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Computation of Optical Energy Gap of Cu_2O Thin Film: Theoretical Estimation

Thin films of cuprous oxide Cu_2O have been prepared using spray pyrolsis technique. Experimentally, the optical energy gap of Cu_2O was about 2.2eV. To achieve and estimate an accurate E_g value, there was problem in the selection of exact tangent point. To overcome this problem, Newton-Raphson method and mean-value theorem were used. It was found that the mean-value theorem can predict correlated nearly satisfactory E_g value than the other method.

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1. Introduction

Determination of the band gap energy of semiconductors and specially semiconductor nanostructures is of great interest since it is directly related to the nanometer sized particles. Therefore, many efforts have been focused on the evaluation of the band gap energy to investigate the optical properties. Semiconductor nanoparticles produced by various methods constituting different sizes, thereby particles size distribution introduces many consequences on the optical properties due to the corresponding band gap. Therefore studying the particle size and their size distribution could be considered a crucial point.

Cuprous oxides Cu_2O and CuO are the main semiconductor phases of copper oxides. Cu_2O form a cubic structure with lattice parameter of 4.27Å [1] and direct band gap of 2.2eV, while CuO has monoclinic crystal structure and indirect band gap of 1.4eV [2]. A metastable copper oxide paramelacouite Cu_4O_3, which is an intermediate compound between the Cu_2O and CuO also been reported [3]. Due to copper oxides potential applications, such as, in solar cells [4], catalysis [5], and magnetic devices [6], much attention has been attracted. Recently, extraordinary efforts have been made to investigate the optical properties of Cu_2O. Mishinia *et al* have studied the structure of Cu/Cu_2O multilayer preparation using nonlinear electrochemical deposition with high precision in control thicknesses and number of layers. Their results lead to significant changes in the linear and nonlinear optical properties of Cu_2O and CuO multilayer structure [7]. Liu *et al* reported the structural and optical properties of films electrodeposited on different substrates. Their results illustrate that, the kind of substrate strongly affect film morphology, crystal structure and optical properties [8]. Prevot *et al* studied the near infrared optical and photoelectric properties of Cu_2O under oxygen atmosphere. The absorption near the fundamental edge was characterized by several absorption bands with peak position at 0.65um, 0.75um, 0.88um, 1.1um with strongest one at 1.28um [9].The aim of this work is to find an appropriate theoretical consideration to obtain the value of the optical energy gap and compare results with experimental values.

2. Experiment

The coatings were deposited on to heated borosilicate glass substrates (Bk-7), aqueous solution containing 2.41gm of $Cu(NO_3)_3.3H_2O$ were used to prepare Cu_2O thin films. The spraying setup and the preparation technique have been described elsewhere [10]. It has found that coatings adherence to substrate were obtained under deposition conditions of substrate temperature T_S=360°C, spraying rate of $10cm^3$/min, air pressure of $10^6 dyne/cm^2$ and distance between nozzle and substrate 28±1.0cm.

The substrate was preheated for 30min before spraying the solution. The period of spraying was about 10s followed by 2min waiting to avoid excessive cooling during spraying process. Weighting method was used to find film thickness, here it is found to be 300nm. With the aid of Pye-Umicom SP-100 sphectrophotometer, the absorption spectrum was recorded within the wavelength region (400-900)nm, knowing that all the prepared samples were done under the same conditions.

3. Results and Discussion

Fig. (1) shows the behavior of absorption coefficient versus photon energy calculated from the equation [11]:

$$\alpha = 2.303(\frac{A}{d}) \quad (1)$$

where α is the absorption coefficient (in cm^{-1}), A the corrected absorbance, and d film thickness (in nm). Fig. (1) illustrates that α rise steeply near the absorption edge and linearly beyond this region. Since $\alpha > 10^{-4} cm^{-1}$, therefore plotting α versus E gives a priory insight of vertical transition at the fundamental absorption edge which is related to the direct energy gap.

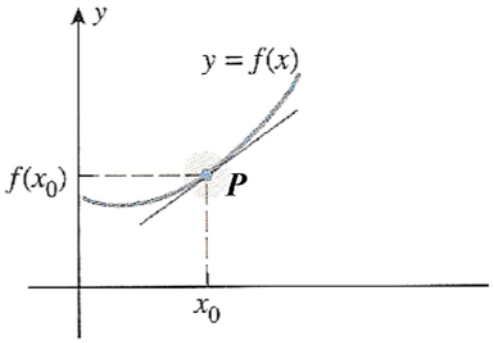

Fig. (1) The behavior of absorption coefficient versus photon energy calculated from equation (1)

The direct energy gap may be found from the relation [12]:

$$\alpha h\nu = B(h\nu - E_g)^{1/2} \quad (2)$$

where B is a constant, E_g energy gap of allowed direct transition and $h\nu$ is the photon energy.

To evaluate the energy gap value E_g many workers used the traditional method, i.e., a plot of $(\alpha h\nu)^2$ versus $(h\nu)$, shown in Fig. (2) [here Matlab [13] and Sigma-plot [14] were used]. This method was based on the fact [15]: "The slope of the curve *y=f(x)* at the point *P=f(x,y)* is defined as the slope of the tangent line to the curve at *P*" as shown.

Therefore, in using this method it's difficult to select the exact tangent point (slope of the graph *y=f(x)* at this point) to achieve an accurate E_g value. This means that the instantaneous rate of change of y with respect to x was evaluated. As a result, an approximated E_g value usually associated with error was obtained. To overcome this problem, we present alternative evaluation methods:

1. Newton-Raphson method (numerical method) [16],
2. Mean-value theorem [15]

The analysis of using these methods was summarized as follows:

Step 1

Using a graphing utility to generate the behavior of experimental data pairs $(\alpha h\nu)^2$ versus $(h\nu)$, shown in Fig. (2). This behavior may be represented in terms of *xy*-plane abbreviation, i.e., *y=f(x)*. Then taking advantage of any general knowledge one have about the function to help in choosing the window.

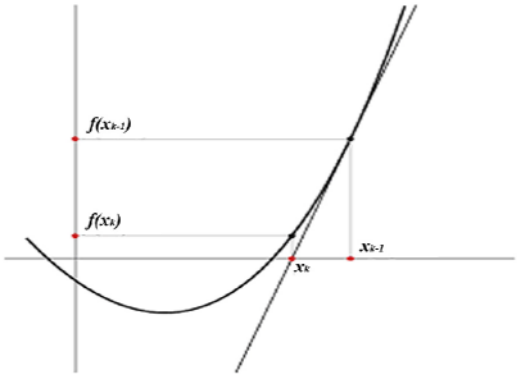

Fig. (2) The behavior of experimental data pairs $(\alpha h\nu)^2$ versus $(h\nu)$

Step 2

Finding the "best fitting" or "good fitting" equation. This may be down with the aid of Matlab or Sigma–plot software package. It is found to be cubic equation yield "best" fitting to experimental data pairs $(\alpha h\nu)^2$ and $(h\nu)$:

Cubic equation: $y = y_0 + ax + bx^2 + cx^3$, where y_0=-0.9891x10^{12}, a=0.2617x10^{12}, b=-1.2150x10^{12}, c=1.8960x10^{12}

Step 3

Finding the "roots", if needed. This may be done using "Matlab" or "advantage plus™" software [17].

Step 4

Calculating first and second derivatives of *y=f(x)* for the cubic equation, this may be done "analytically" or "numerically".

Step 5

Finding the "intercepts", using "Advantage plus™" software, shown in Fig. (3) and the point of intercepts are summarized as follows:

Step 6

Newton-Raphson method:

Usually, this numerical method is used for solving nonlinear algebraic equations. Here, we adapted the basic idea of this method:

- When the real root x_1 is known, then one may easily compute the functional $f(x_1)$. Drawing a line tangent to the curve at point x_1, then the tangent line intersect the x-axis at a point, say x_2, which plays a significant important role in evaluating E_g values, as shown in figure.
- Evaluating intersection point of tangent line with x-axis:

$$x_{K+1} = x_K - \frac{f(x_K)}{f'(x_K)} \quad (3)$$

where, x_{k+1}= approximate root after $k+1$ iterations, x_k= approximate root after k iterations,

$f(x_k)$=functional value at x_k, $f'(x_k)$=first derivative value of the functional at x_k, and $k=1,2,3,...$

As a result, intersection points gives a range of E_g values due to the cases:

a) $f(x)$ and $f''(x)$ [3.5375, 2.8653, 2.4351, 2.1163, 1.8851, 1.6888,…]

b) $f'(x)$ and $f''(x)$ [3.5375, 2.5378, 2.033, 1.7702, 1.615,…]

The *average value* of E_g=2.0746eV, this gives an indication that this method still gives an approximated E_g value.

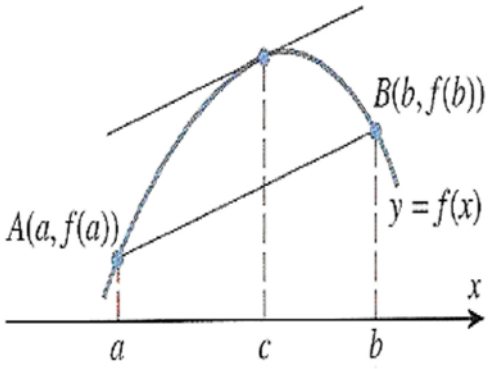

Fig. (3) Finding the "intercepts" using "Advantage plus™" software

Functions	Point of intercept	Decimal Places of accuracy	Number of iterations	Figure
$f(x)$ and $f''(x)$	(1.55089,0.0052) (3.98312,3.8243)	8	4	(3-a)
$f'(x)$ and $f''(x)$	(1.5576,0.0157) (3.5375,3.1246)	8	4	(3-b)

Step 7

Mean-value theorem: This theorem states that "between any points A and B on the graph of a differentiable continuous function $y=f(x)$, there must be at least one place where the tangent line to the curve is parallel to the secant joining A and B" as shown. In this method, the average rate of change of y with respect to x over the interval $[a,b]$ is $\frac{f(b)-f(a)}{b-a}$ equivalent to the slope of the tangent at c, i.e., $f'(c)$. Then E_g values are:

- E_g=2.3674eV, for the case $f(x)$ and $f''(x)$, and
- E_g=2.0370eV, for others

The *average value* of E_g=2.2023eV

From the final result, it is concluded that adapting "mean-value theorem" give results correlate nearly satisfactorily with predicted E_g value [3].

4. Conclusion

From previous results one can conclude that the chemical spray pyrolysis method that has been used to perform the experimental measurements required for this investigation was found to work fairly successfully. As well, E_g value predicted using "mean-value theorem" give good value and fit the experimental results much better and quick than others. It was found that good E_g value may be obtained when the second derivative of the fitting equation considered as a secant line than choosing arbitrary secant. The accuracy of E_g value depends on experimental conditions and deposition technique.

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