Study of structural, optical and electrical properties of thin $Ag_2Cu_2O_4$ films prepared by pulsed laser deposition

Iqbal S. Naji and Shahad H. Abdulwahed

Department of Physics, College of Science, University of Baghdad

E-mail: moonbb_moonaaaa@yahoo.com

Abstract

The influence of sintering and annealing temperatures on the structural, surface morphology, and optical properties of $Ag_2Cu_2O_4$ thin films which deposited on glass substrates by pulsed laser deposition method have been studied. $Ag_2Cu_2O_4$ powders have polycrystalline structure, and the $Ag_2Cu_2O_4$ phase was appear as low intensity peak at 35.57^o which correspond the reflection from (110) plane. Scan electron microscopy images of $Ag_2Cu_2O_4$ powder has been showed agglomerate of oxide particles with platelets shape. The structure of thin films has been improved with annealing temperature. Atomic Force micrographs of $Ag_2Cu_2O_4$ films showed uniform, homogenous films and the shape of grains was almost spherical and larger grain size of 97.85 nm has obtained for film sintered at 600 °C. The optical band gap was increase from 1.6 eV to 1.65 eV when sintering temperature increased to 300 °C and decrease to 1.45 eV at 600 °C for the films deposited at room temperature. Heat treatment of films has been increased the energy band with increasing sintering temperature. Hall coefficient of $Ag_2Cu_2O_4$ films have a positive sign which means the charge carrier is a p-type. The electrical conductivity decreases with increasing of the sintering temperature for as deposited and annealed films.

Key words

Ag-Cu-O films, structure and morphological properties, optical properties, electrical properties.

Article info.

Received: Apr. 2017
Accepted: May. 2017
Published: Sep. 2017

دراسة الخصائص التركيبية، البصرية والكهربائية لأغشية $Ag_2Cu_2O_4$ الرقيقة المرسبة بالليزر النبضي

إقبال سهام ناجي و شهد حسن عبد الواحد

قسم الفيزياء، كلية العلوم، جامعة بغداد

الخلاصة

تم دراسة تأثير درجات حرارة التلبيد والتلدين على الصفات التركيبية والتضاريسية والبصرية لأغشية $Ag_2Cu_2O_4$ الرقيقة والمرسبة على أساس من الزجاج بطريقة الترسيب بالليزر النبضي. يمتلك مسحوق $Ag_2Cu_2O_4$ تركيبا متعدد التبلور، وان طور $Ag_2Cu_2O_4$ ظهر كقمة منخفضة الشدة عند 35.57^o والتي تمثل الانعكاسات عن مستوى (110). أظهرت صور المجهر الالكتروني الماسح للمسحوق $Ag_2Cu_2O_4$ تكتل جزيئات الأوكسيد على شكل صفائح. إن تركيب الاغشيه الرقيقة تحسن مع درجة حرارة التلدين. وضحت صور مجهر القوة الذرية للأغشية $Ag_2Cu_2O_4$ بان الأغشية منتظمة ومتجانسة وشكل الحبيبات على الأغلب كروي، وان اكبر حجم حبيبي هو 97.85 nm تم الحصول عليه للغشاء عند درجة حرارة تلبيد تساوي 600°C. أن فجوة الطاقة البصرية ازدادت من 1.6 eV الى 1.65 eV عند زيادة درجة حرارة تلبيد إلى 300°C وتقل إلى 1.45 eV عند 600 °C للأغشية المرسبة عند درجه حرارة الغرفة. المعاملة الحرارية للأغشية تزيد فجوة الطاقة عند زيادة درجة حرارة التلبيد. معامل هول لاغشية $Ag_2Cu_2O_4$ تمتلك إشارة موجبة وهذا يعني إن نوع حاملات الشحنة هو من النوع القابل. أن التوصيلية الكهربائية تنقص عند زيادة درجه حرارة التلبيد للأغشية المرسبة والملدنه.

Introduction

Copper and silver belong to the same family, share common features, and readily form alloys in their metallic states. Nevertheless, it seems a different story. When it form ternary compounds, only a few simple silver copper compounds were known [1]. The silver-copper-oxygen (Ag-Cu-O) system consists of various ternary compounds $Ag_2Cu_2O_3$, $Ag_2Cu_2O_4$, and $AgCuO_2$ [2]. These compounds derived from the binaries of Ag_2O, AgO, Cu_2O, Cu_4O_3 and CuO [3]. The groups studying silver copper oxides as new promising materials for photovoltaic applications. The silver copper oxides are p-type semiconductors, which could potentially be used as absorber material for future generation photovoltaic devices [4]. Munoz-Rojas et.al prepared a new silver copper oxide, formulated as $Ag_2Cu_2O_4$ by Electrochemical oxidation at room temperature of a slurry of $Ag_2Cu_2O_3$, with one more atom of oxygen per unit formula, that can in turn revert to the original precursor [5]. The $Ag_2Cu_2O_4$ phase was synthesised by modification of oxygen content in $Ag_2Cu_2O_3$ using electrochemical method. As a preliminary study in that line of work, electrochemical characterization of the phase $Ag_2Cu_2O_3$ by cyclic voltammetry at low temperature showed the existence of reduction and oxidation waves that could make possible the obtention of new phases either by reduction or oxidation [6]. In a first approach the powder diffraction pattern of $Ag_2Cu_2O_4$ can be fitted to a primitive monoclinic cell. The transformation from $Ag_2Cu_2O_3$ to $Ag_2Cu_2O_4$ phase have been synthesized by ozonization of the solid state precursor at room temperature [7]. In particular electrochemical oxidation of $Ag_2Cu_2O_3$ has allowed intercalation of oxygen but with a final change in structure to $Ag_2Cu_2O_4$ with an extra oxygen atom per unit formula (this formula can be simplified to the empirical $AgCuO_2$) [8].

In this paper, Ag-Cu-O powder was synthesized by solid state reaction and their films were deposited on glass substrates by pulsed laser deposition method. The effect of sintering temperature on the structural, surface morphology and optical properties of the deposited films was studied.

Experimental procedure

The new phase of $Ag_2Cu_2O_4$ was synthesized by solid state reaction in a various sintering temperature (200, 300, and 600) °C for two hours using AgO (98 %) and CuO (Fluka AG, Buchs SG, Made in Switzerland, 99%) with appropriate atomic percentage. The binary compounds (AgO and CuO) mixed and crushed for an hour then pressed under 5 ton to form a target with a pellet shape (13mm) diameter and (5mm) thickness. The Silver-Copper-Oxide ($Ag_2Cu_2O_4$) thin films were deposited by pulsed laser deposition (PLD) method on glass substrates at room temperature. The thickness of the deposited films was in the range of (100± 5) nm. The focused Nd:YAG SHG Q-switching laser beam (pulse width 10 nsec and repetition frequency 6Hz) with a wavelength 1064 nm incident on the target surface with an angle equal to 45^o. The deposition was carried out inside a vacuum chamber (10^{-2} mbar). The crystal structure analysis of these films was obtained by using x-ray diffractometer type (D_2Phaser, Bruker company, Germany) for powder and (Miniflex II Rigaku company, Japan)for thin film was used with CuK_α target of wavelength 0.154nm and $2\theta = 20^o - 80^o$. Surface morphology measurement was done by using atomic force microscopy (AFM) type CSPM-AA 3000 contact

mode spectrometer, Angstrom Advanced Inc. Company, USA. The optical transmittance of the films was recorded using UV-VIS spectrophotometer type (SP8001 Metertech, USA) over the wavelength range (300-1100) nm. Electrical properties were carried out by using Hall Effect measurement system (3000 HMS, VER 3.5, supplied with Ecopia company).

Results and discussion

Fig.1 shows EDS spectrum of $Ag_2Cu_2O_4$ powder at sintering temperature equals to 200 °C. From this figure, we can recognize the peaks of Ag, Cu and O elements, and this means that the films quality is good since there is no other compounds presence in the spectrum.

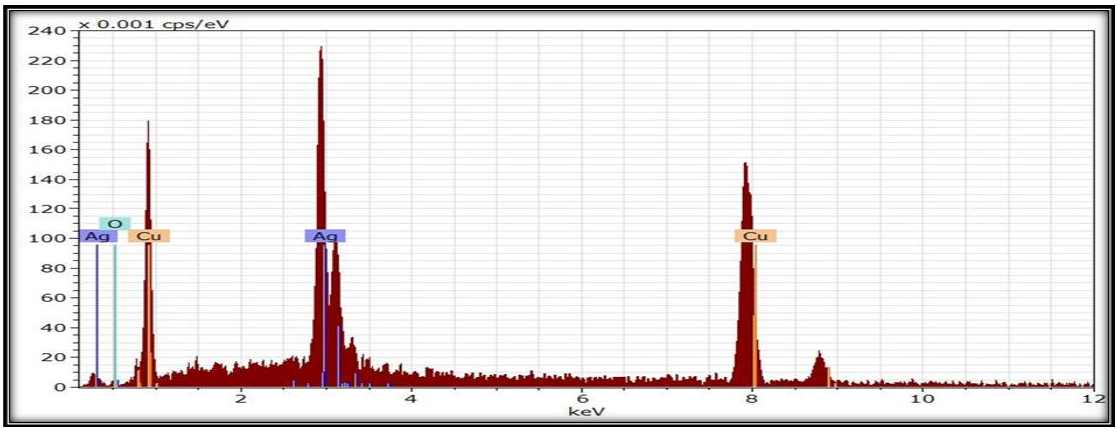


Fig.1: EDS chart of $Ag_2Cu_2O_4$ compound sintered at 200°C.

The structure properties of powder and films of $Ag_2Cu_2O_4$, In general the compound has a polycrystalline structure. The x-ray diffraction pattern of $Ag_2Cu_2O_4$ powder which sintered at 200°C was shown in Fig. 2. Generally the intensity of $Ag_2Cu_2O_4$ peak is low and this peak appeared at 35.579° reflected from (110) plane. The larger peak represent the position of two binary compounds cubic Ag_2O and monoclinic CuO at reflection surfaces (111) and (110) respectively, and probably these binary compounds become ternary compound at different ratios when their presence at the same peak. Another peak was detected by XRD analysis. This peak was correspond to $Ag_2Cu_2O_3$ compound at 29.5° reflected from (013) plane which has tetragonal structure. The XRD analysis results are shown in Table 1.

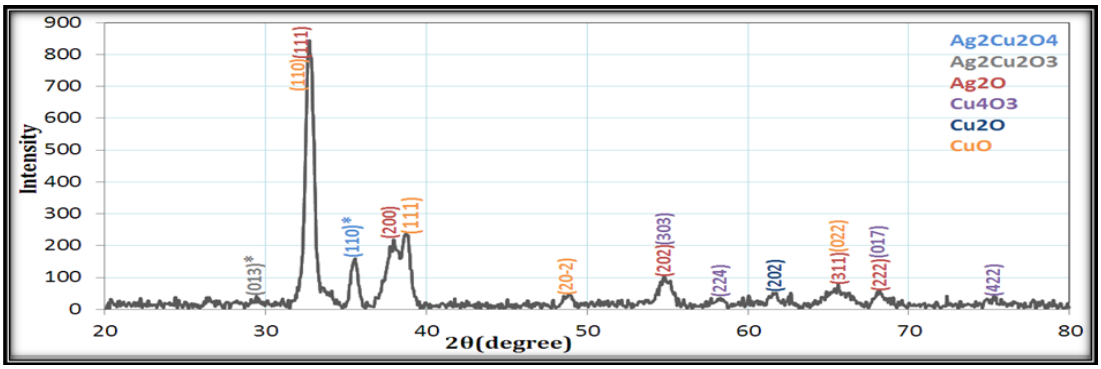


Fig.2: The X-ray diffraction pattern of $Ag_2Cu_2O_4$ powder sintered at 200 °C.

Table 1: Structural parameters viz. inter-planar spacing, crystallite size and miller indices of $Ag_2Cu_2O_4$ powder at sintered at 200 °C.

compounds	2θ (Deg.)	d_{hkl} Exp.(Å)	d_{hkl} Std.	hkl	FWHM (Deg.)	G.S (nm)	phase	card No.
$Ag_2Cu_2O_4$	35.579	2.5213	2.5212	110	0.4838	17.2	monoclinic	-----
$Ag_2Cu_2O_3$	29.5	3.0255	3.0481	013	0.9677	8.5	tetragonal	96-431-9055
Ag_2O	32.719	2.73485	2.7312	111	0.6129	13.5	Cubic	96-431-8189
	38	2.3660	2.3653	200	0.9677	8.7		
	54.85	1.6724	1.6725	202	1.2903	6.9		
	65.6	1.4220	1.4263	311	1.6129	5.9		
	68.2	1.3740	1.3741	222	0.9677	9.9		96-101-0605
Cu_4O_3	54.85	1.6724	1.6774	303	1.2903	6.9	tetragonal	96-900-0604
	58.195	1.5840	1.5871	224	0.6571	13.8		
	68.2	1.3740	1.3787	017	0.9677	9.9		
	74.864	1.26731	1.2623	422	0.9677	10.3		
Cu_2O	61.5	1.5066	1.5061	202	0.8064	11.5	Cubic	96-101-0942
CuO	32.719	2.73485	2.7372	110	0.6129	13.5	monoclinic	96-101-1149
	38.711	2.32417	2.3212	111	0.6451	13.1		96-101-1195
	48.8	1.8647	1.8617	20-2	0.8064	10.8		
	65.6	1.4220	1.4186	022	1.6129	5.9		

Fig. 3 shows the X-ray diffraction pattern for $Ag_2Cu_2O_4$ powder treated at sintering temperature 300°C. It is clear that the intensity of the $Ag_2Cu_2O_4$ peak which correspond the reflection from (110) plane was improved. The larger peak represent the position of two binary compounds cubic Ag_2O and monoclinic CuO at reflection surfaces (111) and (110) which was increased with increasing the sintering temperature to 300 °C. Sharp peak of cubic Ag_2O phase was appeared at 38.270° reflected from (020) plane. The tetragonal $Ag_2Cu_2O_3$ phase was observed at 64.614° which correspond to reflections from (035) plane. Also many binary phase appeared in this pattern such as (Ag_2O, AgO, Cu_4O_3, Cu_2O, CuO) as shown in Table 2. Ag appear at 2θ =44.478° of surface reflection (200) match with Petitjean et al. [9], this is not surprising because silver oxide that is known to decompose into metallic silver at temperature as low as 250 ^oC.

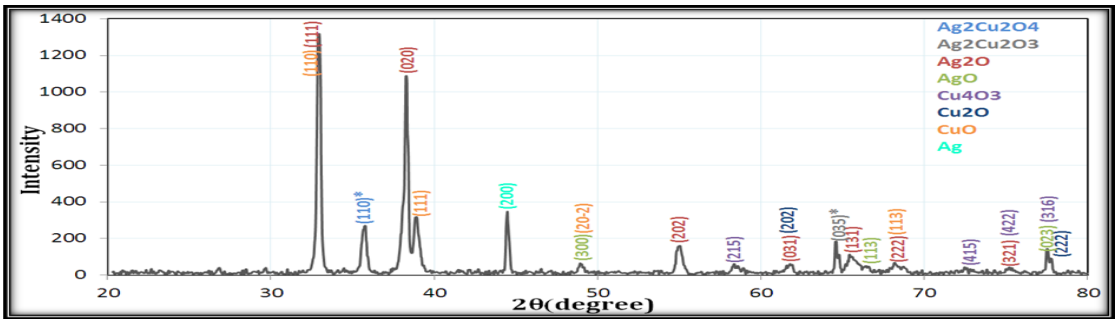


Fig.3: The X-ray diffraction pattern of $Ag_2Cu_2O_4$ powder at sintered at 300°C.

Table 2: Structural parameters viz. inter-planar spacing, crystallite size and Miller indices of $Ag_2Cu_2O_4$ powder at sintered 300 °C.

compounds	2θ (Deg.)	d_{hkl} Exp.(Å)	d_{hkl} Std.	hkl	FWHM (Deg.)	G.S (nm)	phase	card No.
$Ag_2Cu_2O_4$	35.579	2.5213	2.5212	110	0.3428	24.3	monoclinic	------
$Ag_2Cu_2O_3$	64.614	1.44127	1.4455	035	0.1428	65.8	tetragonal	96-431-9055
Ag_2O	32.911	2.71934	2.7239	111	0.2285	36.3	Cubic	96-101-0487
	38.270	2.34994	2.3590	020	0.2285	36.8		
	54.966	1.66918	1.6681	202	0.4	22.4		
	65.503	1.42385	1.4225	131	0.7142	13.2		
	61.655	1.50316	1.5052	031	0.4285	21.6		96-101-0605
	68.184	1.37425	1.3741	222	0.5714	16.8		
	75.2	1.2625	1.2643	321	0.7142	14.0		96-431-8189
AgO	48.935	1.85982	1.8604	300	0.4	21.8	monoclinic	96-900-8963
	66.5	1.4049	1.4084	113	0.2857	33.2		
	77.537	1.23017	1.2324	023	0.1428	71.4		
Cu_4O_3	68.5	1.5765	1.5808	215	0.5142	17.7	tetragonal	96-900-0604
	72.520	1.30239	1.3017	413	0.2857	34.5		
	75.2	1.2625	1.2623	422	0.7142	14.0		
	77.537	1.23017	1.2324	316	0.1428	71.4		
Cu_2O	61.655	1.50316	1.5033	202	0.4285	21.6	Cubic	96-100-0064
	77.79	1.2268	1.2274	222	0.1428	71.5		96-101-0927
CuO	32.911	2.71934	2.7372	110	0.2285	36.3	monoclinic	96-900-8962
	38.877	2.31463	2.3118	111	0.5714	14.7		
	48.935	1.85982	1.8553	20-2	0.4	21.8		
	68.184	1.37425	1.3726	113	0.5714	16.8		
Ag	44.478	2.03529	2.0389	200	0.2285	37.6	Cubic	96-901-2432

The XRD pattern for $Ag_2Cu_2O_4$ powder which sintered at 600°C was shown in Fig. 4. It is clear that the intensity of the fundamental peak of $Ag_2Cu_2O_4$ which correspond to the reflection from (110) plane was increased and appear a new peak at 48.757° for (003) plane. Ag_2O phase appeared with sharp and high intensity at 38.08° for reflection from (020) plane. Also there are two peaks for $Ag_2Cu_2O_3$ tetragonal phase presented at 53.46° and 64.40°. Many binary phases were appeared such as (AgO, Cu_4O_3, Cu_2O, and CuO) as shown in Table 3.

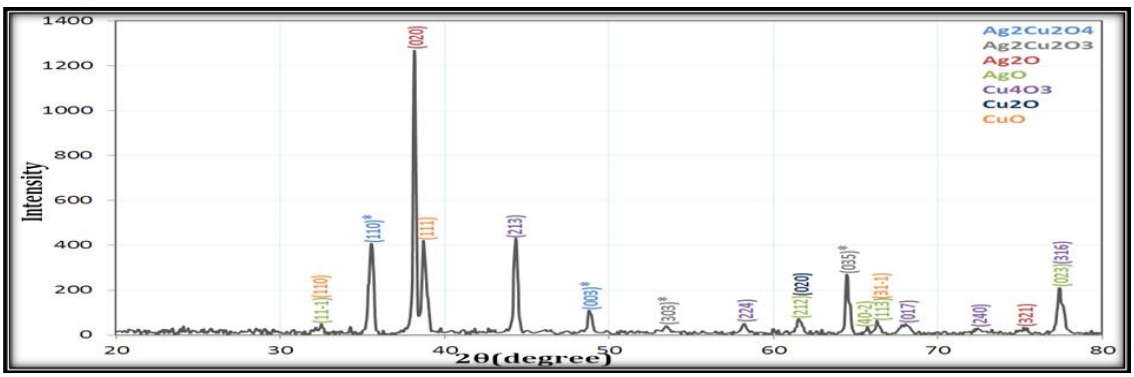


Fig. 4: The X-ray diffraction pattern of $Ag_2Cu_2O_4$ powder sintered at 600 °C.

Table 3: Structural parameters viz. inter-planar spacing, crystallite size and Miller indices of $Ag_2Cu_2O_4$ powder at sintered at 600 °C.

compounds	2θ (Deg.)	d_{hkl} Exp.(Å)	d_{hkl} Std.	hkl	FWHM (Deg.)	G.S (nm)	phase	card No.
$Ag_2Cu_2O_4$	35.579	2.5213	2.5212	110	0.3355	24.9	monoclinic	--------
	48.757	1.86621	1.8636	003	0.4026	21.7		-------
$Ag_2Cu_2O_3$	53.469	1.71233	1.7187	303	0.5033	17.7	tetragonal	96-431-9055
	64.406	1.44543	1.4455	035	0.1677	56.0		
Ag_2O	38.083	2.36104	2.3590	020	0.1677	50.1	Cubic	96-101-0487
	75.01	1.2652	1.2643	321	0.8389	11.9		96-431-8189
AgO	32.459	2.75613	2.7669	11-1	0.3355	24.7	monoclinic	96-900-8963
	61.532	1.50586	1.5093	212	0.4026	23.0		
	65.749	1.41911	1.4216	40-2	0.3355	28.2		
	66.219	1.41019	1.4084	113	0.2684	35.3		
	77.352	1.23264	1.2324	023	0.3355	30.3		
Cu_4O_3	44.266	2.04456	2.0498	213	0.2684	32.0	tetragonal	96-900-0604
	58.190	1.58415	1.5871	224	0.3355	27.1		
	68	1.3775	1.3787	017	0.6711	14.3		
	72.25	1.3066	1.3052	240	0.3355	29.3		
	77.352	1.23264	1.2324	316	0.3355	30.3		
Cu_2O	61.532	1.50586	1.5054	020	0.4026	23.0	Cubic	96-101-0964
CuO	32.459	2.75613	2.7509	110	0.3355	24.7	monoclinic	96-101-1195
	38.654	2.32746	2.3212	111	25.1	25.1		
	66.219	1.41019	1.4085	31-1	0.2684	35.3		96-410-5686

Fig. 5 shows the XRD pattern for $Ag_2Cu_2O_4$ thin films prepared by pulsed laser deposition (PLD) (a) deposited at room temperature (b) annealing at 200°C for half an hour at sintering temperature 200°C. The films have polycrystalline nature. In general the peaks which appeared in this pattern are not sharp and have low intensity. The pattern of the film deposited at room temperature revealed $Ag_2Cu_2O_4$ phase as a fundamental peak at 37.15^o which correspond to reflection from ($\bar{2}02$) plane. Also there are two small peaks related to tetragonal $Ag_2Cu_2O_3$ phase appeared at 35.8° and 43.021° which correspond to reflections from (202) and (213) planes respectively as shown in Table 4.

The heat treatment at 200 °C made the fundamental peak decompose to the binary compound (Ag_2O and CuO) which appeared at the same position (38.18°) and with a small shift to higher 2θ when compared with the former peak. On the other hand the heat treatment at 200°C improve the structure and many peaks appeared. There are three peaks for tetragonal phase of $Ag_2Cu_2O_3$ at 2θ equal to 43.32°, 64.48° and 81.62°. Also there are two peaks related to diffraction from (200) and (111) planes of Ag and Cu respectively as shown in Table 5. The position of the diffraction peaks of the annealing film shifted towards higher angle side.

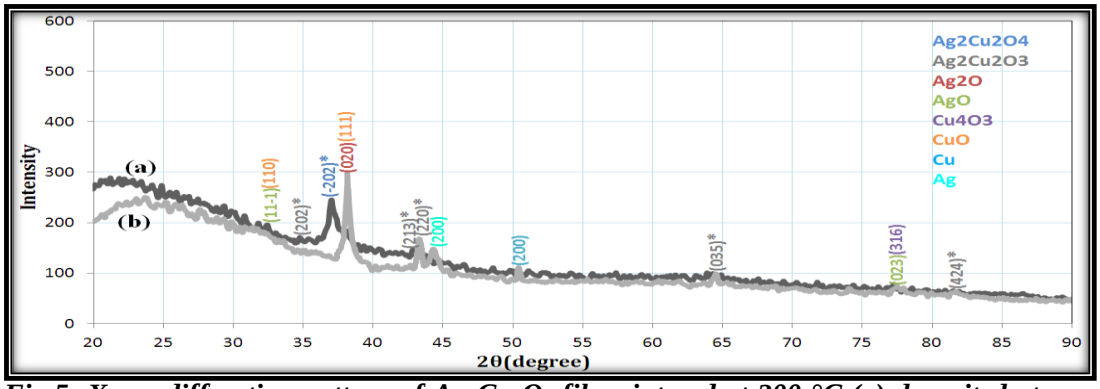


Fig.5: X-ray diffraction pattern of $Ag_2Cu_2O_4$ film sintered at 200 °C (a) deposited at room temperature (b) annealing at 200°C for half an hour.

Table 4: Structural parameters viz. inter-planar spacing, crystallite size and Miller indices of $Ag_2Cu_2O_4$ films sintered at 200 °C and deposited at room temperature.

compounds	2θ (Deg.)	d_{hkl} Exp.(Å)	d_{hkl} Std.	hkl	FWHM (Deg.)	G.S (nm)	phase	card No.
$Ag_2Cu_2O_4$	37.15	2.4182	2.4125	-202	0.612	13.7	monoclinic	--------
$Ag_2Cu_2O_3$	35.8	2.5062	2.5781	202	0.52	16.1	tetragonal	96-431-9055
	43.021	2.1008	2.1172	213	0.4	21.3		
Ag_2O	38.360	2.3446	2.3590	020	0.471	17.9	Cubic	96-101-0487
AgO	32.4	2.7610	2.7669	11-1	0.52	15.9	monoclinic	96-900-8963
CuO	32.4	2.7610	2.7531	110	0.52	15.9	monoclinic	96-410-5683
	38.360	2.3446	2.3395	111	0.471	17.9		

Table 5: Structural parameters viz. inter-planar spacing, crystallite size and Miller indices of $Ag_2Cu_2O_4$ films sintered at 200 °C and annealing at 200 °C for half an hour.

compounds	2θ (Deg.)	d_{hkl} Exp.(Å)	d_{hkl} Std.	hkl	FWHM (Deg.)	G.S (nm)	phase	card No.
$Ag_2Cu_2O_3$	43.320	2.0869	2.0811	220	0.494	17.3	tetragonal	96-431-9055
	64.480	1.4439	1.4455	035	0.565	16.6		
	81.62	1.1786	1.1807	424	0.714	14.7		
Ag_2O	38.180	2.3553	2.3590	020	0.565	14.9	Cubic	96-101-0487
AgO	77.43	1.2316	1.2324	023	0.738	13.8	monoclinic	96-900-8963
Cu_4O_3	77.43	1.2316	1.2324	316	0.738	13.8	tetragonal	96-900-0604
CuO	38.180	2.3553	2.3395	111	0.565	14.9	monoclinic	96-410-5683
Ag	44.340	2.0413	2.0430	200	0.729	11.8	Cubic	96-901-3046
Cu	50.440	1.8078	1.8085	200	0.494	17.8	Cubic	96-710-1265

The X-Ray diffraction pattern of $Ag_2Cu_2O_4$ films (a) deposited at room temperature (b) annealing at 200°C for half an hour for sintered at 300°C are shown in Fig. 6. The $Ag_2Cu_2O_4$ film deposited at room temperature has an amorphous structure. The structure improve with heat treatment where a diffraction peak appeared at 2θ= 37.16° for $Ag_2Cu_2O_4$ phase at surface reflection ($\bar{2}02$) of annealing film. Two small peaks related to $Ag_2Cu_2O_3$ phase were appeared as shown in Table 6.

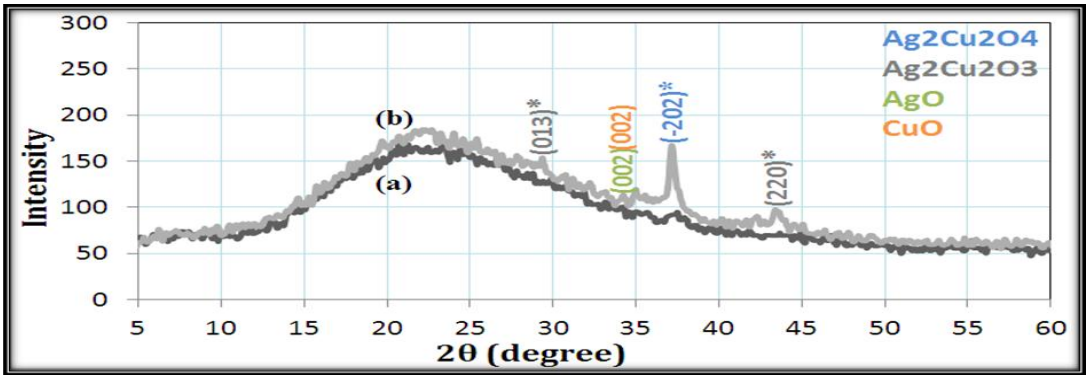


Fig.6: X-ray diffraction pattern of $Ag_2Cu_2O_4$ film sintered at 300 °C (a) deposited at room temperature (b) annealing at 200°C for half an hour.

Table 6: Structural parameters viz. inter-planar spacing, crystallite size and Miller indices of $Ag_2Cu_2O_4$ films sintered at 300°C and annealing at 200°C for half an hour.

compounds	2θ (Deg.)	d_{hkl} Exp.(Å)	d_{hkl} Std.	hkl	FWHM (Deg.)	G.S (nm)	phase	card No.
$Ag_2Cu_2O_4$	37.16	2.4175	2.4125	$\bar{2}02$	0.871	9.6	monoclinic	------
$Ag_2Cu_2O_3$	29.27	3.0488	3.0481	013	0.871	9.4	tetragonal	96-431-9055
	43.41	2.0829	2.0811	220	0.871	9.8		
AgO	34.03	2.6324	2.6203	002	0.822	10.1	monoclinic	96-900-8963
CuO	34.03	2.6324	2.5641	002	0.822	10.1	monoclinic	96-410-5683

Fig.7 shows the X-ray diffraction pattern of $Ag_2Cu_2O_4$ films (a) deposited at room temperature (b) annealing at 200°C for half an hour sintered at 600°C. The film deposited at room temperature has an amorphous structure. The film which annealed at 200°C have a small peak at 2θ=38.16° which related to binary compounds (Ag_2O and CuO). Also very small two peaks appeared at 34.28° and 36.56° which represent AgO and Cu_2O phase respectively as shown in Table 7. The presence of Cu element was due to decompose the ternary and binary compounds at 600 °C, this means the ratio of oxygen un sufficient and there is no pumping O_2 gas during sintering operation and absence the diffraction peaks related to $Ag_2Cu_2O_4$.

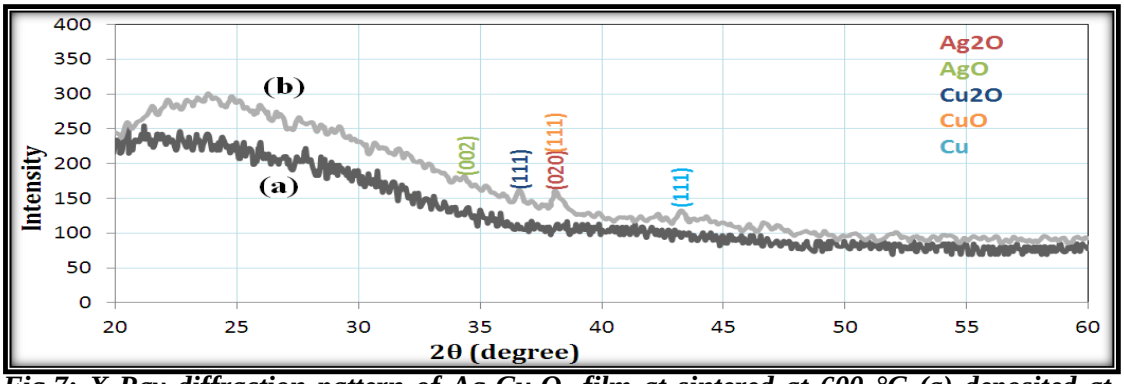
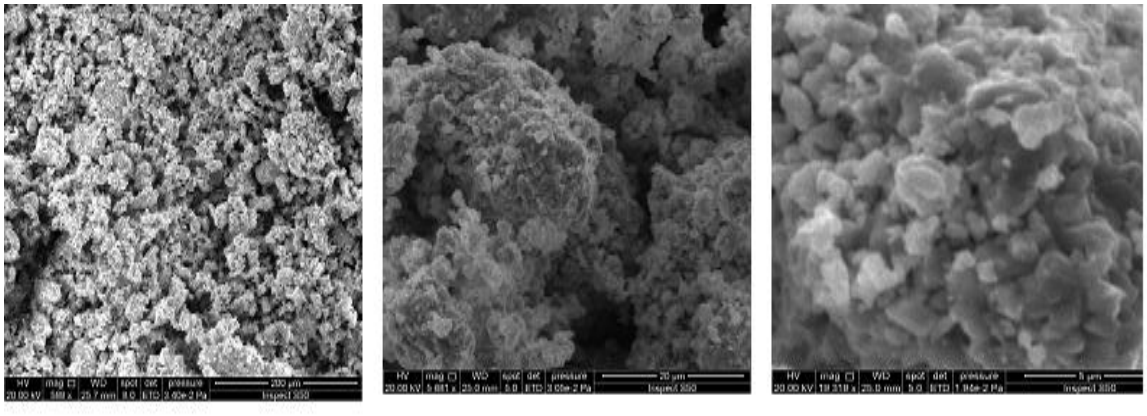


Fig.7: X-Ray diffraction pattern of $Ag_2Cu_2O_4$ film at sintered at 600 °C (a) deposited at room temperature (b) annealing at 200 °C for half an hour.

Table 7: Structural parameters viz. inter-planar spacing, crystallite size and miller indices of $Ag_2Cu_2O_4$ films sintered at 600 °C and annealing at 200 °C for half an hour.

compounds	2θ (Deg.)	d_{hkl} Exp.(Å)	d_{hkl} Std.	hkl	FWHM (Deg.)	G.S (nm)	phase	card No.
Ag_2O	38.160	2.3576	2.3590	020	0.518	16.2	Cubic	96-101-0487
AgO	34.280	2.6137	2.6203	002	0.588	14.1	monoclinic	96-900-8963
Cu_2O	36.56	2.4558	2.4549	111	0.679	12.3	Cubic	96-100-0064
CuO	38.160	2.3576	2.3395	111	0.518	16.2	monoclinic	96-410-5683
Cu	43.260	2.0897	2.0883	111	0.447	19.1	Cubic	96-701-1265

The surface morphological results of prepared powder were studied by SEM images. Fig.8 shows the microstructure with different magnification (588x, 5681x, 19319x) of $Ag_2Cu_2O_4$ powder which sintered at 200 °C observed by SEM analysis. It is obvious there is agglomerate of oxide particles with platelets shape, and the agglomerate of particles is bigger than the $Ag_2Cu_2O_3$ one.



(a) **(b)** **(c)**

Fig.8: SEM photograph of $Ag_2Cu_2O_4$ sintered at 200°C with magnification (a) 588x, (b) 5681x and (c) 19319x.

Atomic force microscopy (AFM) is a useful technique for determining surface topography and regarded the most effective ways due to its high resolution and powerful analysis. The three dimensional AFM images and histogram of $Ag_2Cu_2O_4$ thin film prepared by pulsed laser deposition (PLD) is shown in Fig.9. These images revealed that the film has uniform, homogeneous and tightly adherent, having spherical grains without any voids or cracks. The root mean square roughness (RMS) was decrease with increasing of sintering temperature as shown in Table 8, this means that the average roughness decreased with increase of sintering temperature. The films exhibited differing morphology of surface grains depending on the sintering temperature. The grain size is 95.44 nm, 92.44 nm and 97.85 nm at different sintering temperature 200 °C, 300 °C and 600 °C respectively. The films showed larger grain size of 97.85 nm for film at 600 ^{o}C. This may be due to the coexistence of silver oxide and silver phases or the presence of silver clusters due to low oxygen ratio.

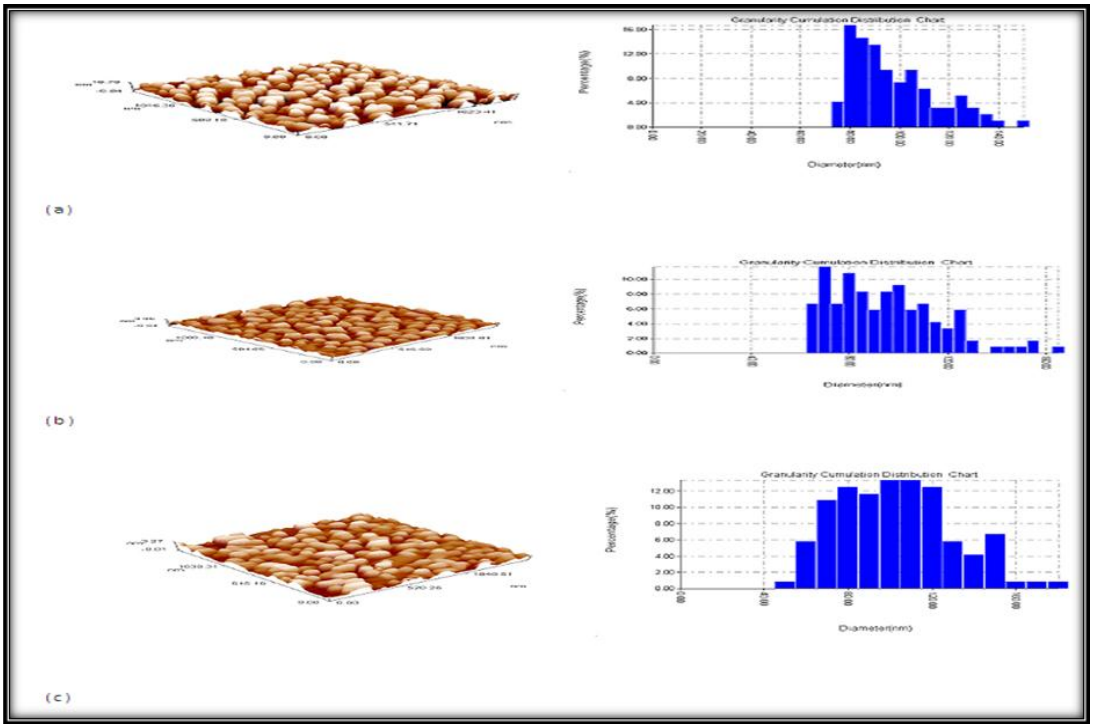


Fig.9: AFM image and histogram for $Ag_2Cu_2O_4$ films deposited at room temperature sintered at (a) 200 °C (b) 300 °C and (c) 600 °C.

Table 8: Average grain size, average roughness , and root mean square for Ag-Cu-O films sintered at (200 °C, 300 °C and 600 °C) respectively.

Thin films	Sintering Temp.(°C)	Root mean square(nm)	Grain size(nm)	Roughness average(nm)
$Ag_2Cu_2O_4$	200	3.01	95.44	3.43
	300	0.59	92.44	0.702
	600	0.54	97.85	0.631

The aim of studying the optical properties is to determine the energy gap and optical constants (extinction coefficient (k), refractive index (n), real and imaginary dielectric constants). The optical properties have been studied for as deposited and annealed $Ag_2Cu_2O_4$ films at 200 °C for half hour which sintered at different temperatures (200, 300 and 600) °C, using UV-visible absorbance spectrum in the region of (300–1100) nm. The optical properties is involve the optical energy gap (E_g) and optical constants.

Fig.10 (a and b) shows the optical transmittance spectra as function of wavelength for $Ag_2Cu_2O_4$ films sintered at different temperatures (200, 300 and 600) °C which deposited at room temperature and annealed at 200 °C for half an hour respectively. In general it is clear that the transmittance increases with increasing the sintering temperature.

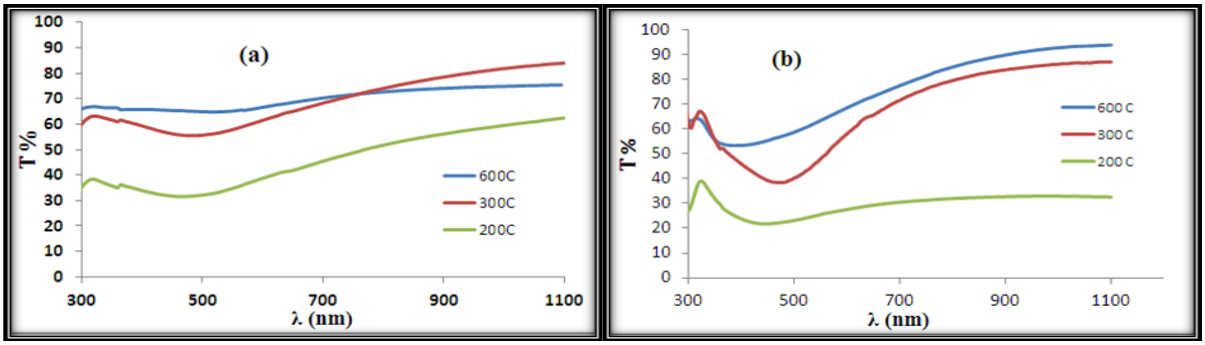


Fig.10: Optical transmittance versus wavelength of $Ag_2Cu_2O_4$ thin films sintered at different temperature (a) as deposited (b) annealed at 200°C for half an hour.

The optical absorption coefficient (α) was calculated from the optical transmittance (T) data using the relation [10]:

$$\alpha = (1/t) \ln T \quad (1)$$

where t is the film thickness. Fig.11 (a and b) shows the optical absorption coefficient (α) as a function of wavelength sintered at different temperature (200, 300 and 600 °C) for as deposited and annealed $Ag_2Cu_2O_4$ films at 200 °C for half an hour. In general the optical absorption coefficient of $Ag_2Cu_2O_4$ films decreases with increasing the sintering temperature. The highest peak absorption was at wavelength range of (410-610) nm. The optical absorption edge of the films deposited at room temperature shifted towards higher wavelength side with increasing sintering temperature. On the other hand the absorption edge of annealed films shifted towards lower wavelength with increasing sintering temperature.

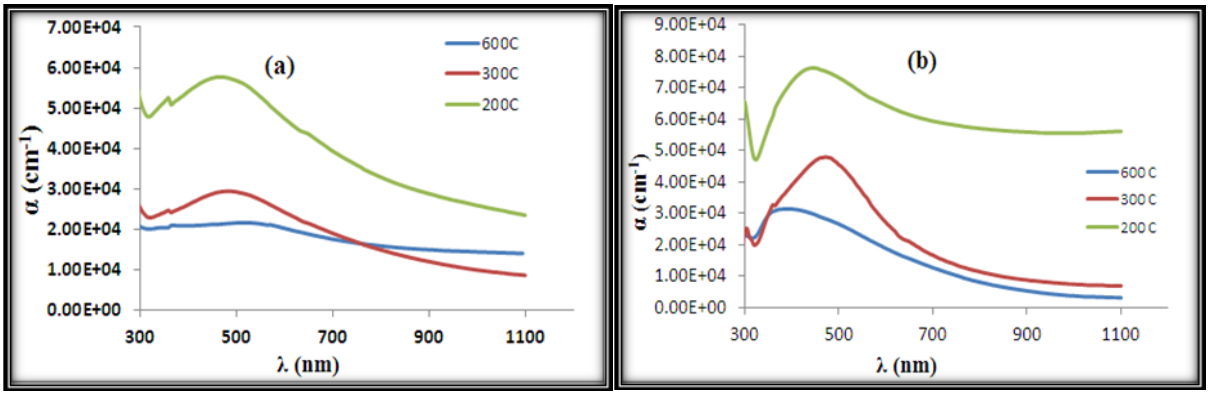


Fig.11: Absorption coefficient versus wavelength of $Ag_2Cu_2O_4$ thin films sintered at different temperature (a) as deposited (b) annealed at 200 °C for half an hour.

The optical direct band gap (E_g) of $Ag_2Cu_2O_4$ films has been determined from the plot of $(\alpha h\upsilon)^2$ versus photon energy ($h\upsilon$) using Tauc's relation [10]:

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

where B is a constant inversely proportional to amorphousity. Extrapolation of the linear portion of the plots of $(\alpha h\upsilon)^2$ versus photon energy to $\alpha = 0$ yields the optical band gap of the $Ag_2Cu_2O_4$ films. Fig.12 (a and b) show the plot of $(\alpha h\upsilon)^2$ versus photon energy ($h\upsilon$) of as deposited and annealed $Ag_2Cu_2O_4$ films formed at different sintering temperature respectively. The optical band gap of $Ag_2Cu_2O_4$ films deposited at room

temperature increase from 1.6 to 1.65 eV with increasing sintering temperature from 200 to 300 °C, and decrease to 1.45 eV at 600 °C. It is clear from Fig. 12 (b) that the energy gap increases when the films annealed at 200 °C for half an hour.

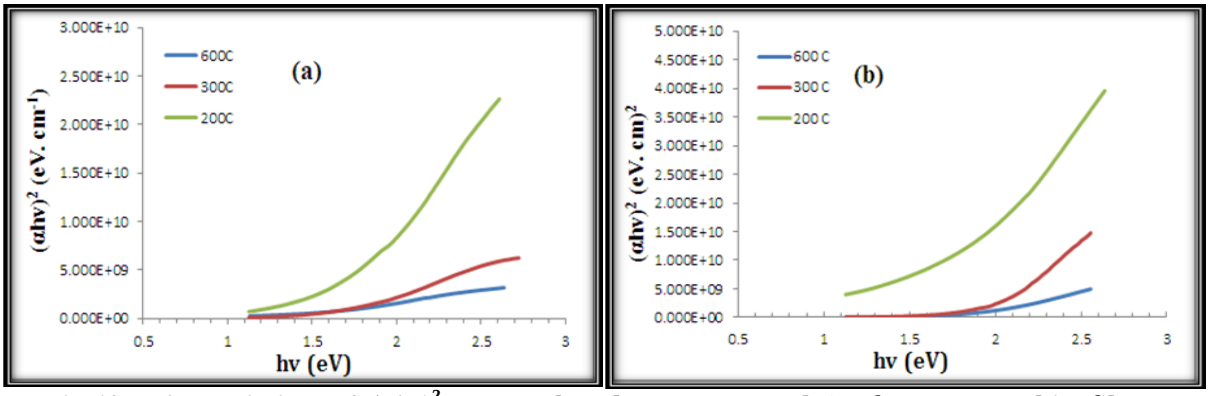


Fig.12: The variation of $(\alpha hv)^2$ versus the photon energy (hv) of $Ag_2Cu_2O_4$ thin films sintered at different temperature (a) as deposited (b) annealed at 200 °C for half an hour.

Fig. 13 (a and b) show the variation of refractive index(n) with wavelength(λ) of as deposited and annealed $Ag_2Cu_2O_4$ thin films sintered at different temperature (200, 300, 600) °C respectively. In general it clear that the refractive index decreases with increasing the sintering temperature. The higher value of refractive Index(n) was at sintering temperature 200°C of the film deposited at room temperature and the annealing film at 200 °C.

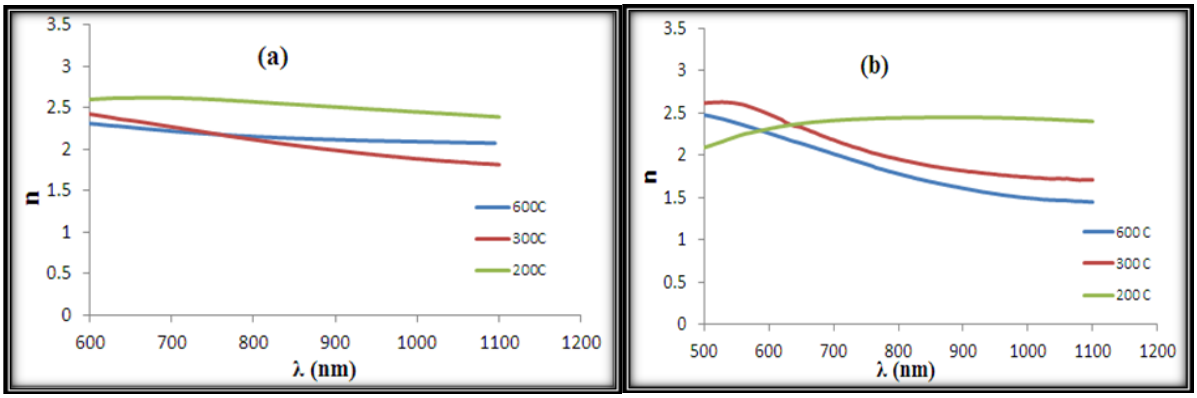


Fig.13: The variation of refractive index (n) with wavelength (λ) of $Ag_2Cu_2O_4$ thin films sintered at different temperature (a) as deposited (b) annealed at 200°C for half an hour.

Fig.14 (a and b) shows the variation of extinction coefficient (k) with wavelength (λ) of as deposited and annealed $Ag_2Cu_2O_4$ thin films sintered at different temperature (200, 300, 600) °C respectively. It is obvious that the extinction coefficient takes the similar behavior of the corresponding absorption coefficient. The extinction coefficient (k) at wavelength 1000 nm of the $Ag_2Cu_2O_4$ films deposited at room temperature decrease from 0.206 to 0.115 with increasing sintering temperature from 200 °C to 600 °C respectively. The extinction coefficient (k) has the best value in the visible region.

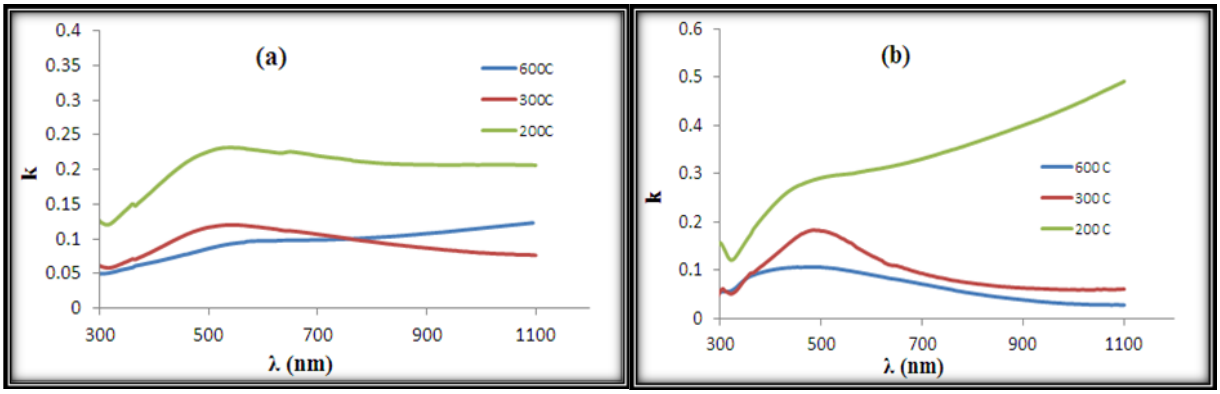


Fig.14: The variation of extinction coefficient (k) with wavelength (λ) of $Ag_2Cu_2O_4$ thin films sintered at different temperature (a) as deposited (b) annealed at 200 °C for half an hour.

The complex dielectric constant is a fundamental material property, the real part of it is associated with term of how much it will slow down the speed of light in the material and the imaginary part gives that how a dielectric absorb energy from electric field due to polarization in it. The behavior of ε_r similar to refractive index because the smaller value of k^2 comparison of n^2, while ε_i is mainly depends on the k values, which are related to the variation of absorption coefficient.

The optical properties parameters including, energy gap, absorption coefficient, refractive index, extinction coefficient, real and imaginary part of the dielectric constant at wavelength equals to 1000 nm for as deposited and annealed $Ag_2Cu_2O_4$ films are listed in Table 9.

Table 9: The optical properties for $Ag_2Cu_2O_4$ thin film at wavelength (λ=1000nm).

Thin film	Sintering Temp.(°C)	E_g(eV)	$\alpha \times 10^4 (cm)^{-1}$	k	n	ε_r	ε_i
As deposited	200	1.6	2.60	0.206	2.450	5.959	1.013
	300	1.65	1.0	0.079	1.883	3.542	0.3
	600	1.45	1.45	0.115	2.09	4.357	0.482
annealed at 200°C	200	1.64	5.56	0.442	2.437	5.743	2.155
	300	1.92	7.48	0.059	1.744	3.039	0.207
	600	1.95	3.77	0.029	1.497	2.241	0.089

The type of charge carriers, concentration (n_H) and Hall mobility (μ_H), have been estimated from Hall measurements. Table 10 illustrates the main parameters estimated from Hall Effect measurements for $Ag_2Cu_2O_4$ thin films sintered at different temperature deposited at room temperatures and annealed at 200°C for half an hour. It is clear from this table, all films have a positive Hall coefficient (p-type) this result is in agreement with P. Narayana Reddy et al. [4].

In general the $Ag_2Cu_2O_4$ films which deposited at room temperature showed that the carrier concentration (n_H) increase with increasing sintering temperature. The mobility of carriers take the opposite behavior, where it decrease with increasing the temperature of sintering as shown in Table 10. The carrier concentration and the mobility decrease with increasing sintering temperature for $Ag_2Cu_2O_4$ films annealing at 200 °C for half an hour as shown in the Table 10.

Table 10: Hall Effect measurements for $Ag_2Cu_2O_4$ film deposited at room temperature and annealing at 200 °C for half an hour with different sintering temperature.

Thin films	Sintering temp.(°C)	σ (1/Ω cm)	n(cm^{-3})	μ(cm^2/V.sec)	Type
as deposited	200	7.115×10^{-6}	3.007×10^{10}	1.477×10^{3}	p-type
	300	8.214×10^{-6}	5.871×10^{11}	8.733×10^{1}	
	600	1.777×10^{-7}	7.988×10^{11}	1.388	
annealed at 200 °C	200	2.640×10^{-4}	7.007×10^{11}	2.352×10^{3}	p-type
	300	3.940×10^{-5}	3.515×10^{11}	6.997×10^{2}	
	600	5.906×10^{-6}	2.649×10^{11}	1.392×10^{2}	

Conclusions

Pulsed laser deposition technique was employed for deposition of Ag-Cu-O films on glass substrates using $Ag_2Cu_2O_4$ powder formed by solid state reaction at different sintering temperatures. The effect of sintering and annealing temperature on the crystallographic structure and surface morphology, optical and electrical properties was investigated. X-ray diffraction studies of the powder showed polycrystalline structure with mixed many phases. The films have low intensity peak of $Ag_2Cu_2O_4$ phase and the structure was improved with annealing for sintering temperature equal to 200 °C and 300 °C, while the film sintered at 600°C has amorphous structure.

AFM analysis showed the larger grain size (97.85 nm) obtained for film sintered at 600 °C. The optical band gap increase from 1.6 eV to 1.65 eV with increasing the sintering temperature to 300°C and decrease to 1.45 eV when temperature of sintering equal to 600 °C. The heat treatment of these films make the band gap wider. The electrical resistivity of these films increase with increasing the sintering temperature for as deposited and annealed.

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