Laser annealing effect on the optical properties of $CuAlO_2$ thin film

The 5th International scientific Conference on Nanotechnology& Advanced Materials Their Applications (ICNAMA 2015)3-4 Nov, 2015

Dr. Azhar A. Hassan
School of Applied sciences, University of Technology/Baghdad
Email: Azhar.Hassan@yahoo.com
Nuha F. Abd Al-Rasheed
School of Applied sciences, University of Technology/Baghdad

Abstract

Transparent conducting oxides thin films of copper aluminium oxide ($CuA1O_2$) were prepared from mixture of $CuCl_2$ and Al_2Cl_3 salts by spray pyrolysis technique on a glass substrate at temperature (500°C). The as-deposited film show pure delaffosite phase of $CuAlO_2$ by XRD spectra, also many peaks of $CuAlO_2$ were appeared after annealing at different energy fluence. The optical transmission of thin films was measured by UV-VIS spectrometer and reach to 74% in visible region. The direct and indirect optical band gaps of the films are found in the range of (3.4-3.1) eV, and (2.1-1.5) eV, respectively depending on the annealing energy fluence at (300, 600, 900, 1200) mJ/cm^2.

Keywords: TCO; $CuAlO_2$ thin film; Laser annealing; Optical properties.

تأثير التلدين بالليزر على الخصائص البصرية لأغشية $CuAlO_2$ الرقيقة

الخلاصة

في هذا البحث تم تحضير أغشية رقيقة لاكاسيد شفافة موصلة من اكاسيد ألمنيوم- نحاس خليط من أملاح كلوريد النحاس وكلوريد الالمنيوم باستخدام تقنية الرش الحراري على قواعد زجاجية عند درجة حرارة (500 م°). الغشاء المرسب يظهر طور delaffosite النقي من $CuAlO_2$ بواسطة أطياف حيود الاشعة السينية, وقد ظهرت قمم عديدة من $CuAlO_2$ بعد التلدين عند كثافات طاقة مختلفة. تم قياس النفاذية البصرية للاغشية الرقيقة بواسطة الطيف المرئي - الأشعة فوق البنفسجية وقد وصلت الى 74% في المنطقة المرئية. وجدت فجوات الطاقة البصرية المباشرة وغير المباشرة للاغشية ضمن المدى (3.4-3.1) الكترون فولت, (2.1 - 1.5) الكترون فولت, على التوالي اعتمادا على كثافات طاقة التلدين عند (300, 600, 900, 1200) ملي جول / سم2 .

INTRODUCTION

Transparent conducting oxides (TCOs) are very important for various kinds of devices and are commonly used in transparent electronics 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

https://doi.org/10.30684/etj.33.5B.15
2412-0758/University of Technology-Iraq, Baghdad, Iraq

attention as p-type TCOs since it was firstly prepared in 1997 by Hosono and Coworker [2]. Properties of TCO material has found extensive applications in optoelectronic devices such as solar cell, liquid crystal display, heat mirrors, photovoltaic cell, low emissivity window, transparent electronics, electro chromic devices and many others different applications depending on the type of conduction in the material [3, 4]. There are several type have been used to prepared $CuAlO_2$ thin films such as sol-gel [5], pulsed laser deposition [6], Chemical solution deposition (CSD) [7], radio frequency (r.f) magnetron sputtering [8], and spray pyrolysis [9].The spray pyrolysis has some advantages 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 [4,10]. In this work $CuAlO_2$ thin film was prepared by spray pyrolysis and performed annealing treatment the films. We focused on the effect of annealing energy fluence on the structure, and optical properties of the films.

Experimental

$CuAlO_2$ thin films were deposited on glass substrate using spray pyrolysis process. The starting solution was prepared using $CuCl_2$ and Al_2Cl_3 salts dissolved in distilled water in the ratio (0.1: 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. After deposition, the samples were annealed at different energy fluence (300, 600, 900, 1200) mJ/cm^2. 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]:

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

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:

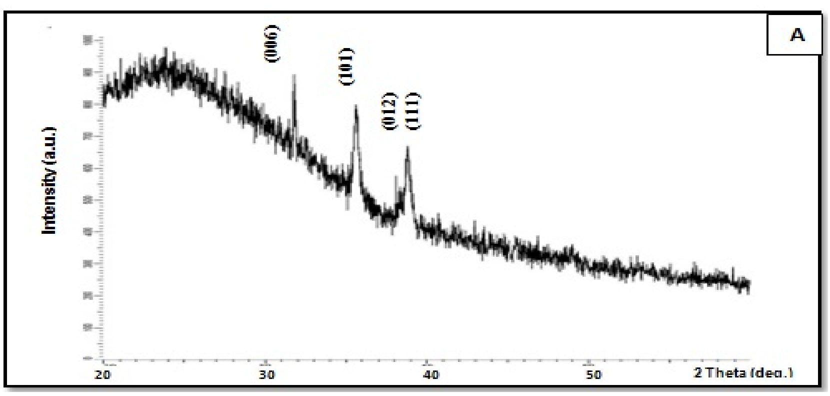
$$2CuCl_2.2H_2O + Al_2Cl_3.2H_2O + 2O_2 \longrightarrow 2CuAlO_2 + 7Cl + 6H_2O \qquad \dots(2)$$

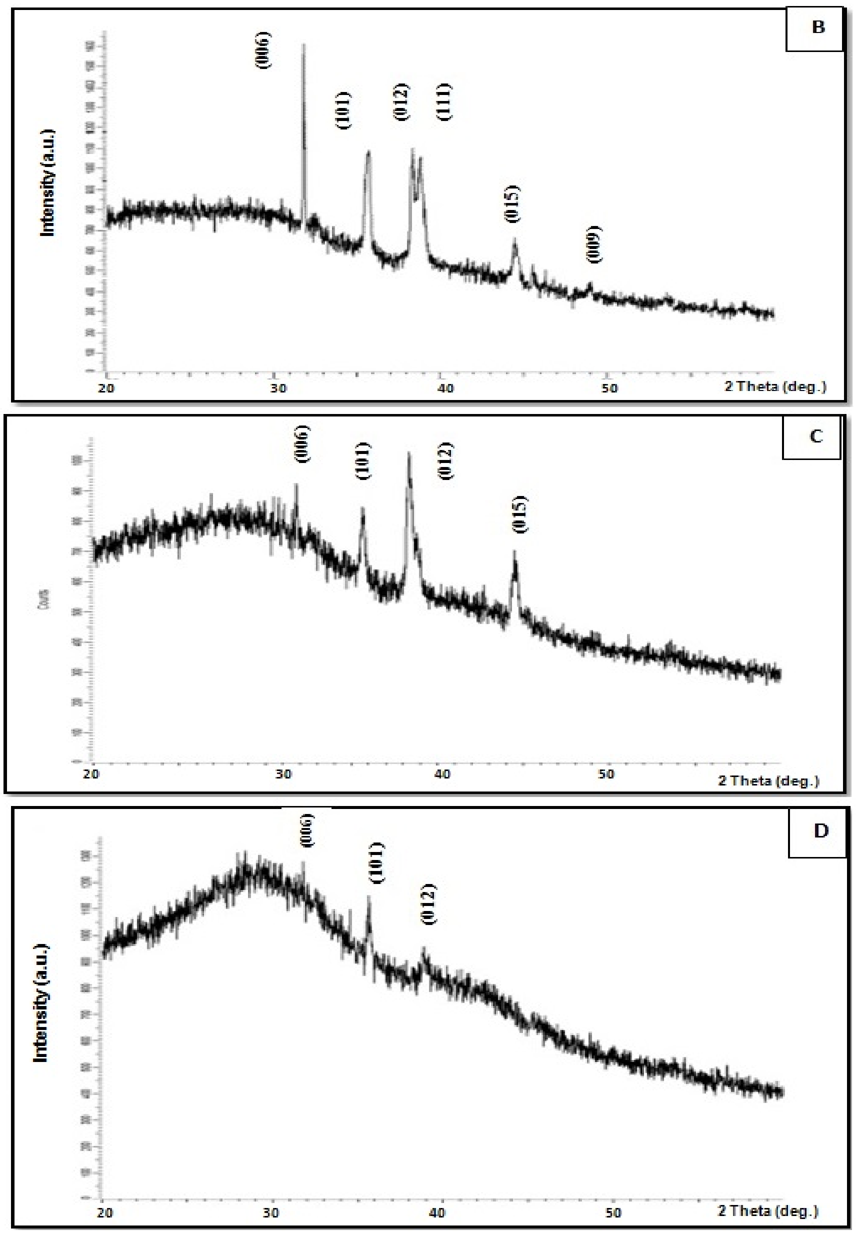
The structural characterization of thin films was studied by using X-ray diffractometer with Cu, BF 2.7KW radiation (λ=1.5418 A°, SHIMADZU, JAPAN), the influence of annealing at differ energy fluence on the optical property were investigated by using (UV-VIS-NIR) spectrophotometer.

Results and Discussion

Structural properties

Figure (1-A) shows the XRD spectra of deposited thin films before annealing, which shows three intensity (006), (101) and (012) of delafossite $CuAlO_2$ at (2θ= 32°, 36°, 38.5°) and low intensity (111) of CuO at (2θ= 39°). The effect of laser annealing at different energy fluence on the structural properties of $CuAlO_2$ thin films can be understood from figures (1- B,C,D,E). It is seen that increasing in intensity of (006) orientation may be due to annealing energy fluence decreasing the defect in the $CuAlO_2$ films and improving quality of films, also when annealing energy fluence increased the CuO phase begin disappear and $CuAlO_2$ phase was dominated. Figure (1-B) presents the XRD results of the prepared film at (300 mJ/cm^2) which shows a high intensity of $CuAlO_2$ delafossite at (2θ= 32°) reflected from (006) plane, and other peaks of these phase appeared at (2θ=36°, 38.5°, 44.8°, 49°) with orientation (101), (012), (015) and (009) respectively, at (2θ=39°) CuO phase reflected from (111) plane were found to agree with [12]. The diffraction pattern of the film annealing at (600 mJ/cm^2) shows high peak (012) orientation and (006), (101), (015) peaks of $CuAlO_2$ at (2θ=38.5°, 32°, 36°, 44.8°) respectively, in figure (1-C). While figure (1-D) represents this film in annealing energy fluence (900 mJ/cm^2) has three peaks of $CuAlO_2$ (006), (101) and (012) at (2θ=32°, 36°, 38.5°) respectively. Three peaks of delafossite $CuAlO_2$ (006), (101) and (012) plane were appeared in figure (1-E) when the film annealed at (1200 mJ/cm^2) energy fluence. We noticed that pure $CuAlO_2$ films are obtained and the crystallization quality of CAO decreases with the increase of the annealing energy fluence. In general, the crystallinity of thin film should be improved with increase in annealing, but the weakened crystallinity of our films may be due to the poor morphology induced by quick rearrangement and coalescence of $CuAlO_2$ grains in the film at high energy fluence, agree with [13].




B
(006)
(101)
(012)
(111)
(015)
(009)
Intensity (a.u.)
20
30
40
50
2 Theta (deg.)
C
(006)
(101)
(012)
(015)
20
30
40
50
2 Theta (deg.)
D
(006)
(101)
(012)
Intensity (a.u.)
20
30
40
50
2 Theta (deg.)

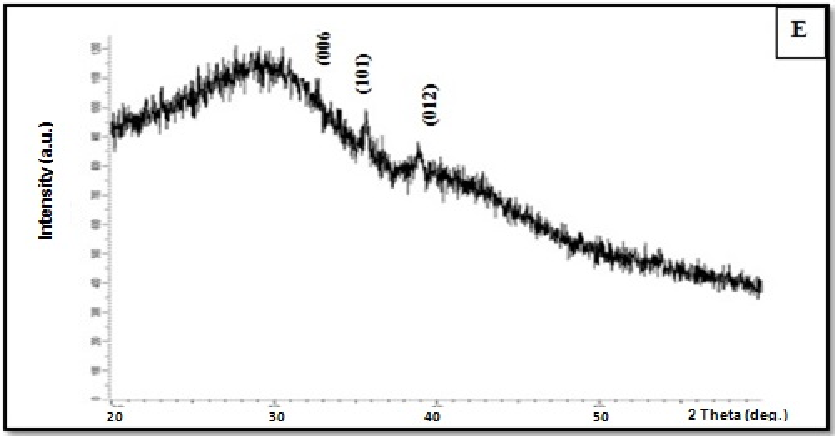


Figure (1):- XRD results of $CuAlO_2$ layer (A) before annealing, (B) after annealing at 300 mJ/cm^2, (C) 600 mJ/cm^2, (D) 900 mJ/cm^2, (E) 1200 mJ/cm^2.

Optical properties

The optical transmission of copper aluminum oxide CAO thin films prepared on glass substrate was measured by UV-VIS spectrometer as a function of a (200-1100) nm wave length range. The transmission is increased with wave length increasing and this is one of a property of semiconductor. Figure (2) display the optical transmission of $CuAlO_2$ films before annealing it is found 38%, while after annealing the value of transmission increasing and reach to 74% at 300 mJ/cm^2 around (500 nm) and a sharp absorption edge is observed at (350 nm) due to improvement the structure of film and reduce of impurities and defects leading to the reduction of reflection and scattering effect. But by rising the fluence, the transmission in the visible region decreases and the absorption edge shifts to the long wave length. The decrease of the crystalline quality and the poor morphology may be the reasons for this reduction, this agrees with [13]. Compared with the films prepared by chemical solution deposition method, T 70% [7] and DC. sputtering process, T 70% [14], the optical transmittance of our films is relatively higher.

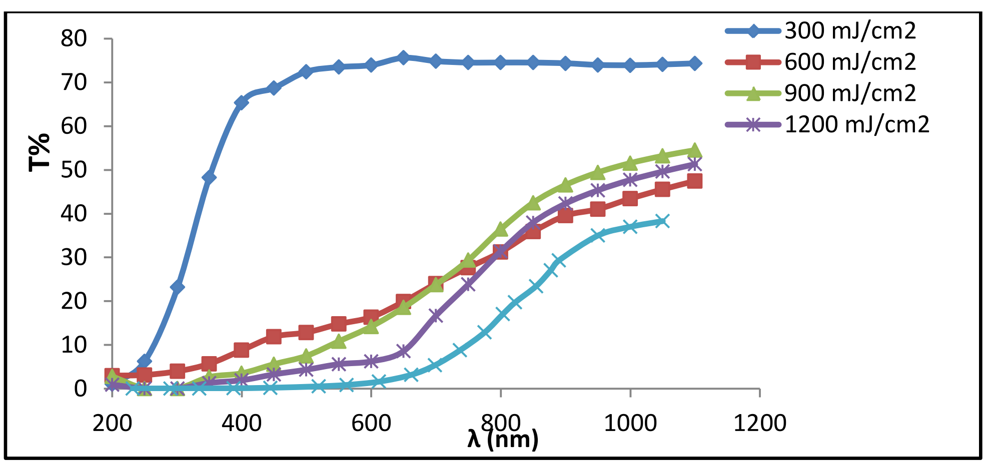


Figure (2):- Transmission as a function of wave length for $CuAlO_2$ thin films.

The optical absorption coefficient (α) for the prepared thin films was calculated using the following equation [15]:

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

Where t is the film thickness and T is the transmittance of the film.
Figure (3) exhibits the variation of the absorption coefficient against wavelength for $CuAlO_2$ films before and after annealing with different laser energy fluence. It is found that the highest absorption coefficient was at short wave length range (300 – 400 nm). The absorption coefficient of $CuAlO_2$ thin films increased sharply in the UV range, and then decreased gradually in the visible region because it is inversely proportional to the transmittance. The absorption coefficient is decreasing by the annealing, then return to increase when the annealing fluencies increases. This can be linked with increase in grain size after annealing.

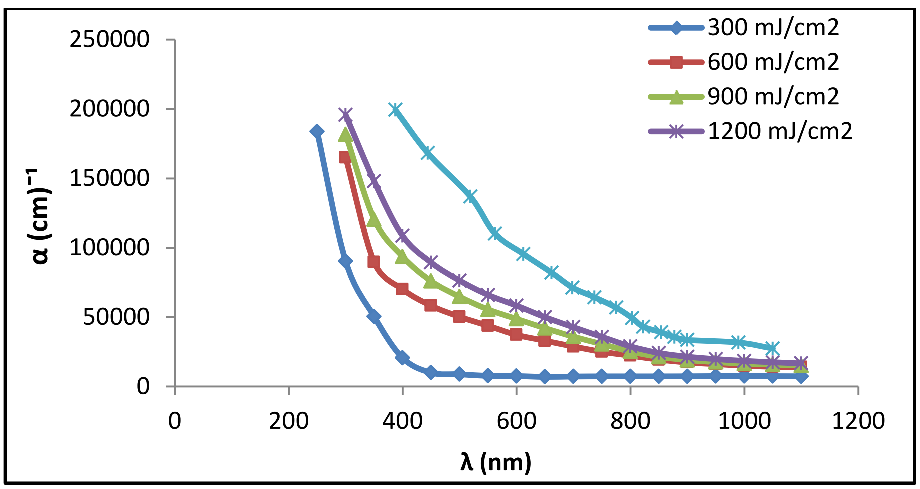


Figure (3) The optical absorption coefficient as a function of wavelength of $CuAlO_2$ films.

The optical energy gap in general depends on the arrangement and distribution of atoms in the crystal lattice and the films crystal structure. The relation between the absorption coefficients (α) and the incident photon energy (*h*ν) can be written as [16].

$$(\alpha h\nu)^{1/n}=A(h\nu-E_g) \qquad \dots (4)$$

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 $(\alpha h\upsilon)^{1/n}$ vs. hυ shown in figure (4,5) gives the direct allowed optical band gap (n=1/2) and the allowed indirect optical band gap (n=2) by extrapolating the linear part of the plot to intercept with (hν) axis when (α=0).

This results refer to a fact that the energy gap increased with the annealing at (300 mJ/cm^2) may be due to the removal of surface defects at annealing and enhancment the crystallinity. While by increased the annealing energy fluence the energy gap reduce because of increase the defect and decreased the crystallinity as shown by XRD. Before annealing the direct energy gap (Eg_d) and indirect energy gap (Eg_{in}) were calculated (3 eV and 1.5 eV) from figures (4-A) and (5-A) respectively. And these values increased by annealing and reached to (3.4 eV and 2.1 eV) for (Eg_d) and (Eg_{in}) at 300 mJ/cm^2 illustrated in figures (4-B), (5-B), when increasing fluence of annealing, these values of direct and indirect energy gap begin to decline to (3.3, 3.2, 3.1) eV, (1.7, 1.6, 1.5) eV at 600, 900, 1200 mJ/cm^2 respectively. These results agree with the results of many studies [16-18]. The band gap values of $CuAlO_2$ thin films are listed in table (1).

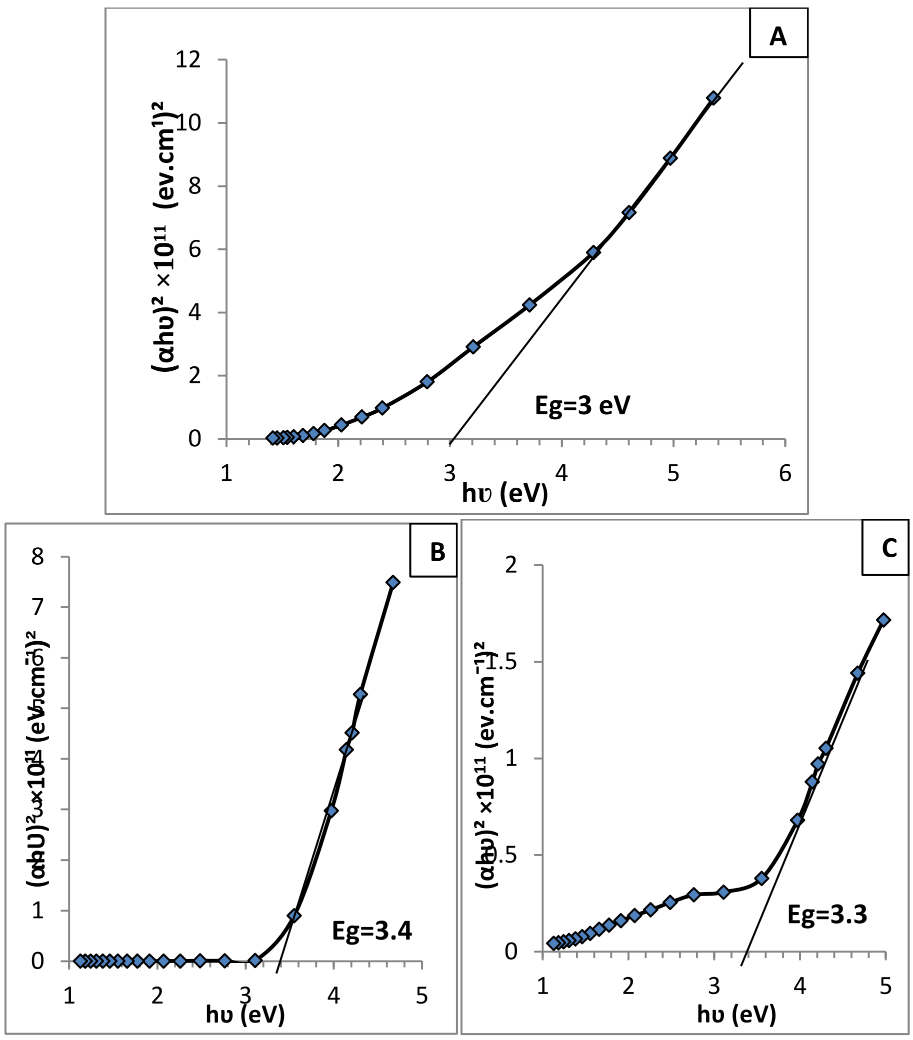
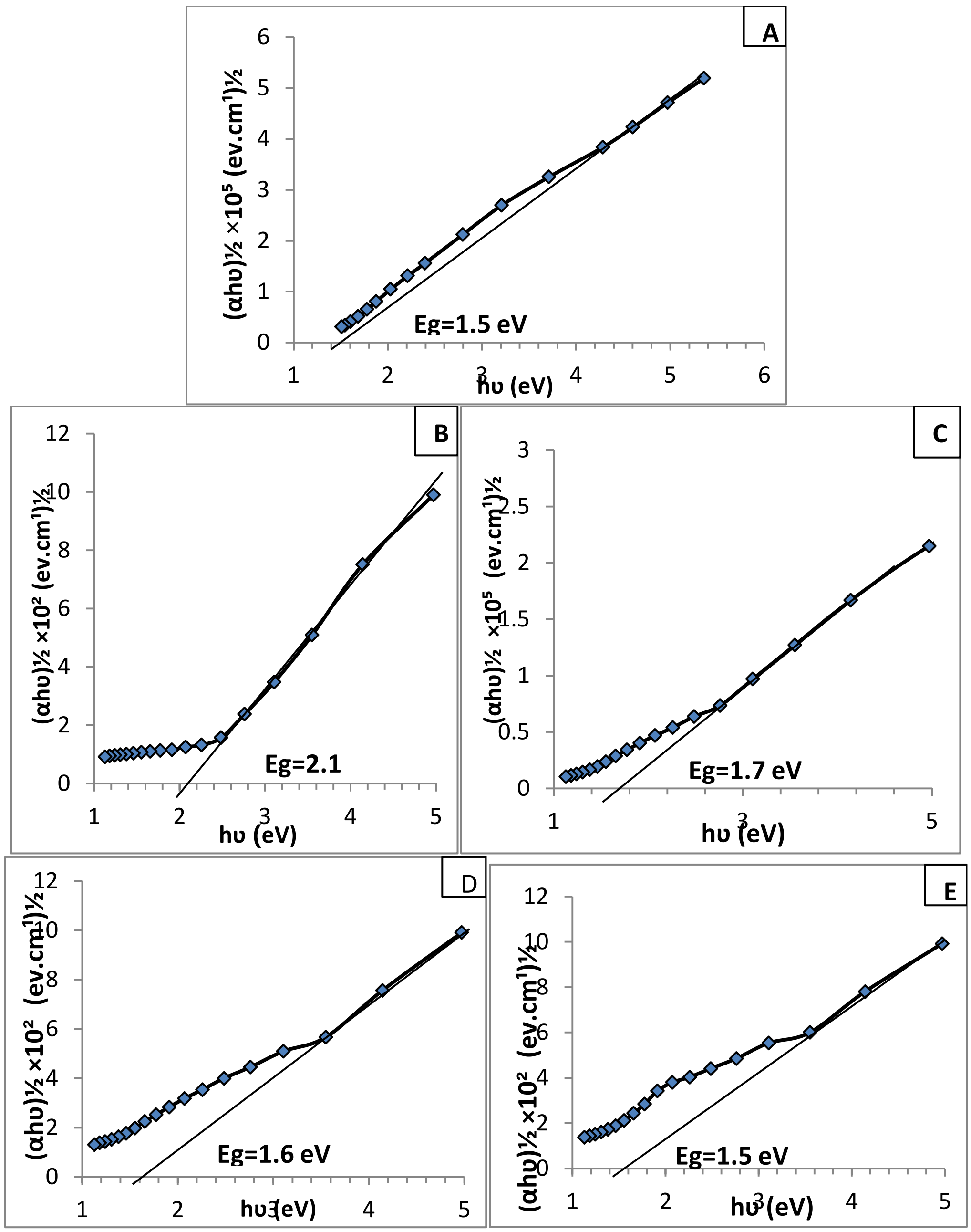


Figure (4) Plots of $(\alpha h\upsilon)^2$ versus ($h\upsilon$) of $CuAlO_2$ thin films at (A) before annealing, (B) 300 mJ/cm^2, (C) 600 mJ/cm^2, (D) 900 mJ/cm^2, (E) 1200 mJ/cm^2.



Figure(5):- Plots of (αhυ)½ versus (hυ) of $CuAlO_2$ thin films at (A) before annealing, (B) 300 mJ/cm^2, (C) 600 mJ/cm^2, (D) 900 mJ/cm^2, (E) 1200 mJ/cm^2.

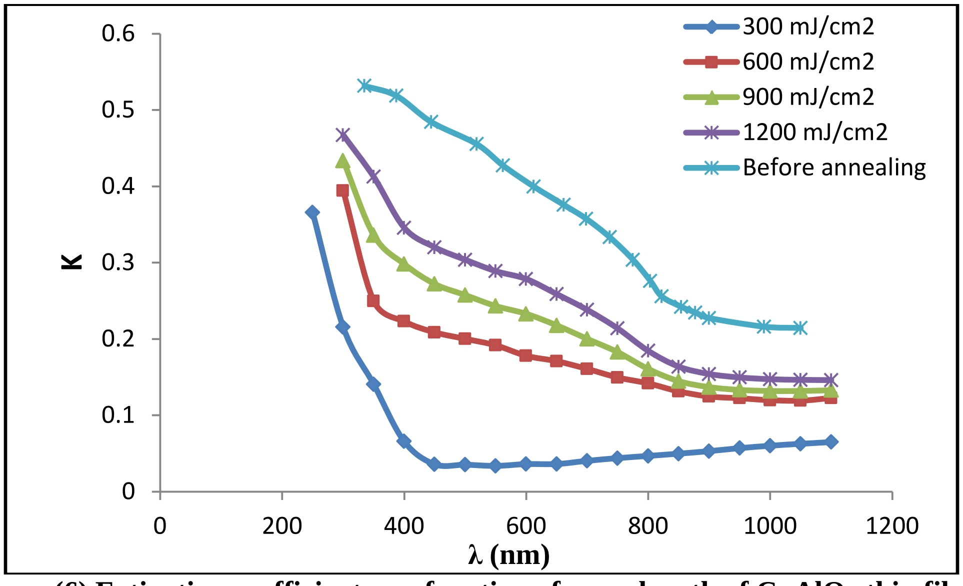
Table (1) The direct and indirect energy gap of $CuAlO_2$ thin films.

sample	Direct energy gap (Eg_d)	Indirect energy gap (Eg_{in})
Before annealing	3 eV	1.5 eV
Annealing at 300mJ/cm^2	3.4 eV	2.1 eV
Annealing at 600mJ/cm^2	3.3 eV	1.7 eV
Annealing at 900mJ/cm^2	3.2 eV	1.6 eV
Annealing at 1200mJ/cm^2	3.1 eV	1.5 eV

The values of extinction coefficient are calculated using the following equation [19] :

$$K = \frac{\lambda\alpha}{4\pi} \quad \dots (5)$$

The K values are plotted vs λ for $CuAlO_2$ thin films before and after annealing at different fluencies as shown in figure (6). Extinction coefficient decreased by annealing. This reduce may be attributed to change in crystalline structure. This result agrees well with literature [20].



Figure(6) Extinction coefficient as a function of wave length of $CuAlO_2$ thin films.

Conclusion

In the study, $CuAlO_2$ delafossite thin films were deposited using $CuCl_2$ and Al_2Cl_3 salts by spray pyrolysis technique with annealing at different energy fluence. The annealing plays an important role in the structure and optical properties of $CuAlO_2$ thin film, where the crystallite of CAO thin films is increased with annealing energy fluence of laser. From UV-VIS transmittance measurements conclude that the transmittance of CAO thin film increased by annealing energy fluence than before the annealing. Also the direct and indirect optical energy gap of synthesize films are increased by annealing energy fluence and reach (3.4) eV and (2.1) eV respectively, than before the annealing, then reduced with continuous in energy fluence. While the optical absorption coefficient and the extinction coefficient values are high before annealing and they decreased with annealing energy fluence.

Reference

[1] Robert M. Pasquarelli, David S. Ginley and Ryan O'Hayre " Solution processing of transparent conductors: from flask to film", The Royal Society of Chemistry, Chem. Soc. Rev., vol. 40, pp.5406–5441, (2011).

[2] Tran V. Thu, Pham D. Thanh, Koichiro Suekuni, Nguyen H. Hai, Derrick Mott, Mikio Koyano ,Shinya Maenosono " Synthesis of delafossite $CuAlO_2$ p-type semiconductor with a nanoparticle-based Cu(I) acetate-loaded boehmite precursor", Materials Research Bulletin, vol. 46, PP. 1819–1827, (2011).

[3] David S. Ginley, Hideo Hosonol, David C. Paine "Handbook of Transparent Conductors", Book, Springer Science +Business Media, (2011).

[4] Antonio Facchetti, Tobin Marks " Transparent Electronics: From Synthesis to Applications", Book, John Wiley & Sons, Inc., pp. 470, (2010).

[5] Sabar D. Hutagalung*, Wu S. Woon, Khatijah A. Yaacob, Zainovia Lockman "Phase formation study of $CuAlO_2$ transparent conductive oxide thin films", Journal of Nuclear and Related Technology, Vol. 4, pp.165-170, (2007).

[6] Jong-Chul Lee, Se-Young Um, Young-Woo Heo, Joon-Hyung Lee *, Jeong-Joo Kim "Phase development and crystallization of $CuAlO_2$ thin films prepared by pulsed laser deposition", Journal of the European Ceramic Society, vol.30, pp. 509–512, (2010).

[7] S.H. Chiu, J.C.A. Huang * "Characterization of p-type $CuAlO_2$ thin films grown by chemical solution deposition", Surface & Coatings Technology, vol. 23, pp.239–242, (2013).

[8] S. Liu, Z. Wu, Y. Zhang, Z. Yao, J. Fan, Y. Zhang, J. Hu, P. Zhang and G. Shao, "Strong temperature-dependent crystallization, phase transition, optical and electrical characteristics of p-type $CuAlO_2$ thin films", Phys. Chem, Vol.17, pp.557-562, (2015).

[9] L. Filipovic, S. Selberherr , G. C. Mutinati , E. Brunet, S. Steinhauer, A. Kck, J. Teva, J. Kraft, J. Siegert, F. Schrank c " Methods of simulating thin film deposition using spray pyrolysis Techniques", Microelectronic Engineering, Vol. 117, pp. 57–66, (2014).

[10] John F. Wager, Douglas A. Keszler, Rick E. Presley , " Transparent Electronics ", Book, Springer Science+ Business Media , (2008).

[11] Yun Lu, Kazunari Maed, Katauhiro Sagara, Liang Hao and Yingrong Jin, "Improvement of Thermoelectric Properties of $CuAlO_2$ by Excess Oxygen Doping in Annealing", Materials Science Forum, Vol. 750 pp 134-137, (2013).

[12] C. Bouzidi, H. Bouzouita, A. Timoumi, B. Rezig " Fabrication and characterization of $CuAlO_2$ transparent thin films prepared by spray technique", Materials Science and Engineering B 118, pp. 259–263, (2005).
[13] Gang Li, Xuebin Zhu, Hechang Lei, Haifeng Jiang " Preparation and characterization of $CuAlO_2$ transparent thin films prepared by chemical solution deposition method", J Sol-Gel Sci Technol, Vol. 53, pp. 641–646, (2010).
[14] A. N. Banerjee, D. Panda, K. K. Chattopadhyay "Fabrication of p-$CuAlO_2$ / n-ZnO: Al heterojunction diodes for Transparent Electronics", Thin Film and Nano-Science Laboratory, Department of Physics, Jadavpur University, Kolkata – 700 032, India.
[15] Adawiya J. Haidar, Jehan A. Saimon, Ali J. Addie "Effect of Mg Concentration MgxZn1-XO nanostructure thin films by PLD on optical and topographical properties", Eng. & Tech.Journal, vol. 31, part (B), No.7, (2013).
[16] A.N. Banerjee, S. Kundoo, K.K. Chattopadhyay " Synthesis and characterization of p-type transparent conducting $CuAlO_2$ thin film by DC sputtering", Thin Solid Films, vol. 440, pp. 5–10, (2003).
[17] W. Lan W. L. Cao M. Zhang X. Q. Liu " Annealing effect on the structural, optical, and electrical properties of $CuAlO_2$ films deposited by magnetron sputtering", J Mater Sci, Vol. 44, PP.1594–1599, (2009).
[18] Chun- Tsung Su, Hsin- Yen Lee, Bin- Kun Wu, Ming Yau Chern "Development of phase-pure $CuAlO_2$ thin films grown on c-plane sapphire substrates prepared by RF sputtering", Journal of Crystal Growth, Vol. 328, pp. 25–29, (2011).
[19] Ping-Hung Hsieh, Yang-Ming Lu, Weng-Sing Hwang, Jing-Jia Yeh, Wei-Luen Jang " Effect of Al content on electrical conductivity and transparency of P-type Cu-Al-O thin film", Surface & Coatings Technology, vol. 205, pp. S206–S209, (2010).
[20] Lawrence V. Olivante, "P-type transparent semiconducting delafossite $CuAlO_{2+x}$ thin film: promising material for optoelectronic devices and field- emission displays", Materials Science Research Trends, Book, pp. 17-132, (2008).