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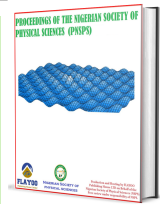

Comparative studies for determining the optical band gap energy of CuSe thin films

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A B S T R A C T

In the present study, copper selenide (CuSe) metal chalcogenide thin films have been fabricated from Se/Cu bilayer deposited using two-step procedure involving thermal evaporation and dip coating followed by thermal annealing. The thermally evaporated Se layer was maintained at a constant thickness of 40 nm while the dip coated layer of copper was carried out for varying time of 40 and 80 min. The prepared CuSe thin film was characterized in terms of its structural and optical properties. The X-ray diffraction spectra revealed post thermal inter-diffusion of the two layers and the production of CuSe thin film exhibiting hexagonal crystal structure. The optical transmission measurements were recorded within the wavelength range of 300 to 1000 nm. Four different methods were employed in ascertaining the direct band gap energies of the prepared CuSe thin films and the results were compared with the famous Tauc's relation. The values of the band gap energy ranges between 3.58 and 3.87 eV for the 40-CuSe sample as well as 3.65 and 3.99 eV for the 80-CuSe sample. The results from the study confirmed that the fabricated films possess wide band gap energy, making them a candidate for window layer in many solar cell applications.

Keywords: Selenium, Tauc's relation, Band gap, Structural property, Thermal evaporation.

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1. INTRODUCTION

Recently, research efforts in materials sciences have been driven towards advances in the renewable energy, solar cell and thermoelectric technology [1], and the thin films of semiconductor metal chalcogenide have received diverse attentions in this regard [2]. Among these metal chalcogenide group is the copper chalcogenide families which has been widely studied due to its efficiency in electronic and optoelectronic devices [3, 4]. Copper selenides (CuSe) that belongs to this family possesses a p-type conductivity and exhibits several crystal structures including, tetragonal, rhombic, cubical and hexagonal [5]. It exists in various stoichiometric forms such as, CuSe, $CuSe_2$, Cu_3Se_2, Cu_5Se_4, Cu_7Se_4 as well as non- stoichiometric forms like, $CuSe_{2-x}$ and $Cu_{2-x}Se$ [3].

Different techniques have been employed in the preparation of CuSe thin films, such as Chemical Bath Deposition (CBD [6], thermal evaporation [5], sputtering [7], spray pyrolysis [8], electrochemical deposition [9], Chemical vapour deposition [10]. The value of the direct band gap energy of copper-selenide films ranged between 2.3 and 2.7 eV while that of indirect band gap energy can vary from 1.1 to 1.5 eV. The band gap energy of semiconducting materials is a very important optical parameter and the determination of its values have received so much efforts due

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to its importance in deducing the quantity of energy that will necessitate the movement of electron from the valence band to the conduction band. In Tauc's extrapolation, the band gap energy can be estimated from the intercept of $(\alpha h\nu)^q$ vs $h\nu$ where q is a quantity that determines the nature of transition. Although, the Tauc's model is commonly used in estimating band gap energies of thin films but it suffers some inadequacies owing to the need for the speculation of the transition mode as well as the extrapolation of the linear part which has a strong sensitivity to the range over which the extrapolation is taken [11].

Furthermore, the need for measurement of the film's thickness is also a requirement which in most cases could not be taken precisely. Derivative of transmittance and DASF procedure directly employ the transmittance and absorption data, avoiding any presumption of the transition mode as well as precise thickness measurement making them more precise procedure for band gap energy determination [12].

The present work has focused on a relatively novel method of CuSe thin film preparation by employing the combination of both physical and chemical techniques; thermal evaporation and dip coating. This procedure will bring about reduction in cost, promote simplicity in thin film fabrication and reduce human exposure to fumes associated with evaporation technique. Additionally, the band gap energies will be estimated using different methods such as, First Derivative of Transmittance, Cody's model and Derivation of Absorption Spectrum Fitting (DASF) and the values from these three methods will be compared with values from the commonly employed Tauc's model.

2. EXPERIMENTAL DETAILS

The Se/Cu bilayer thin films have been prepared onto glass by employing two different techniques - thermal evaporation and dip coating. The glass slides have been previously cleaned using methanol, acetone and distilled water in an ultrasonic bath. Selenium thin film layer of thickness 40 nm was initially evaporated at vacuum pressure of 1.8×10^{-5} Torr with the aid of thermal evaporation machine (Kurt J. Lesker Nano 36 model) using Selenium (Se) powder of 99.99% purity. The second layer of Cu was prepared by dipping the initially prepared glass/Se film vertically into a beaker (100 ml) containing solution of 25 ml, 0.2 M $Cu(CO_2CH_3)_2.H_2O$ and tartaric acid (as a complexing agent). The solution was kept at 60°C and the bilayer films were removed after 40 and 80 min, rinsed with distilled water, dried before annealing at 400°C for 1 hour, and respectively labelled 40-CuSe and 80-CuSe. The optical transmission (T) measurement was recorded using Avantes UV Spectrophotometer in the wavelength range 300-1000 nm. Structural measurement was accomplished with the aid of x-ray diffraction (XRD) machine (EMPYREAN) having Cu-kα radiation, $\lambda = 0.154056$ nm. The step size was taken as 0.0260 and the 2θ angle ranged between 15 to 70°. The surface morphology scanning electron microscope (JEOL, JSM 7600F Field emission SEM).

3. RESULTS AND DISCUSSION

3.1. BAND GAP ENERGY DETERMINATION

3.1.1. Tauc's model

In the semiconductor and nano-material industries, the measurement of the band gap energy is very essential. The Tauc's model

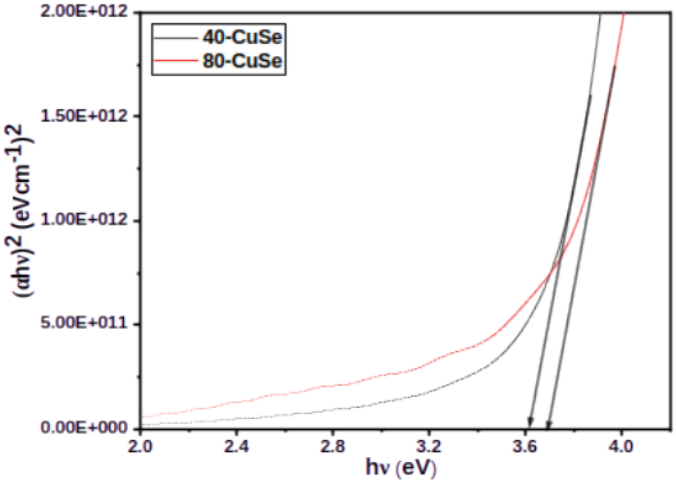

Figure 1. Plot of $(\alpha h\nu)^2$ against $h\nu$ for the prepared CuSe sample.

is the commonly used procedure which allows for the determination of band gap energy as a function of photon energy according to the relation [13]:

$$(\alpha h\nu) = B(h\nu - E_g)^q, \tag{1}$$

where B is a constant, α is the absorption coefficient, $h\nu$ is the photon energy and E_g is the energy gap, q is the transition mode and take the values $\frac{1}{2}$ and 2 for direct and indirect transitions, respectively.

The Tauc's direct optical band gap of the prepared CuSe thin films involves extrapolating the linear portion observed when $(\alpha h\nu)^2$ is plotted against $h\nu$, as shown in Figure 1. The linear nature of this plot over a long range is an indication of existence of direct transition. The value of the band gap energy for the fabricated samples at different Cu^{2+} solution dipping time are obtained from the intersection of the linear part of the curve with the $h\nu$ axis and recorded in Table 1. The result reveals values that are higher than that of the bulk CuSe which may be due to the introduction of more oxygen contents into the films during post-thermal annealing process [14]. Other researcher has earlier reported higher band gap energy values for CuSe thin films [15]. Moreover, the band gap energy is observed to increase with increasing Cu^{2+} solution dipping time and this can be attributed to an increase in Cu content which creates new levels in both valence and conduction bands by reason of a disturbed valence and conduction band edges [16].

3.1.2. Cody's model

The Cody model is based on a constant dipole matrix approximation and it is related to the absorption coefficient by the following expression [17]:

$$\left(\frac{\alpha}{h\nu}\right) = B(h\nu - E_g)^q. \tag{2}$$

Taking into cognizance this expression, the direct band gap energy ($q = \frac{1}{2}$) values are obtained by extrapolating the linear part of the curve of $\left(\frac{\alpha}{h\nu}\right)^2$ against $h\nu$ (Figure 2) to the intersect with $h\nu$ axis. The band gap energy values as estimated from the plot are displayed in Table 1, where good agreement is established and

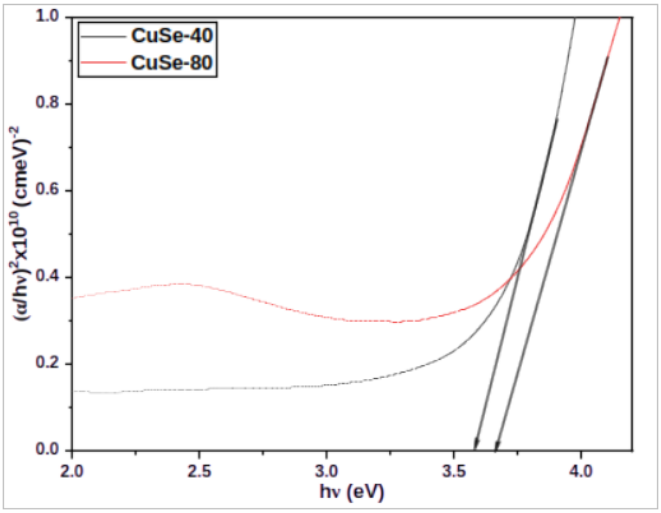

Figure 2. Plot of $(\alpha/h\nu)2$ against $h\nu$ for the prepared CuSe thin film samples.

Table 1. The optical band gap energy values using different methods.

Sample	Tauc's model	Cody's model	DASF	$dT/d\lambda$
40-CuSe	3.61	3.58	3.87	3.66
80-CuSe	3.69	3.65	3.99	3.77

similar trend with Cu^{2+}solution dipping time is confirmed when compared with those obtained from the Tauc's plot.

3.1.3. Derivation of absorption spectrum fitting (DASF) procedure

The band gap energy of the prepared CuSe thin films have also been estimated using DASF method by starting with the Absorption Spectrum Fitting (ASF) model, represented in equation (3). As reported in literatures, the ASF equation has been obtained by the transformation of the Tauc's relation into its absorption equivalent using the Beer-Lambert's law $\alpha(\lambda) = \frac{2.303A}{d}$ [18, 19].

$$\frac{A(\lambda)}{\lambda} = C\lambda\left(\frac{1}{\lambda} - \frac{1}{\lambda_g}\right)^q, \tag{3}$$

where $C = \left[\frac{B(hc)^{q-1}d}{2.3030}\right]$, d and A are the film's thickness and film's absorbance correspondingly.

The DASF started with taken the natural log of both sides of equation (3) leading to an equation of the form [12]:

$$Ln\left(\frac{A(\lambda)}{\lambda}\right) = Ln(C) + qLn\left(\frac{1}{\lambda} - \frac{1}{\lambda_g}\right). \tag{4}$$

Thus, the derivative of equation (4) with respect to the inverse of wavelength gives:

$$\frac{d\left\{Ln\left[\frac{A(\lambda)}{\lambda}\right]\right\}}{d\left(\frac{1}{\lambda}\right)} = \frac{q}{\left(\frac{1}{\lambda} - \frac{1}{\lambda_g}\right)}. \tag{5}$$

Thus, with regards to equation (5), a graph of $\frac{d\left\{Ln\left[\frac{A(\lambda)}{\lambda}\right]\right\}}{d\left(\frac{1}{\lambda}\right)}$ against $\frac{1}{\lambda}$ will produce a discontinuity at $\frac{1}{\lambda} = \frac{1}{\lambda_g}$ as displayed in Figure 3.

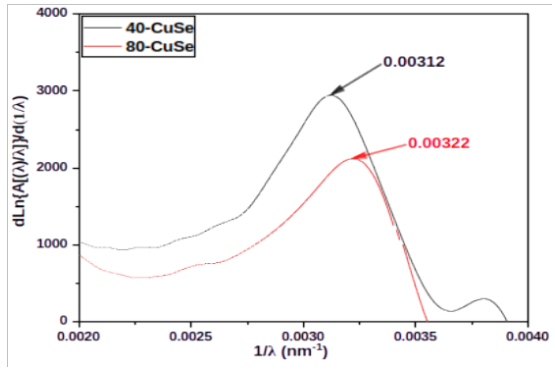

Figure 3. Plot of $\frac{d\left\{Ln\left[\frac{A(\lambda)}{\lambda}\right]\right\}}{d\left(\frac{1}{\lambda}\right)}$ against $\frac{1}{\lambda}$ for the prepared CuSe thin films.

Subsequently, the obtained $\frac{1}{\lambda_g}$ is used to directly determine the value of the band gap energy using $E_g^{DASF} = 1239.83 \times \frac{1}{\lambda_g}$ [20], bypassing the need for least square and avoiding speculation concerning the type of transition. The values of the band gap energies as obtained are shown in Table 1, which shows similar trend with the values determined from the Tauc's model. Comparing with the values obtained from the Tauc's relation, the band gap energies from the DASF procedure is slightly higher; a similar occurrence that has previously been reported by [19]. This slightly higher values of band gap energy may be attributed to the fitting of a broader range (the complete spectrum) of data as occurred in DASF method. In comparison, the Tauc model relies on mere extrapolating a straight line from the absorption curve which is quite sensitive to the range over which the extrapolation is taken [12]

3.1.4. First derivative of transmittance

In another method the transmittance data was used to determine the values of the band gap energy where the need for thickness measurement and least square estimation is avoided. This procedure involves the determination of the absorption edge from the plot of first derivative of transmittance with respect to wavelength $(dT/d\lambda)$ against the photon wavelength [21] as displayed in Figure 4. The maximum peak in the first derivative curve corresponds to the absorption edge (λ_g) from where the band gap energy (E_g) can be determine using the relation, $E_g = \frac{1239.83}{\lambda_g}$. The values of the energy gap are listed in Table 1 where the energy gap is observed to increase with Cu^{2+} solution dipping time; a trend that is in agreement with values obtained from Tauc's plots. Furthermore, there is a close agreement between the band gap energy values obtained from applying the first derivative of transmittance and Tauc's plots taking into consideration the experimental error. This first derivative of transmittance has been previously employed as an alternative method to determine the band gap energy of chitosan biopolymer hybrids and a good agreement was established with the Tauc's values [19].

A graphical representation (bar chart) is created in order to clearly compare the values of the band gap energies obtained using Cody's representation, Differential Absorption spectrum Fitting (DASF), as well as the First Derivative of Transmittance with the Tauc's values, as presented in Figure 5. The height of each bar corresponds to the value of the band gap energy determined us-

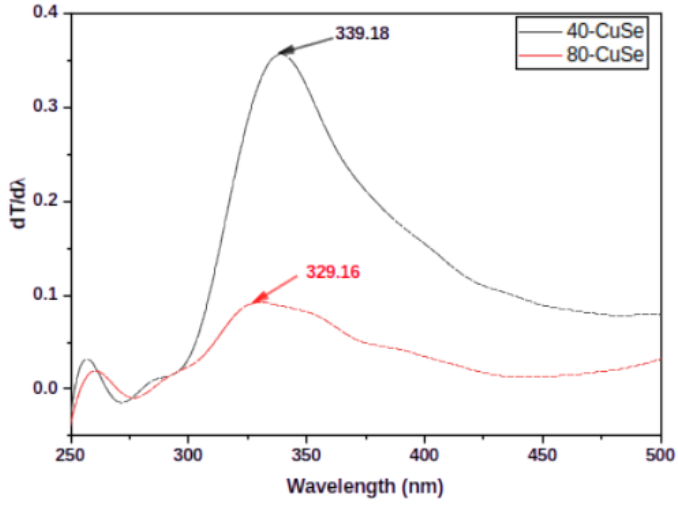

Figure 4. Plot of $\frac{dT}{d\lambda}$ against λ for the prepared CuSe thin film.

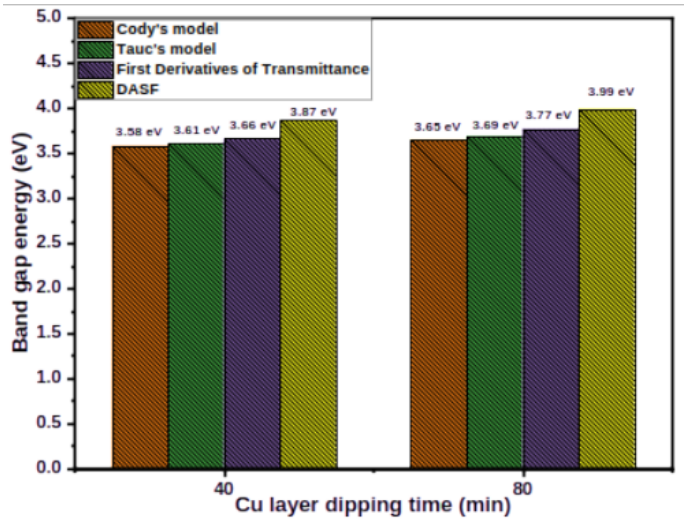

Figure 5. Bar chart showing variation of the band gap energy with Cu layer dipping time.

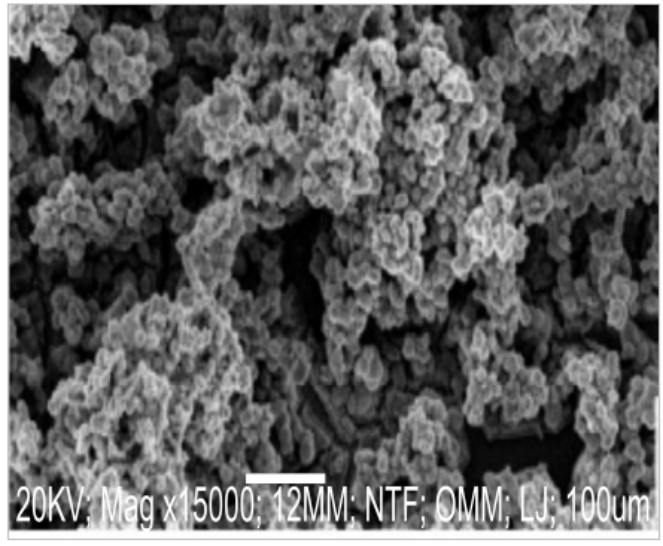

Figure 6. SEM image of the prepared 40-CuSe thin film sample.

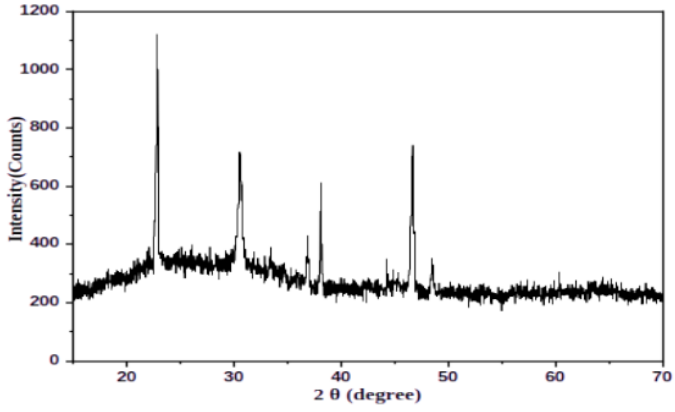

Figure 7. XRD spectra for the prepared 40-CuSe thin film sample.

ing each method. It can be clearly seen from the chart that all the band gap energy values determine using the three methods are in an approximate agreement with those obtained using Tauc's model. The variations are within 0.03 and 0.26 range as well as 0.04 and 0.34 for the 40-CuSe and 80-CuSe samples respectively. The DASF and derivative of transmittance method gave relatively higher values of band gap energy for CuSe thin films, a result that may likely be attributed to the fitting of the entire spectrum, as compared to Tauc's and Cody's models that merely rely on extending the linear portion of the absorption curve [12].

3.2. SURFACE MORPHOLOGY

The thin film surface morphology was inspected at a magnification of x15000 by using scanning electron microscope (SEM), and the image is presented in Figure 6, for the 40-CuSe sample. The morphological image shows that the film was non-uniformly deposited all over the substrate surface with the grains clustering together. Some pores can also be seen on the film surface which may be associated with the type of method used in the preparation. It can also be attributed to an incomplete coverage of the substrate by the deposited film.

3.3. X-RAY DIFFRACTION ANALYSIS

In order to identify the structure of the prepared thin films, an x-ray diffraction analysis was carried out on the 40-CuSe sample and the result (Figure 7) reveal peaks at 2θ angles of 22.8018°, 30.5501°, 36.8757°, 38.0637°, 46.6656° and 48.5025°. These peaks were observed to be in close match with the (004), (103), (104), (105), (110) and (336) plane of hexagonal CuSe compound having a close agreement with the 2θ angles of the standard JPDCS card No. 65-3562 [22]. This observed outcome signifies a complete mixture of the bilayer structure.

4. CONCLUSION

Copper selenide (CuSe) thin film have been successfully prepared via thermally induced inter-diffusion of Se/Cu bilayer fabricated using two different techniques. The band gap energies of the prepared films have been determined using four differ-

ent methods vis-a-vis Tauc, DASF, Cody and first derivative of transmittance. The band gap energy values obtained for the 40-CuSe sample are; 3.58, 3.61, 3.66 and 3.87 eV, while that of 80-CuSe sample are; 3.65, 3.69, 3.77 and 3.99 eV, corresponding to Codys, Tauc's, First derivative and DASF methods respectively. The values obtained from all the four methods are seen to be larger than the value of the bulk CuSe, but follow similar trend as they increase with increasing Cu^{2+}solution dipping time. The X-ray diffraction study revealed that the fabricated film is polycrystalline in nature with hexagonal structure. The results from the three other methods are compared with that of Tauc, and slight variations are confirmed. DASF and derivative of transmittance methods are considered more precise owing to the fitting of the entire absorption spectrum, avoidance of errors which might accompany the measurement of film's thickness, as well as the need to bypass linear extrapolation and optical transition nature. Consequently, the results from this study might be seen as a move towards a new approach in CuSe thin films preparation and the precise estimation of its band gap energy.

DATA AVAILABILITY

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

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