The impact temperature of substrate on the basic and optical properties of CuO slender movies acquired by shower pyrolysis technique

تأثيردرجة حرارة الاساس على الخواص التركيبيه والبصريه لغشاء رقيق أوكسيد النحاس المرسب بطريقة رش الانحلال الحراري

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Abstract
In this research the structural and optical Properties of copper oxides, Cu_2O and CuO semiconductor films had been concentrated on, which arranged with 300 nm thickness by spray pyrolysis method at 200, 250 and 300°C substrate temperatures on glass substrates from 0.2M ($CuCl_2$•$2H_2O$) broke down in refined water. The phase existed were studied by the X-ray diffraction analysis and their effect on the optical properties.
Keywords: CuO, Cu_2O spray pyrolysis, optical properties, substrate temperature.

الخلاصه :
تمت دراسة الخواص التركيبيه والبصريه لمركب شبه الموصل كبريتيد النحاس وكبريتات النحاس (cu₂o, cuo) المرسب على الزجاج غشاء رقيق بسمك nm 300 بطريقة رش الانحلال الحراري لدرجات حرار للاساس C°(200و 250 300) الاطوار الـ تي وجدت من خلال حيود الاشعه السينيه وكذلك تأثير درجات الحراره الاساس على الخواص البصريه للغشاء

Introduction
Copper has two known oxides, cuprite (Cu_2O) and tenorite (CuO) [1]. The two oxides can coexist with copper, annealing Cu_2O films in air at 300°C converts it to CuO [2]. Cupric oxide (CuO) is a p-sort semiconductor having a band crevice of 1.21–1.51 eV and monoclinic gem structure [3].Cuprous oxide (Cu2O) is likewise a p-sort semiconductor having a band hole of around 2.0 eV and a cubic precious stone structure [3]. Its high optical ingestion coefficient in the obvious reach and sensibly great electrical properties constitute imperative favorable circumstances and render Cu2O as the most fascinating period of copper oxides [4]. CuO is alluring as a specific sunlight based safeguard since it has high sun oriented permeableness and a low warm emittance [5]. What's more, its reasonable optical Properties with a dark shading and a fractional straightforwardness in the obvious extent [6].

Various techniques have been used to synthesize Cu_2O and CuO films such as: thermal oxidation [7]; electrodeposition [8]; spraying [9]; chemical vapor deposition [10]; plasma evaporation [11]; reactive sputtering [12]; and molecular beam epitaxy [13]. The simplest one is the spray pyrolysis method with excellent features such as the need for no sophisticated equipment, and quality targets or substrates; also, film thickness and stoichiometry are easy to control and the resulting films are well compacted. We have used this coating method to prepare of Cu2O and CuO thin films.

Experimental procedure
Copper oxide movies have been delivered by splashing fluid arrangement of 0.2M of CuCl2.2H2O onto glass substrates (1x25x75mm3) at 200, 250 and300°C substrate temperature. The substrate

temperature was kept up to inside ±5oC. 50 ml refined water was utilized for setting up the arrangements. The used $CuCl_2.2H_2O$ mass was figured utilizing the accompanying condition:
*WEIGHT (G) =MOLARITY (MOL/L) *VOLUME (L)*MOLECULAR WEIGHT (G/MOL)… … …1*
Prior to deposition, the substrates were cleaned with cleaner solution, distilled water and followed by alcohol using ultrasonic bath.
The schematic plan of shower pyrolysis set-up is appeared in Fig. (1). Shower pyrolysis is essentially a concoction procedure, that is the splashing of the arrangement onto a substrate held at high temperature, where the arrangement responds framing the coveted film.

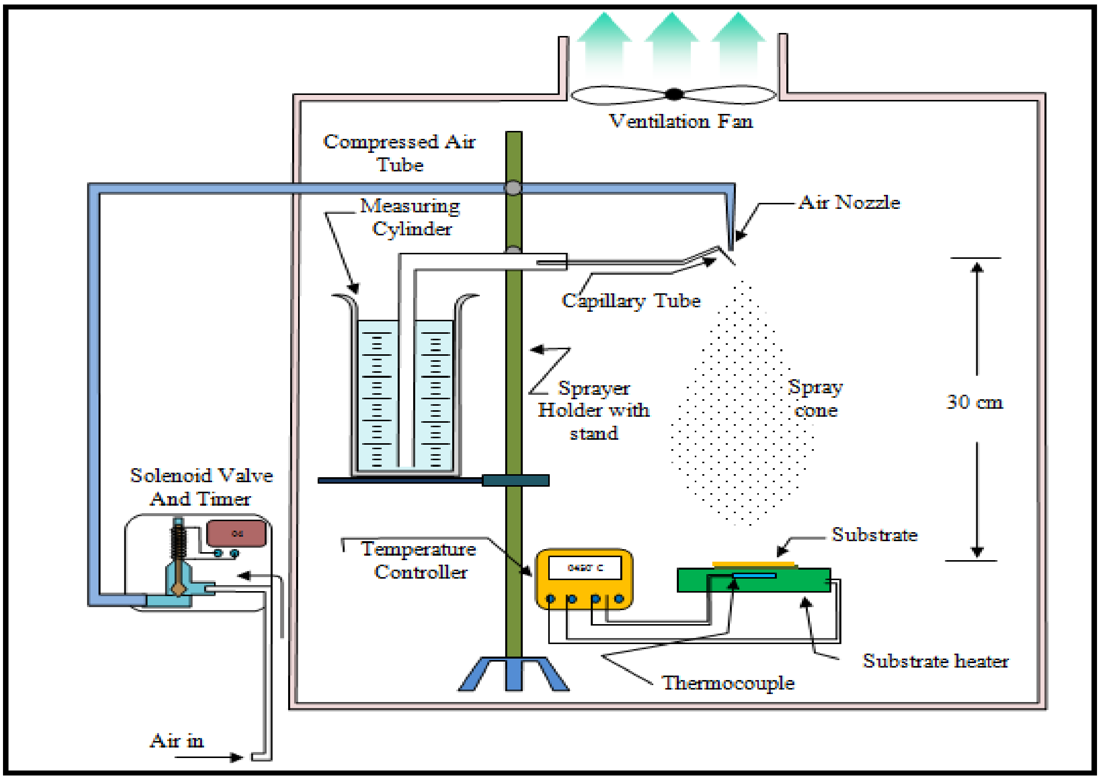


Figure (1) Schematic of the spray pyrolysis system.

The spray rate of the solution was adjusted to be five sprinkling in minute, the sprinkling time about ten second. The standardized separation between the shower spout and the substrate is 30cm. Compressed air was utilized as the bearer gas. The temperature of the substrate was controlled by an Iron-Constantan thermocouple. The thickness of the films (t) was resolved utilizing the measuring technique and by Michelson interferometer. X-beam diffraction (XRD) pattern of the deposited films on corning glass substrate were examined by SHIMADZU XRD-6000 X-beam diffract meter ($Cu_{k\alpha}$ radiation λ=0.154nm) in 2θ range from 20° to 60°. The interplaner distanced d_{hkl} for different planes is measured using Bragg law [15]

$$2d \sin\theta = m\lambda \qquad \ldots\ldots 1$$

while The average crystallite size estimated by Scherrer's formula [16]:

$$b = \frac{0.89\,\lambda}{\Delta(2\theta).\cos(\theta)} \qquad \ldots\ldots 2$$

Optical transmittance ranges were recorded, at room temperature, in the wavelength range 300-1100nm utilizing OPTIMA SP-3000 UV-VIS spectrophotometer. The absorption coefficient (α) of copper oxides thin films were calculated from the optical transmittance spectrum measurements using the formula [17]:

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

where t is the thickness of meager films , and T is the transmittance force. The vitality crevices were computed as a component of various Ts (temperature substrate).

Results and Discussion

It can be observed the change in films color from brown to black in appearance when increasing the substrate temperature from 473 to 573 K.

Fig. (2) Shows XRD for 300 nm thin film deposited on glass from 0.2 M $CuCl_2{:}2H_2O$. At 473 K T_s three peaks can be seen for (Cu_2O) phase located at 2θ=36.64^o , 42.49^o and 52.67^o with hkl (111), (020) and (121) respectively, While at 523 K the two oxides Cu_2O and CuO peaks were existed where two peaks new appeared 35.52 ^{o} and 38.73^o idicates the CuO phase existance with hkl (11-1) and (111). When the T_s increase to 573 K only CuO phase peaks were exist located at 32.41, 35.52, 38.72, 48.75, 53.48 and 58.37 with hkl (110), (11-1), (111), (20-2), (020) and (202) respectively.

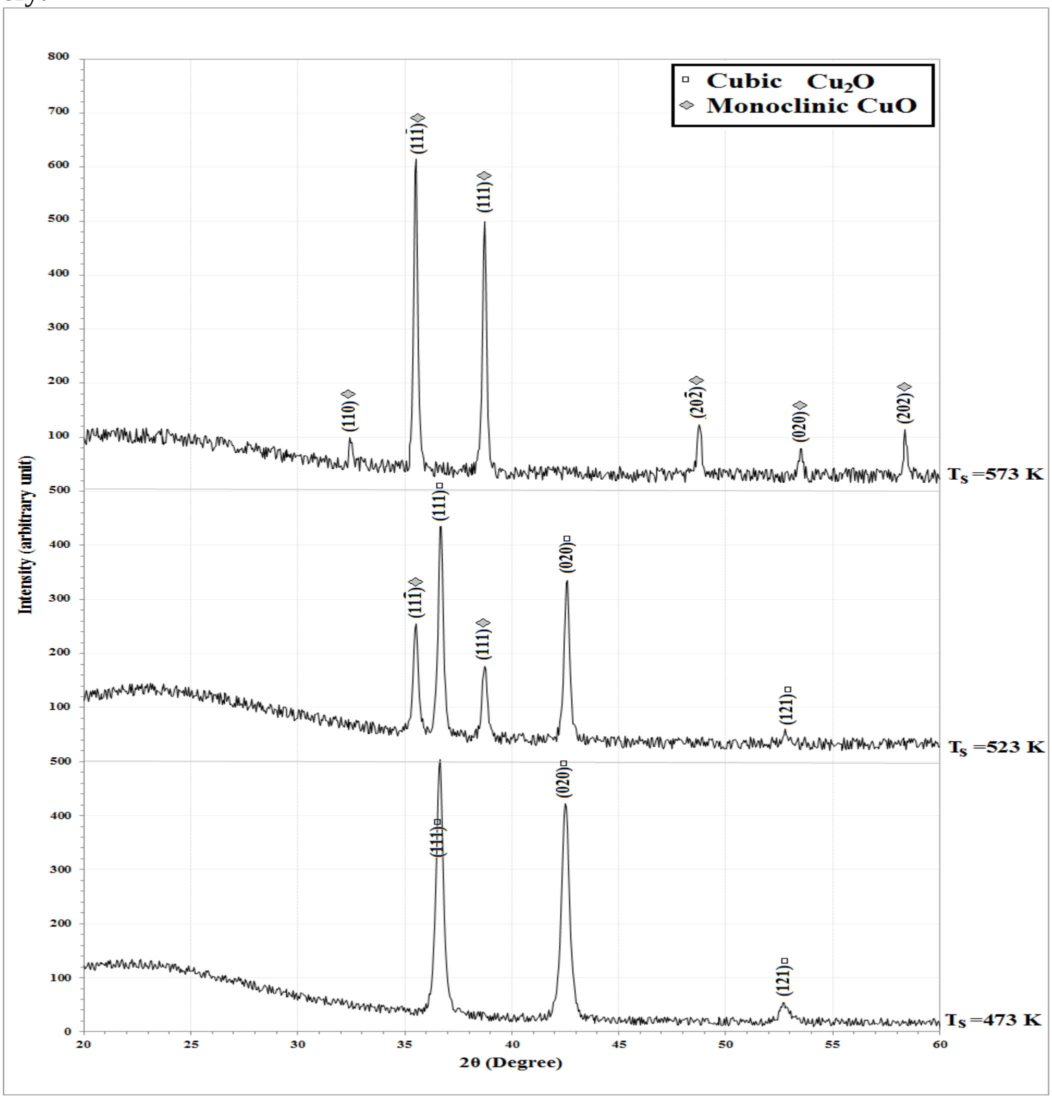


Fig. (1) X-beam diffraction designs for copper oxide movies with various Ts

Table (2) shows the experimental peaks, observe at XRD patterns, and the standard peaks from International center for diffraction data (JCPDS) for coper oxides films.

Table (1) Structural parameters: Inter-planar spacing, crystalline size of copper oxide films with different T_s

T_s (K)	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	d_{hkl} Std.	hkl	phase	card No.
473	36.6412	0.4580	2.4506	18.3	2.4584	(111)	Cub. Cu_2O	96-101-0964
	42.4936	0.4580	2.1256	18.6	2.1290	(020)	Cub. Cu_2O	96-101-0964
	52.6718	0.5598	1.7363	15.8	1.7383	(121)	Cub. Cu_2O	96-101-0964
523	35.5216	0.3053	2.5252	27.3	2.5228	(11-1)	Mono.CuO	96-101-1195
	36.6412	0.3053	2.4506	27.4	2.4584	(111)	Cub. Cu_2O	96-101-0964
	38.7277	0.3053	2.3232	27.6	2.3212	(111)	Mono.CuO	96-101-1195
	42.5954	0.3562	2.1208	23.9	2.1290	(020)	Cub. Cu_2O	96-101-0964
	52.7735	0.3053	1.7332	29.0	1.7383	(121)	Cub. Cu_2O	96-101-0964
573	32.4173	0.3053	2.7596	27.1	2.7509	(110)	Mono.CuO	96-101-1195
	35.5216	0.2545	2.5252	32.8	2.5228	(11-1)	Mono.CuO	96-101-1195
	38.7277	0.3053	2.3232	27.6	2.3212	(111)	Mono.CuO	96-101-1195
	48.7532	0.3053	1.8663	28.6	1.8617	(20-2)	Mono.CuO	96-101-1195
	53.4860	0.3562	1.7118	25.0	1.7150	(020)	Mono.CuO	96-101-1195
	58.3715	0.2545	1.5796	35.8	1.5764	(202)	Mono.CuO	96-101-1195

Optical study of copper oxide movies is completed in the wavelength range 200–900 nm at room temperature for the film kept on glass substrate.

Figures (9) demonstrate the room-temperature transmission spectra of three examples at various substrate temperature (473, 523 and 573) K

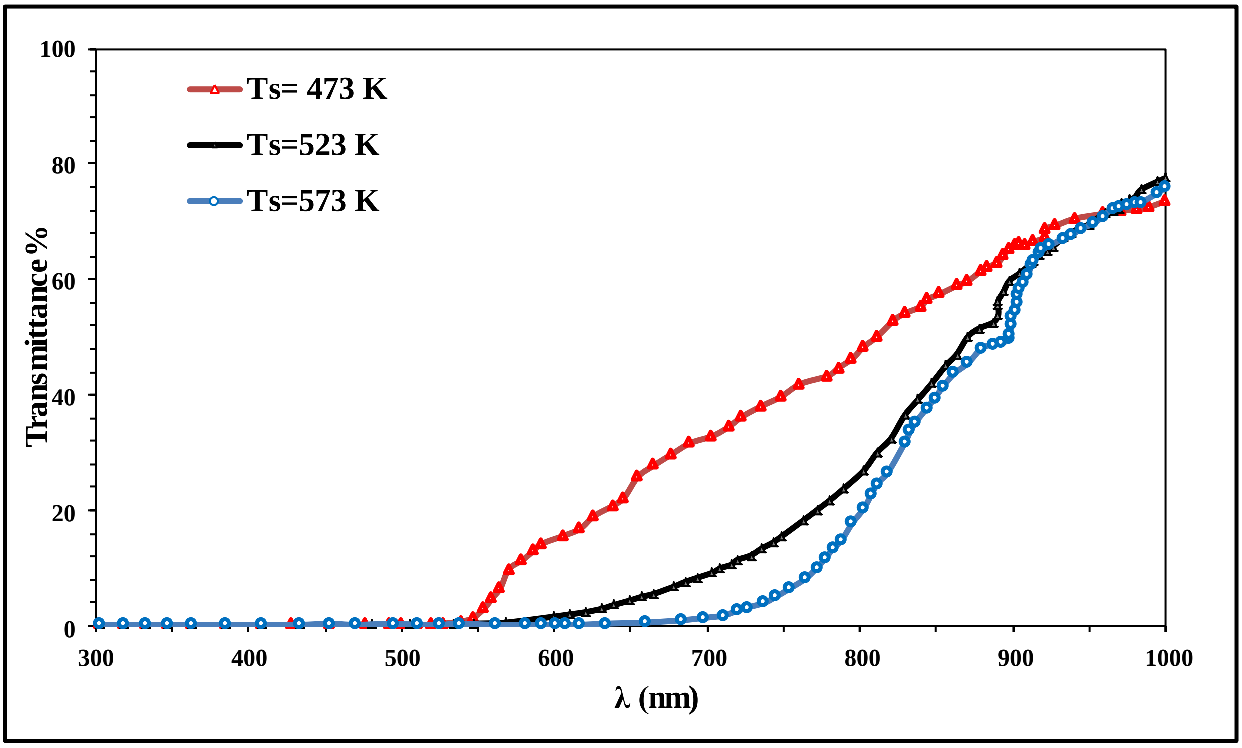


Fig.(2) the transmission variation with the wave length for copper oxide films at different T_s

The optical vitality hole values (Egopt) for copper oxide films have been controlled by utilizing Tauc condition. This is utilized to discover the kind of the optical move by plotting the relations (αhυ)1/2,(αhυ)1/3,(αhυ)2/3,and (αhυ)2 versus photon vitality (hυ).This condition additionally chooses the ideal direct part. It is found that the connection for r=1/2 yields straight reliance, which depicts the permitted direct move. Egopt is then controlled by the extrapolation of the bit at (α =0 as appeared in Figure 3).

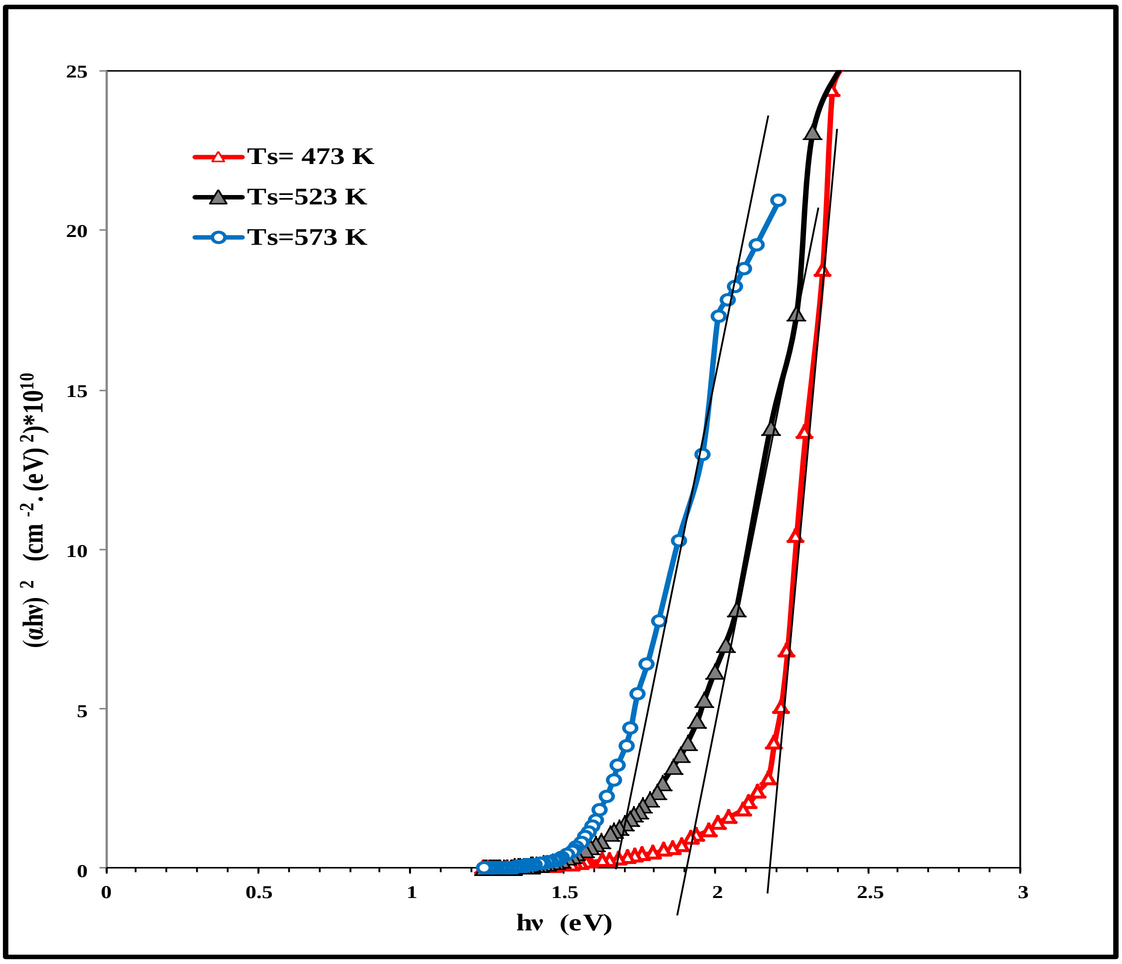


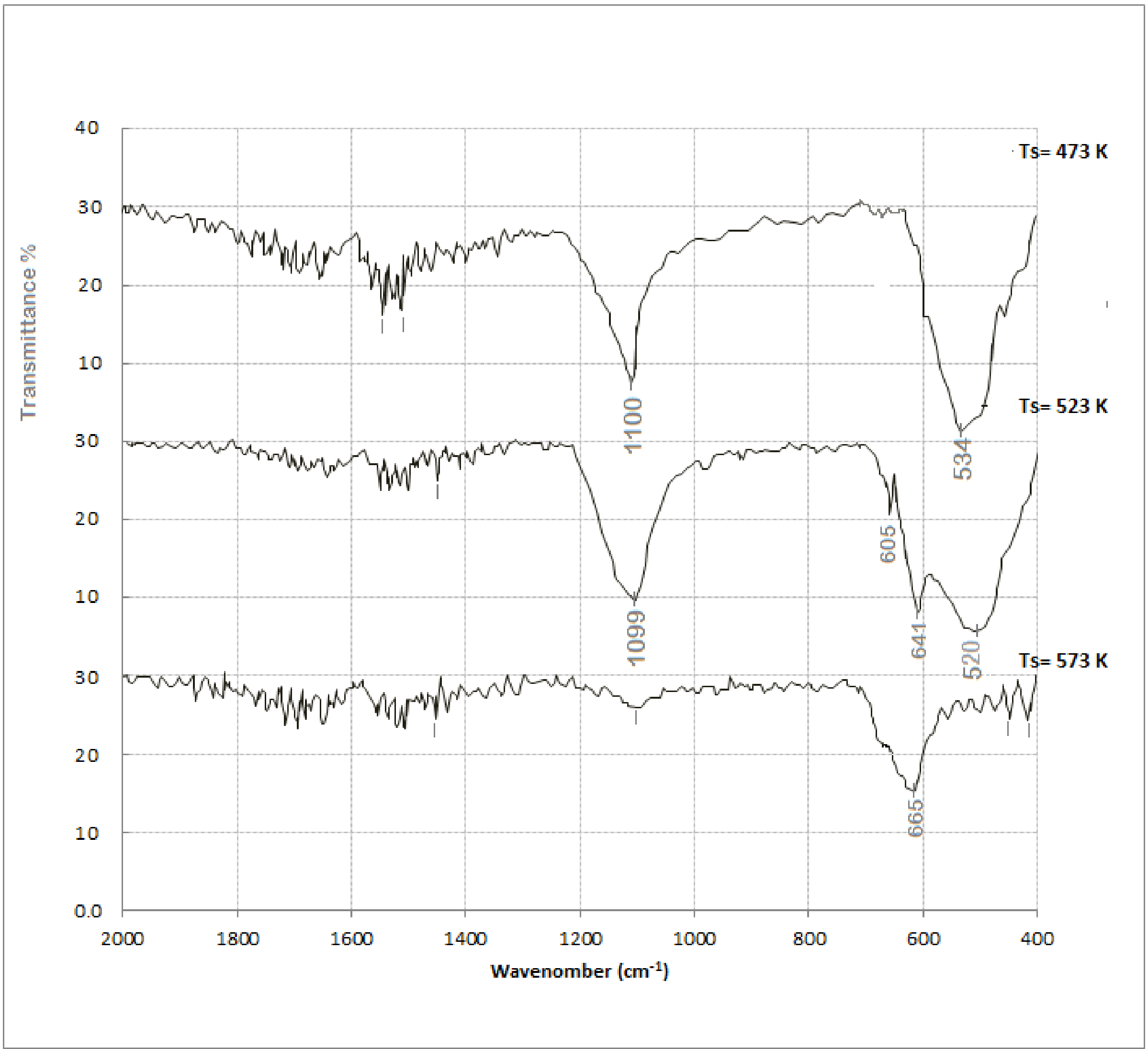
Fig. (3) The variation of $(\alpha h\upsilon)^2$ versus photon energy (hυ) for copper oxide films at different T_s

When T_s increase the band gap is shifted to lower energies due to change in the composition from Cu_2O to CuO. The films deposited at 473K show a band gap of 2.20 eV which identical with Cu_2O energy gap, while when increasing the T_s to 523K leads to decrease the energy gap to 1.7 eV which identical with CuO. This is in agreement with the XRD results given in Fig. (1). The lower band gap of the oxide films deposited at 573K may indicate better oxidation. The different in the calculated and reported energy gap values may be attributed to physical properties of the films, which are subsequently affected by the deposition conditions [18].

Table (2) Optical band gap (Eg) values for copper oxide meager films at various substrate temperatures

T_s (K)	Eg (eV)
473	2.20
523	1.90
573	1.70

The FTIR spectra of deposited films shown in Fig.(4). This figure shows that the deposited film at 473 K are described by a solid band with one transmittance least of around 665 cm-1. Balamurugan et al [16] watched the same band credited to the extending of Cu2O and the range likewise affirms the nonattendance of CuO where band is around 530 cm-1.



Fig(4) FTIR spectra of copper oxide dainty film stored at different substrate temperatures

Conclusions

For the film stored at 523K there are two crests at wavenumber of around 605 cm-1 (the phonon range of Cu2O) and 520 cm-1 (the phonon range of CuO). For the movies kept at 523K more extensive crests at around 534 cm-1 are likewise credited to the CuO. It is likewise watched a top at around 1100 cm-1 for substrate temperatures 523 and 573 K created by imperfections and the crests related to Cu2O was vanished. The consequences of FTIR affirmed the stage move from Cu2O to CuO in the wake of expanding Ts from 473 to 573 K.

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