Structural and Optical Properties of CuAlO$_2$ Thin Film Prepared by Spray Pyrolysis

Dr. Azhar A. Hassan
Applied Sciences Department, University of Technology/Baghdad
Email:Azhar.Hassan@yahoo.com
Nuha F. Abd Al-Rushed
Applied Sciences Department, University of Technology/Baghdad
Email:neenoo_999@yahoo.com

Abstract

Transparent conducting oxides thin films of copper aluminium oxide (CuA1O$_2$) were prepared by spray pyrolysis technique on a glass substrate at temperature (500°C). The precursor solution was mixture of CuCl$_2$ and anhydrous AlCl$_3$ salts with different concentration (1:1), (1:2), and (2:1) of (Cu: Al) ratio. It appears that from XRD spectra the pure delaffosite phase of CuAlO$_2$ was dominate at the ratio (1:1). UV-visible spectrum measurement showed highest absorption coefficient in the visible region at ratio (1:1). The optical allowed direct and indirect band gap of thin films at ratio (1:1), (1:2) and (2:1) were estimated to be (2.9, 3, 2.6 and 1.2, 1.5, 1.4) eV respectively. The extinction coefficient was also studied for different ratio. The effective ratio is (1:1) for photoelectric application.

Keywords: TCO; CuAlO$_2$; Thin film; Delaffosite structure.

الخصائص التركيبية والبصرية لأغشية CuAlO$_2$ الرقيقة المحضرة بالرش الكيميائي الحراري

الخلاصة

في هذا البحث تم تحضير أغشية رقيقة لاكاسيد شفافة موصلة من اكاسيد ألمنيوم- نحاس (CuAlO$_2$) باستخدام تقنية الرش الكيميائي الحراري على قواعد زجاجية عند درجة حرارة (500 م°). المحلول الاساس عبارة عن خليط من ملح كلوريد النحاس وملح كلوريد الالمنيوم اللامائي مع تراكيز مختلفة (1:1), (2:1), و(1:2) لنسبة (نحاس: المنيوم). أظهرت أطياف حيود الاشعة السينية الطور النقي (delaffosite) لاكاسيد ألمنيوم- نحاس عند النسبة (1:1). كما أظهر قياس الطيف المرئي - الأشعة فوق البنفسجية أعلى معامل الامتصاص في المنطقة المرئية عند النسبة (1 :1). وحسبت الفجوة الطاقة البصرية المسموحة المباشرة وغير المباشرة للأغشية الرقيقة عند نسب (1:1), (2:1) و(1:2) لتكون (2.9 , 3 , 2.6) و (1.2، 1.5، 1.4) ألكترون فولت على التوالي ,كما درس معامل الخمود عند النسب المختلفة. النسبة الفعالة هي (1:1) للتطبيقات الكهروضوئية.

INTRODUCTION

Transparent conducting oxides (TCOs) play a critical role in emerging opto-electronic devices due to their unique combination of electronic conductivity and transparency in the visible region of the spectrum [1]. CuAlO$_2$ thin films with delafossite structure have attracted much attention as p-type TCOs since it was firstly prepared in 1997 by Hosono and Coworker [2]. It was found that the electrical and optical properties of CuAlO$_2$ films heavily depend on their structural characterization, so far several growth methods have been investigated in deposition of CuAlO$_2$ thin films, such as pulsed laser deposition [3], radio frequency (r.f) magnetron sputtering [4], sol-gel [5], spray pyrolysis [6] and Chemical solution deposition (CSD) [7].

Their ability to collect and deliver electricity while allowing light in and out of a device makes CuAlO$_2$ thin films ideal for applications in optoelectronic devices [1], solar cells, gas sensors, p-n junctions, organic light-emitting diodes (OLEDs), and flat panel display (FPD) [8].

In this work CuAlO$_2$ thin film was prepared by spray pyrolysis because it was one of the major techniques to deposit a wide variety of materials, Simple, inexpensive, the final product composition can be easily controlled, and has the ability to produce chemically homogeneous multi-metal oxides [6,9]. CuAlO$_2$ thin films prepared with different concentration of (Cu:Al), and studying the effect on the structural and optical properties of thin films. Physical properties of the prepared films by spray pyrolysis affected significantly by concentrations salts that involved in the preparation [10].

Experimental

CuAlO$_2$ thin films were deposited on cleaned glass substrate using a simplified spray pyrolysis technique. The starting solution was prepared using different concentration of CuCl$_2$ and anhydrous AlCl$_3$ salts dissolved in distilled water in the ratio (0.1:0.1)M, (0.1:0.2)M, (0.2:0.1)M. This solution was mixed by using a magnetic stirrer until the solution has been cleared. the solution was sprayed on a glass substrate heated to temperature (~500 C°) measured by (Infrared Thermocouple AR 350) with compressed air as a carrier gas. The distance between the nozzle tip and the substrate surface kept at 30 cm, and spray rate was 5 ml/min, the time of the deposition was (5sec) each (60 sec). After deposition, thin film was stay on heater even the temperature down to room temperature. Thickness of deposited thin film was (0.37μm) determined by optical interference methode (Fizeau method). This method based on interference of the light beam reflected from thin film surface and substrate bottom. The thickness is determined using the formula [11]:

$$t = \frac{\Delta x}{x} \cdot \frac{\lambda}{2}$$ .... (1)

Where (x) is fringe width, Δx is the distance between two fringes, and λ is wavelength of laser light (He-Ne laser 632.8 nm).

The reaction may be represented by the following equation:

$$2CuCl_2.2H_2O + Al_2Cl_3.2H_2O + 2O_2 \longrightarrow 2CuAlO_2 + 7Cl + 6H_2O$$ ......(2)

The structural characterization of thin films was studied by using X-ray diffractometer with Cu, BF 2.7KW radiation (λ=1.5418 A°, SHIMADZU, JAPAN), the influence of differ concentration on the optical property were investigated by using (UV-VIS-NIR) spectrophotometer.

Results and Discussion

Figure (1) shows the XRD spectra of thin films prepared from different concentration of (Cu:Al). Fig (1-b) represent the ratio (1:1), show a preferential orientation with high intensity (006) and (101) of delafossite CuAlO₂ at (2θ= 32°, 36°), and small peak (111) of CuO at (2θ= 38.78°). While in fig (1-a) at ratio (1:2) the orientation (006), (101), (009) of CuAlO₂ phase were found at (2θ= 32°, 36° ,49°) respectively, and high intensity peak of CuO phase with (111) orientation was appear, also low intensity (015) of CuAl₂O₄ at (2θ=46°) was show. Fig (1-c) show the ratio (2:1) concentration thin film had high intensity peaks of CuAlO₂ and CuO phases at (2θ=36°, 38.78°) with orientation (101) and (111) respectively, this is agrees with literature [3,8,10]. The result above show the ratio (1:1) is the best to obtain delafossite CuAlO₂ which important in photoelectric application.
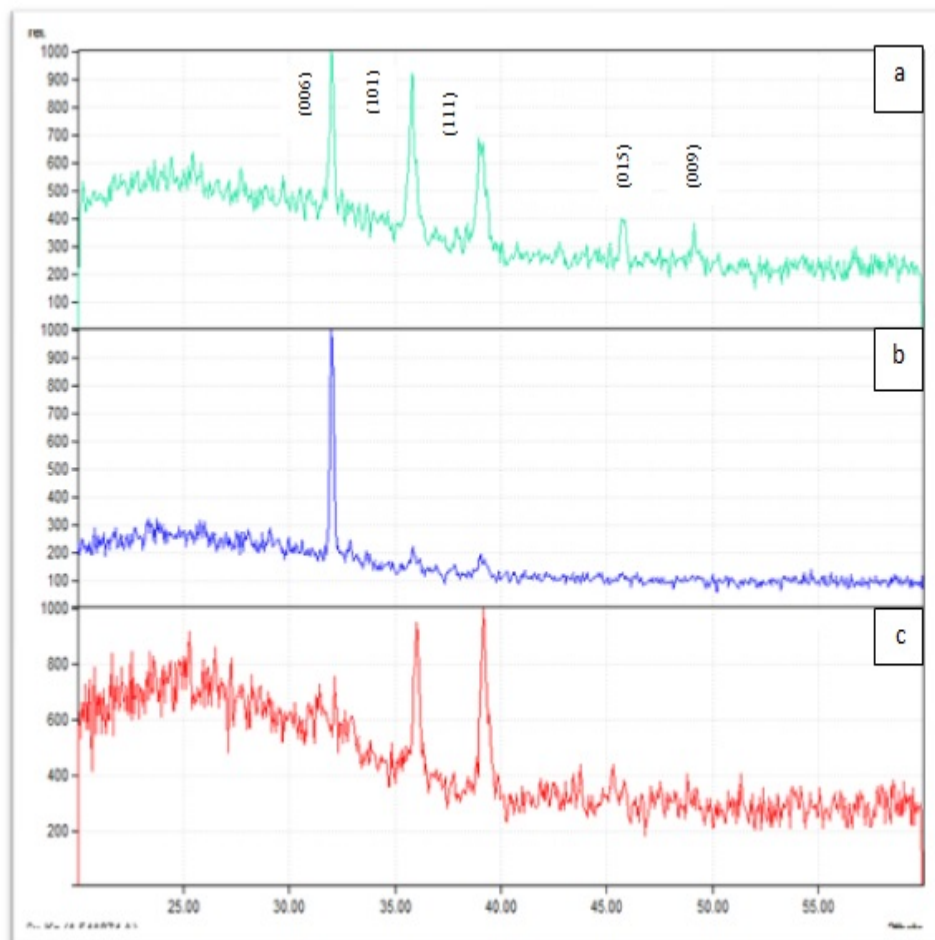

Figure(1): XRD pattern of thin film prepared from copper chloride and aluminium chloride with different concentration a (1:2), b (1:1), c (2:1).
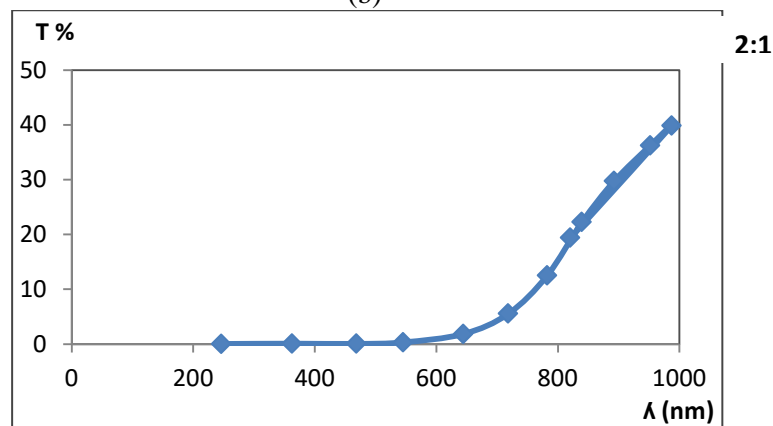
The optical transmission of the CuAlO$_2$ Thin films was recorded from (250-900 nm) wavelength, figure (2) present the optical transmittance spectra of the CuAlO$_2$ films at different concentration on glass substrate. The film with concentration ratio (1:1), (1:2) exhibited lower transmission. The film with concentration ratio (2:1) has an optical transmission above 40% at wavelength (950nm) because of increase Cu ratio and due to existence high intensity phase of CuO.
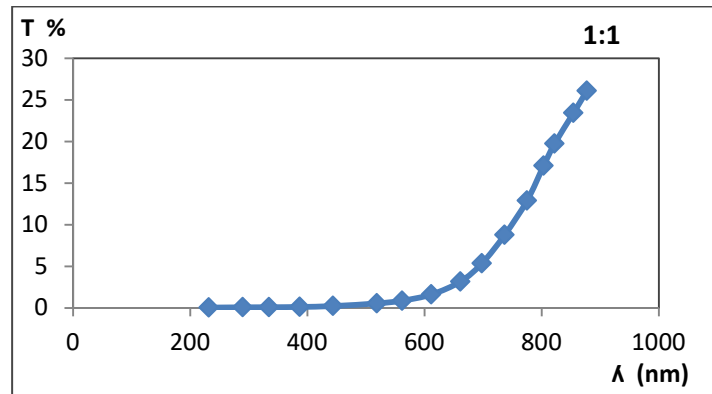
(a)
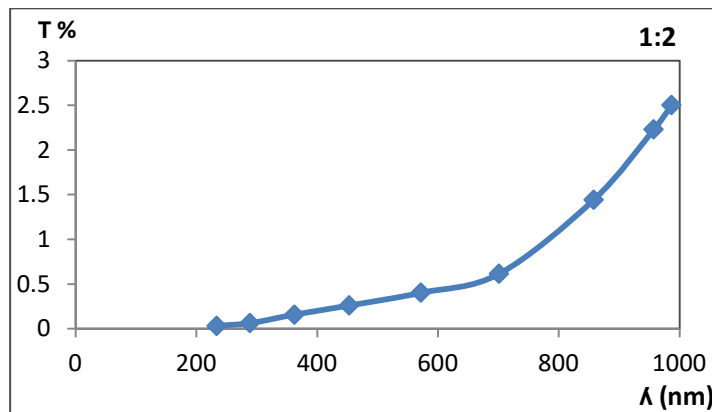
(b)

(c)

Figure(2): (a, b, c) represent optical transmittance of CuAlO$_2$ thin film with differ concentration.

The fundamental absorption, which corresponds to electron excitation from the valance band to conduction band, can be used to determine the nature and value of the optical band gap. The optical absorption coefficient (α) of the films can be calculated using the following equation [12]:

$$\alpha = \frac{1}{t}\ln\left(\frac{1}{T}\right) \qquad\qquad ……… (3)$$

Where t is the film thickness and T is the transmittance of the film.

Figure (3) represent the optical absorption coefficient of the CuAlO$_2$ films at different concentration. The film with concentration ratio (1:1) has high optical absorption coefficient at (230 nm) wavelength due to presence high intensity phase of CuAlO$_2$ compared with (1:2), (2:1) concentration.


(a)

(b)
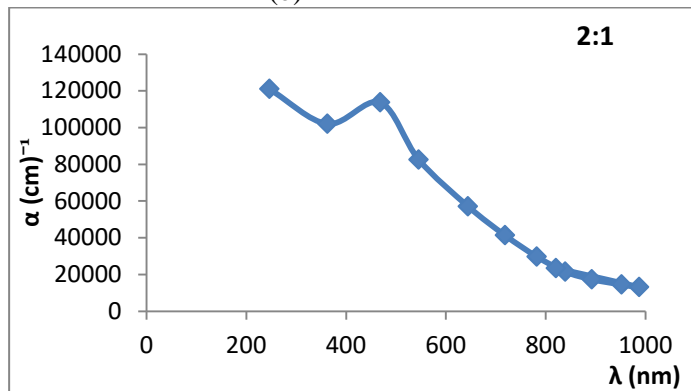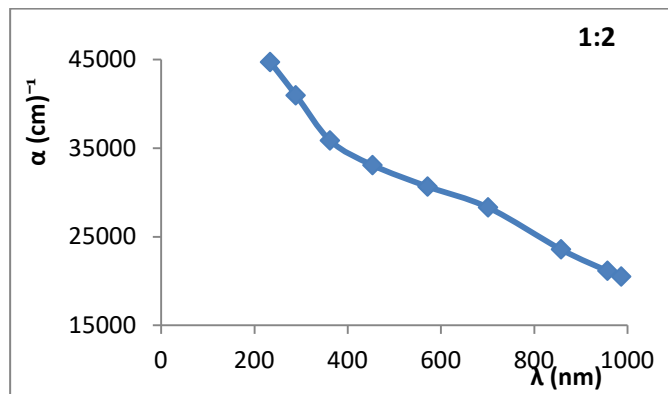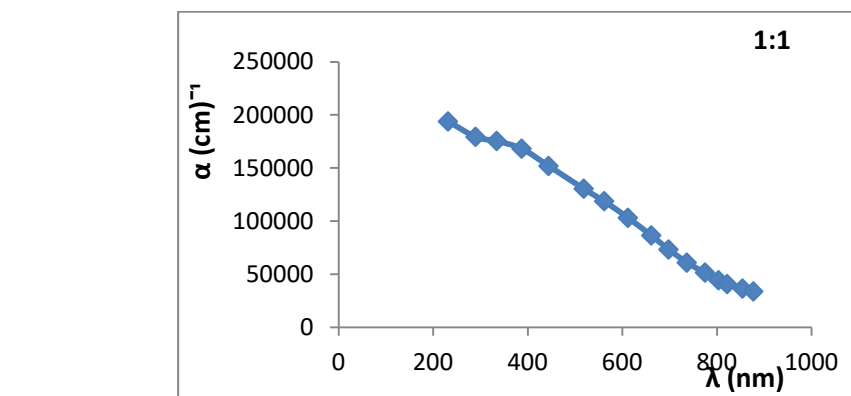
(c)

Fig.3: (a, b, c) represent relationship between the optical absorption coefficient and wave length.

The extinction coefficient (k) which is defined as amount of loss in energy that electromagnetic wave suffer it   when pass through material was determined, it is related with the wavelength (λ) and absorption coefficient (α) by the following equation [13] :

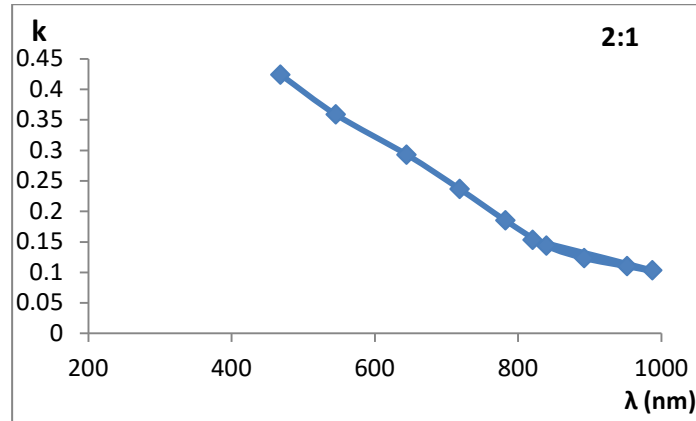$$K = \frac{\lambda \alpha}{4\pi}$$ .... (4)

Fig (4) shows the variation in extinction coefficient with wavelength for different concentration (1:1), (1:2) and (2:1) respectively, the higher value of (k) was for the ratio (1:1) at (λ=500 nm), and all curves related with behavior of absorption coefficient as shown in fig (3) according to equation (4).
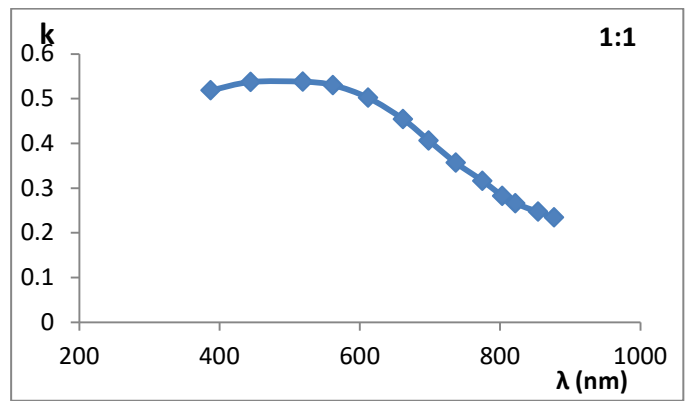
(a)
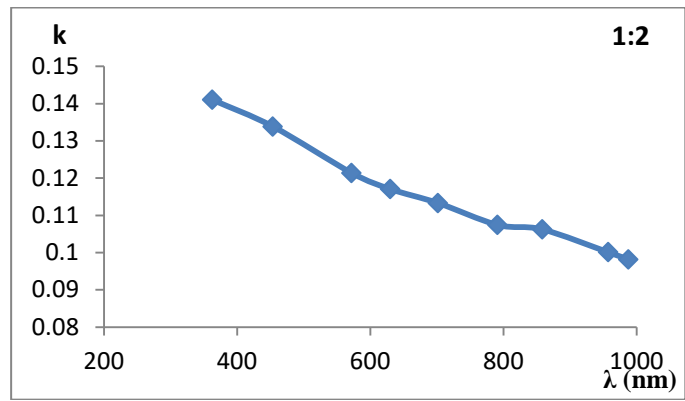
(b)

(c)

Fig.4: a, b, c shows relation between Extinction Coefficient and wave length.

The incident photon energy (*hv*) can be calculated from fllowing equation [14]:

$$E \text{ (eV)} = \frac{1240}{\lambda \text{ (nm)}} \qquad \text{......... (5)}$$

While the relation between the absorption coefficients (α) and the incident photon energy (*hv*) can be written as [15].

$$(\alpha h v)^{1/n} = A(h v - E_g) \qquad \text{......... (6)}$$

Where A is a constant, Eg is the optical band gap of the material and exponent n depends on the type of transition. A plot of $(\alpha h v)^{1/n}$ vs. hυ shown in fig (5,6) gives the optical band gap by extrapolating the linear part of the plot to intercept with (hv) axis when (α=0).the direct allowed optical band gap (n=1/2) is observed in fig (5) to be (2.9, 3, 2.8) eV for ratios (1:1), (1:2), (2:1) respectively. Which is in a good agreement with [13,16], the allowed indirect optical band gap (n=2) were (1.6, 1.7, 1.5) eV as illustrated in the fig (6), it is agree with the result by [4], and low compare with [15,17].
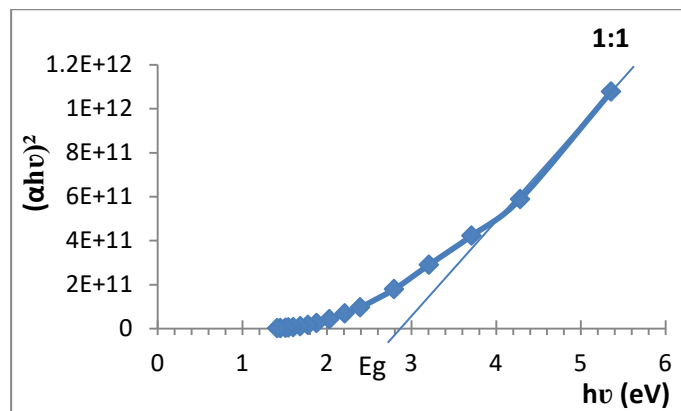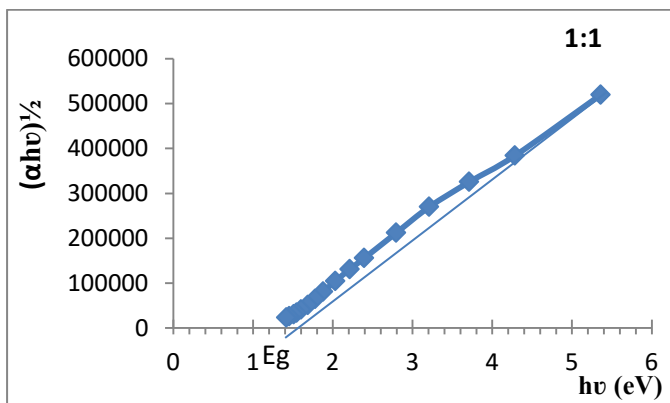

(a)
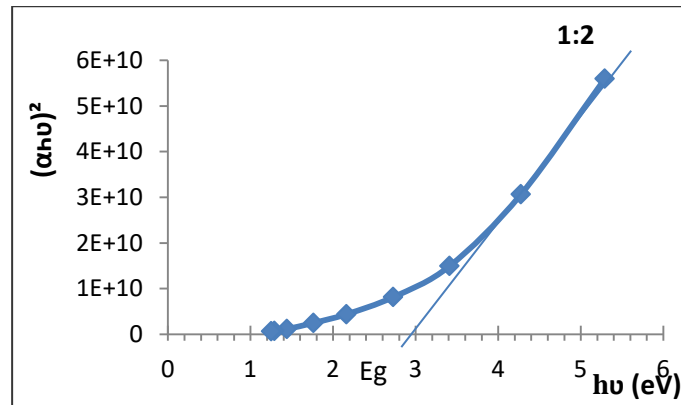
(b)
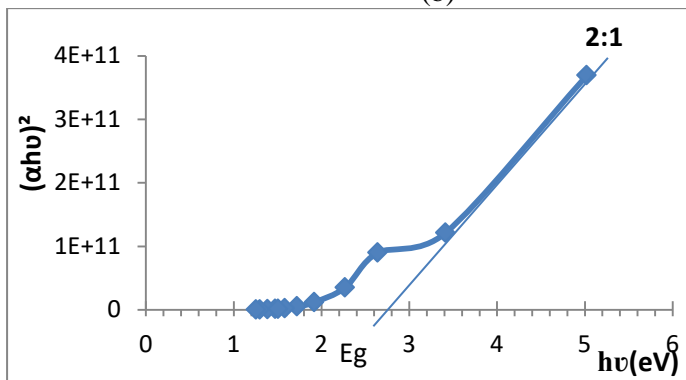
(c)

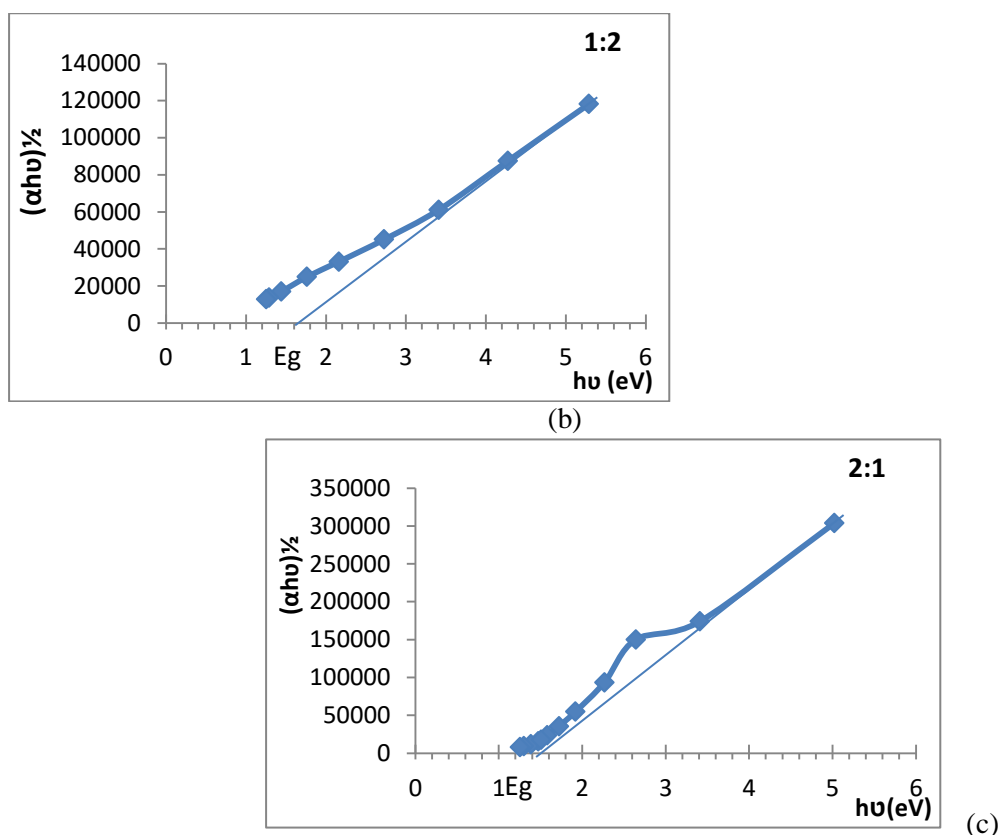**Fig.5: direct allowed energy gap of the thin films with different concentration.**

(a)

(b)

(c)

Fig.6: indirect allowed energy gap of the thin films with different concentration.

CONCLUSION

In the study, CuAlO$_2$ delafossite thin films were deposited by spray pyrolysis with different concentration of salts used in pressure spray solution. The structure and optical properties of thin films were examined and result can be summarized as follows: the films with concentration (2:1) and (1:2) were found to consist of a mixture of CuO and CuAlO$_2$, while the result of (1:1) confirms. That CuAlO$_2$ is the dominant phase of the films, and these films have highest value of absorption coefficient and the optical band gap was increase with increasing of Cu salt, and these ratio (1:1) is important used as a detector in visible region.

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