\text{v} - E_g)^n \quad (6)$$

where A = parameter that depends on transition chance and n = value that depends on transition type. The number $n = 2$ represents direct band gap transition and $n = \frac{1}{2}$ represents indirect band gap transition. For the determination of band gap, the direct ($n = 2$) transitions was considered. The plot obtained indicates the start of the light absorption spectra with a clearly defined linear segment. The abscissa axis and the extrapolated linear part's junction yield the band gap, or E_g value. The optical band gap energy of a material can be obtained by extrapolating its linear region to the abscissa.

Photon energy loss resulting from scattering and absorption is quantified by the extinction coefficient k. The thin films' extinction coefficient was calculated using the connection:

$$k = \frac{\alpha\lambda}{4\pi} \quad (7)$$

where α = absorption coefficient (attenuation coefficient) while λ = incident photon wavelength.

The electrical characterization was examined with the use of Keithley 4ZA4 2400 Sourcemeter four-point probe machine, for measurement of voltage and current and other electrical properties were calculated using Equations (9) – (11). The sheet resistance, R_s of the films were obtained using the relation:

$$R_s = K \frac{\text{V}}{\text{I}} \quad (9)$$

where $K = 4.533$, a constant.

The resistivity, ρ, of the grown films was obtained using equation (10);

$$\rho = R_s\, x\, t \quad (10)$$

And the conductivity, σ, was determined using the relation;

$$\sigma = \frac{1}{\rho} \quad (11)$$

4. RESULTS AND DISCUSSION

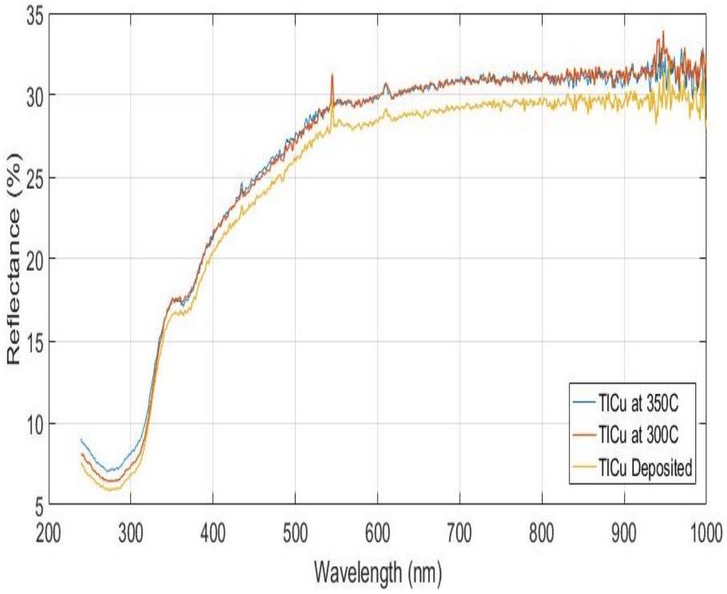

Figure 2. Reflectance (R) against wavelength of the deposited thin films.

The results of the reflectance spectra (Figure 2) demonstrate that heat causes Tl_2Cu thin film reflectance to rise in the visible region. This demonstrates that, despite the low values, the annealing temperature has a linear proportional impact on the reflectance characteristics of the deposited thin film samples. This is consistent with the findings of Wanjala *et al*. (2016), who assert that for solar applications, reflectance must be as low as feasible. Consequently, it demonstrates that thin films are a good material choice for the solar cell's window layer.

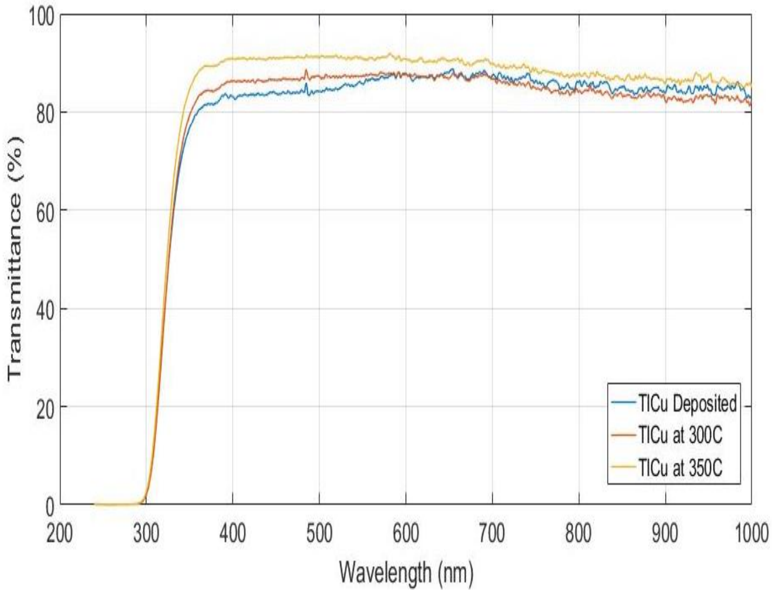

Figure 3. Transmittance (T) against wavelength of the deposited thin films.

Transmittances greater than 40% were observed in all film samples at wavelengths greater than 350 *nm*. A significant increase in photon absorption is shown by the films' % transmittance falling sharply below 320 *nm* (Kim *et al*., 2009). It means that in the Fermi-level between the valence and conduction bands, certain states have been formed. As photon striking rises with increasing carrier concentration, this can also be explained by an increase in fundamental absorption (Kumar and Sankaranarayanan, 2009). The average transmittances at λ = 800 *nm* for Tl_2Cu films were found to be 90%, as illustrated in Figure 3. These relatively high transmittance values contrast with those for doped ZnS thin films deposited by Wanjala *et al*., 2016, but the high values indicate the films' suitability for window layers in solar cells.

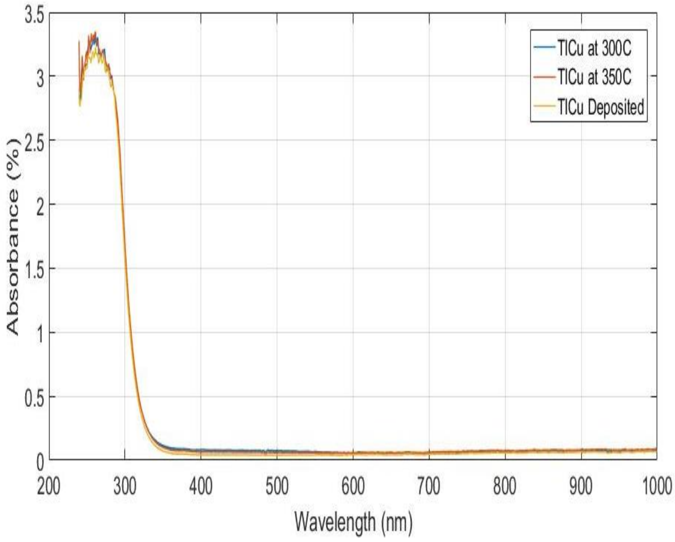

Figure 4. Absorbance (A) against wavelength of the deposited thin films.

The results presented in Figure 4 clearly demonstrate the good absorption of Tl_2Cu thin films at short wavelengths, which are around 3.25%, 3.28%, and 3.3% for *TlCu Deposited*, *TlCu at 300C*, and *TlCu at 350C*, respectively. With longer solar radiation wavelengths, there was less absorption. When the photon energy exceeds the energy gap, which is the threshold where electronic exchanges between the valence band and conduction band take place, absorption increases dramatically. With *TlCu Deposited*, the lowest absorbance was 0.2%, while with *TlCu at 350C*, and 900 nm wavelength, the greatest absorbance was 0.25%.

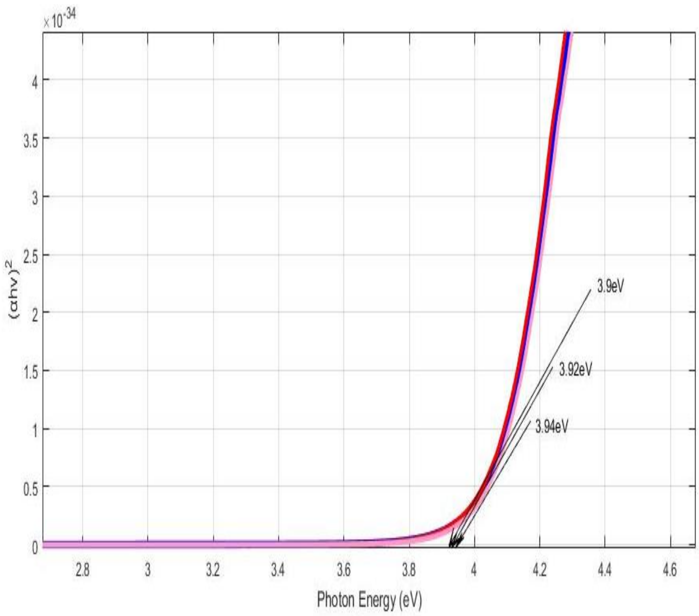

Figure 5. $(\propto hv)^2$ against wavelength for the deposited thin films.

Figure 5 displays the band-gap graphs for Tl_2Cu, indicating comparatively high energy values. For the *TlCu Deposited*, *TlCu at 300C* and *TlCu at 350C*, the energy varied from 3.9 *eV*, 3.92 *eV*, and 3.94 *eV*, respectively. These band gap values match those of Rahdar *et al*. (2012), who found that the optical characteristics of ZnS thin films ranged from 3.64 *eV* to 4.00 *eV*. To maintain low series resistance, the window layer's band-gap should be as high as feasible, and the layer should be as thin as possible (Banerjee and Chopra, 1985). This is done to make sure that none of the incident light is absorbed by the window layer and to maximize the amount of photon energy that reaches the absorber layer, which is where electron creation occurs.

Table 1. Electrical results of the Tl_2Cu thin films.

Thin film Samples	Voltage (v)	Current (A)	Sheet resistance, R_s (Ωm^{-2})	Resistivity (Ωm)	Conductivity $(\Omega m)^{-1}$
TlCu Deposited	4.87×10^{-1}	9.87×10^{-8}	2.24×10^{7}	4.48×10^{6}	2.20×10^{-7}
TlCu at 300C	2.30×10^{-1}	4.57×10^{-8}	2.29×10^{7}	4.57×10^{6}	2.19×10^{-7}
TlCu at 350C	1.81×10^{-1}	1.29×10^{-8}	6.35×10^{7}	1.27×10^{6}	7.87×10^{-7}

To evaluate the film current and voltage, the Tl_2Cu samples were inspected using a four-point probe (FPP) apparatus. With resistivities decreasing with an increase in annealing temperature from 4.48×10^6 Ωm to 1.27×10^6 Ωm, Table 1 displays the I-V characteristics for Tl_2Cu samples: *TlCu Deposited*, *TlCu at 300C*, and *TlCu at 350C*, that were as deposited, annealed at 300ºC and annealed at 350ºC, respectively. Additionally, shown in the table are the values for conductivity (σ), resistivity (ρ), and sheet resistance (Rs). The findings of Shinde *et al*. (2011) indicate that resistivity shouldn't be excessively high in order to allow for inevitable flaws to occur throughout the production process. At 2.2×10^{-7} $(\Omega m)^{-1}$ to 7.87×10^{-7} $(\Omega m)^{-1}$ in temperature, the associated conductivity rises rapidly. This improves the film's electrical characteristics and qualifies it as a suitable material for solar applications.

CONCLUSION

It has been shown that the chemical bath deposition technology is a practical and affordable way to deposit thin films at low temperatures on both tiny and large surfaces. This suggests that a number of thin-film semiconductors can be produced at a low cost and consistent level. Tl_2Cu thin films produced using CBD exhibited high absorbance in the UV-VIS light spectrum, which is the photon-rich region required for solar application. As such, they are prefabricated materials intended for use in solar cell absorber layers. The thin films' high band-gaps, which are derived from their absorption coefficients, indicate that they are suitable for window layers, which are layers that are not intended to absorb photons in order to produce carriers.

As expected, thin films of Tl_2Cu could find application in solar energy absorbers where solar energy can be directly converted to electrical energy. They have the high band gap energy, high transmittance, and low electrical resistivities that are necessary for window layers, making them viable window layer materials in hetero-junction solar cells. Hence, additional thin-film deposition techniques, such as spray pyrolysis, co-precipitation, etc., are suggested for the formation of Tl_2Cu thin films. Teflon, copper, and silicon wafer are examples of additional substrate types that may be utilized, and the outcomes of these techniques can be compared with the findings of this work. For additional research, X-Ray Diffraction (XRD), Energy Dispersive X-ray Analysis (EDX), and Scanning Electron Microscopy (SEM) could be used.

ACKNOWLEDGEMENTS

The authors are thankful to the Departments of Physics and Chemical Sciences, Tai Solarin University of Education, Ijagun, Nigeria and Department of Physics, Olabisi Onabanjo University, Ago-Iwoye, Nigeria, for creating an enabling environment for this study.

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