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# INFLUENCE OF ANNEALING TEMPERATURE ON THE STRUCTURAL AND OPTICAL PROPERTIES OF COPPER IODIDE THIN FILMS

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## Abstract

Copper Iodide (CuI) nanoparticles with (250 nm) thickness have been prepared at RT on glass substrate using PLD technique with focused Nd:YAG laser beam at (800 mJ) with a frequency second radiation at (1064 nm) (pulse width 9 ns) repetition frequency (6 Hz), for 500 laser pulses incident on the target surface . The films annealed to different annealing temperatures (423K )and(523K). The structural and surface morphology properties of the deposited CuI thin films were examined by X-ray diffraction analysis (XRD) and Atomic force microscope (AFM). The X-ray diffraction show that structure is a cubic phase with (111) plane preferential orientation direction. AFM was used to examine and measure the morphology and average diameter for CuI thin films respectively. It is observed that the average nanoparticles size increases with increasing of annealing temperature. The optical measurements showed that CuI thin films have direct allowed energy gap transition and the energy gap (Eg) decreases from (3.2eV) to (2.8 eV) with increasing annealing temperatures from RT to (532 K) for all samples.

**Keywords**: Copper Iodide, Optical Properties ,PLD Technique ,Annealing.

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## 1. Introduction

Copper iodide (CuI) is a chemical compound that is shaped like a white crystalline powder nailed,the copper iodide compound is brought from the reaction of potassium iodide with copper sulfate Duo[1]. The wide-gap for the CuI (3.1ev)and the excitation binding energy(62meV) [2]. CuI have three crystalline phases, α and γ phase is cubic structure , βphase is hexagonal structure . [ 3]. The optical transparencies for CuI thin film is a high over 80% in the visible region and high conductivity there is useful in solar cell [4, 5] , light-emitting devices [6] and organic photo cell [7,8]. Pulse laser deposition is technique that allows stoichiometric a physical vapor deposition process and nanoparticles generation for high quality thin film of a huge of composite materials [9]. In pld the laser beam is focused onto the surface of the target by interaction with a high fluency. pulsed laser beam, plasma formation, and then deposited in pulses on a substrate surface in sufficiently energy density high and pulse duration short, according gas dynamic law [10]. PLD involves stages of target heating, melting, evaporation, ionization, re-solidification/re-crystallization and condensation [11,12]. In this research was studied the effect of the change temperature of the structural, Optical and Photoluminescence of CuI thin film prepared by PLD technique on glass substrate.

## Expermintal Part

CuINanopowder with a purity of 99.99% were mixed together using a gate mortar for one hour. It was pressed into pellets with (1cm) diameter and (0.2 cm) thick, using hydraulic piston type (SPECAC), under pressure of 5 tons for 10 minute. The pellets were sintered in air to temperature (773 K) for 1 hours then cooled to room temperature. The glass substrates slides made in china from " AFCO", have dimension (75 × 25 × 1.2 mm) were cleaned in a beaker have distilled water and put rinsed in ultrasonic for 15 minutes. After immersed in alcohol and washing substrates in ultrasonic for 15min to get rid fat and some oxide. PLD technique was used to deposit thin film inside a vacuum chamber 10-3 Torre. Using Nd: YAG focused laser an angle of 45° at 1064 nm, repetition frequency 6 Hz and laser pulse energy 800 mJ. The CuI thin film thickness measured using optical Interferometer technique utilize. The structural morphological and optical properties have been investigated.The prepared films were annealed and according to the value of x using a tube electric furnace at a temperature of (400 ° C) for one hour.

Results and Discussion:

The x-ray diffraction (XRD) patren of CuI thin films deposited at different temperature (RT,423K and 523K) is shown in figure (1). Obviously, these figure exhibits significant sharp diffraction peaks at (1 1 1), 30◦ (020), 42◦(20 2) and 50◦(311) ,52◦ (222), 61◦ (040) ,67◦ (313), 6◦9(402) and 77◦ (242) corresponding to 2Ɵ= 25◦, 30◦ , 42◦, , 50◦,,52◦ , 61◦ , ,67◦ , 6◦9, and 77◦ according to (JCPDS ## 96-901-3912).Also The identification of the crystalline phases leads to the conclusion that the major phase consists of the CuI thin films with cubic structure (Fiche No. 403-413) and have a polycrystalline structure with preferred orientation along (111) direction at 2θ around 25◦ this means that this plane is suitable for crystal growth. It is clear that the annealing temperatures for CuI films has significant influence on the quality of the films. The highest of predominant peak of CuI at 25◦ (1 1 1) was increased after annealing and the FWHM decreased with annealing temperatures .Table(1) shows the values of all parameters that calculated from XRD results.

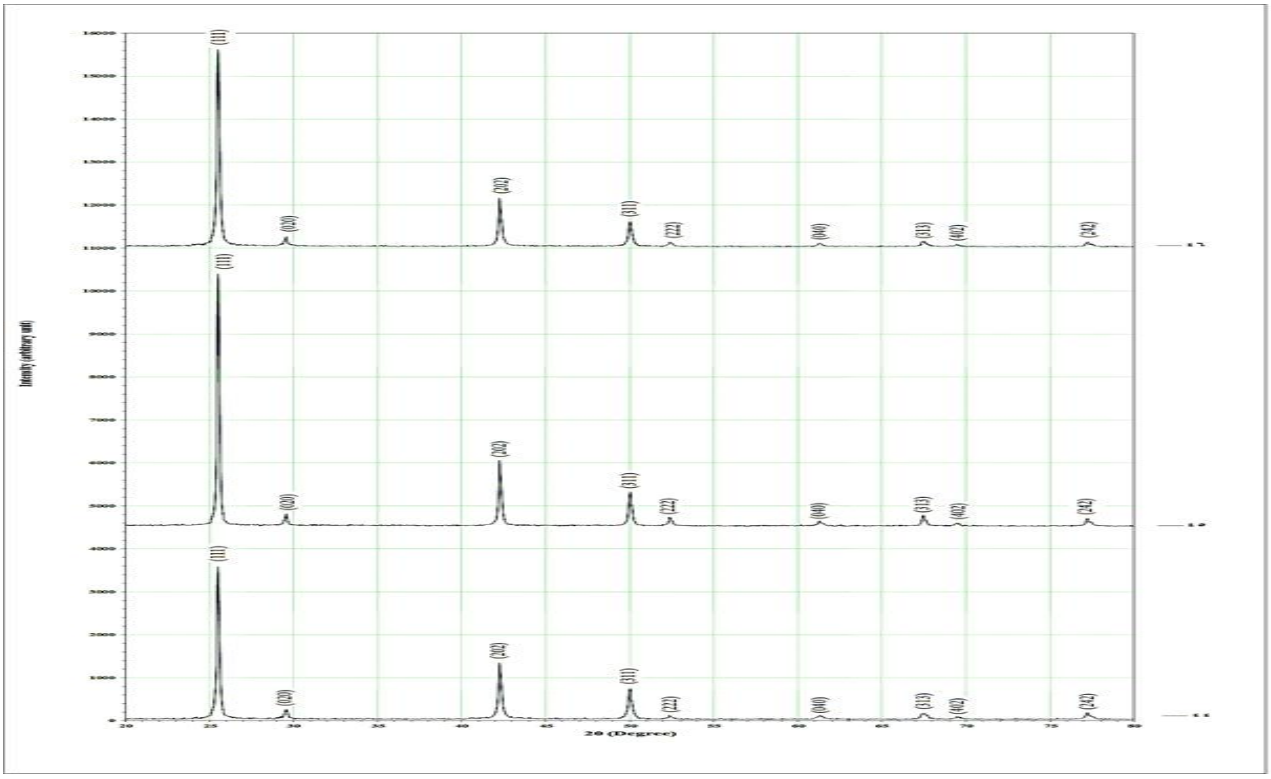



**Figure.(1) The XRD patterns for CuI thinfilms deposited by PLD**

Table(1) the results of XRD indicate grain size the diffraction angle forCuI thin films

| concent. | 2θ (Deg.) | FWHM (Deg.) | Int (Arb. Unit) | $d_{hkl}$ Exp.(Å) | G.S (nm) | $d_{hkl}$ Std.(Å) | hkl | phase | card No. |
|---|---|---|---|---|---|---|---|---|---|
| 44 | 25 | 0.2310 | 1751.0 | 3.5000 | 35 | 3.4956 | (111) | CuI | 96-901-3921 |
| | 30 | 0.2887 | 241.2 | 3.0169 | 28.5 | 3.0273 | (020) | CuI | 96-901-3921 |
| | 42 | 0.2310 | 1307.4 | 2.1381 | 37 | 2.1406 | (202) | CuI | 96-901-3921 |
| | 50 | 0.3465 | 716.0 | 1.8217 | 25.3 | 1.8255 | (311) | CuI | 96-901-3921 |
| | 52 | 0.2887 | 101.2 | 1.7466 | 31 | 1.7478 | (222) | CuI | 96-901-3921 |
| | 61 | 0.5775 | 93.4 | 1.5100 | 16.0 | 1.5136 | (040) | CuI | 96-901-3921 |
| | 67 | 0.5197 | 140.1 | 1.3871 | 18 | 1.389 | (313) | CuI | 96-901-3921 |
| | 69 | 0.4620 | 77.8 | 1.3516 | 20.9 | 1.3538 | (402) | CuI | 96-901-3921 |
| | 77 | 0.4042 | 155.6 | 1.2343 | 25 | 1.2359 | (242) | CuI | 96-901-3921 |
| 45 | 25 | 0.1732 | 3182.9 | 3.5000 | 47 | 3.4956 | (111) | CuI | 96-901-3921 |
| | 30 | 0.2310 | 280.2 | 3.0227 | 35.6 | 3.0273 | (020) | CuI | 96-901-3921 |
| | 42 | 0.2310 | 1525.3 | 2.1381 | 37 | 2.1406 | (202) | CuI | 96-901-3921 |
| | 50 | 0.2887 | 786.0 | 1.8217 | 30.4 | 1.8255 | (311) | CuI | 96-901-3921 |
| | 52 | 0.3465 | 202.3 | 1.7466 | 26 | 1.7478 | (222) | CuI | 96-901-3921 |
| | 61 | 0.4042 | 132.3 | 1.5112 | 22.8 | 1.5136 | (040) | CuI | 96-901-3921 |
| | 67 | 0.4042 | 264.6 | 1.3871 | 24 | 1.389 | (313) | CuI | 96-901-3921 |
| | 69 | 0.3465 | 77.8 | 1.3516 | 27.9 | 1.3538 | (402) | CuI | 96-901-3921 |
| | 77 | 0.3465 | 163.4 | 1.2335 | 29 | 1.2359 | (242) | CuI | 96-901-3921 |
| 46 | 25 | 0.1732 | 4575.9 | 3.4922 | 47 | 3.4956 | (111) | CuI | 96-901-3921 |
| | 30 | 0.2310 | 217.9 | 3.0227 | 35.6 | 3.0273 | (020) | CuI | 96-901-3921 |
| | 42 | 0.2310 | 1136.2 | 2.1381 | 37 | 2.1406 | (202) | CuI | 96-901-3921 |
| | 50 | 0.2887 | 575.9 | 1.8217 | 30.4 | 1.8255 | (311) | CuI | 96-901-3921 |
| | 52 | 0.3465 | 108.9 | 1.7448 | 26 | 1.7478 | (222) | CuI | 96-901-3921 |
| | 61 | 0.2887 | 93.4 | 1.5112 | 32.0 | 1.5136 | (040) | CuI | 96-901-3921 |
| | 67 | 0.3465 | 147.9 | 1.3871 | 28 | 1.389 | (313) | CuI | 96-901-3921 |
| | 69 | 0.3465 | 77.8 | 1.3516 | 27.9 | 1.3538 | (402) | CuI | 96-901-3921 |
| | 77 | 0.3465 | 132.3 | 1.2335 | 29 | 1.2359 | (242) | CuI | 96-901-3921 |

The grain size and average roughness of CuI thin films for different annealing temperatures prepared by PLD technique have been measured using AFM, as show in figure (2). Observed that the different temperature have important effect in topography of the CuI thin film surface and the average diameter. When the temperature increases the surface roughness increases also and thus affects the distribution of nanoparticles and hence increases their size and the structure is vertical Columnar .The effect of annealing temperature can be interpreted that at the high annealing temperature atoms gain more energy, enabling them to grow and diffuse rapidly which leads to the aggregation among them to form large nanoparticles. It is clear from the table (2) that the relationship is proportional between the Nano particles size and annealing temperature , the higher the annealing temperature the greater the nano particles size, this is due to the enhancement of crystalline and particles gain high energy which enable them to combine with each other and form large nano particles.

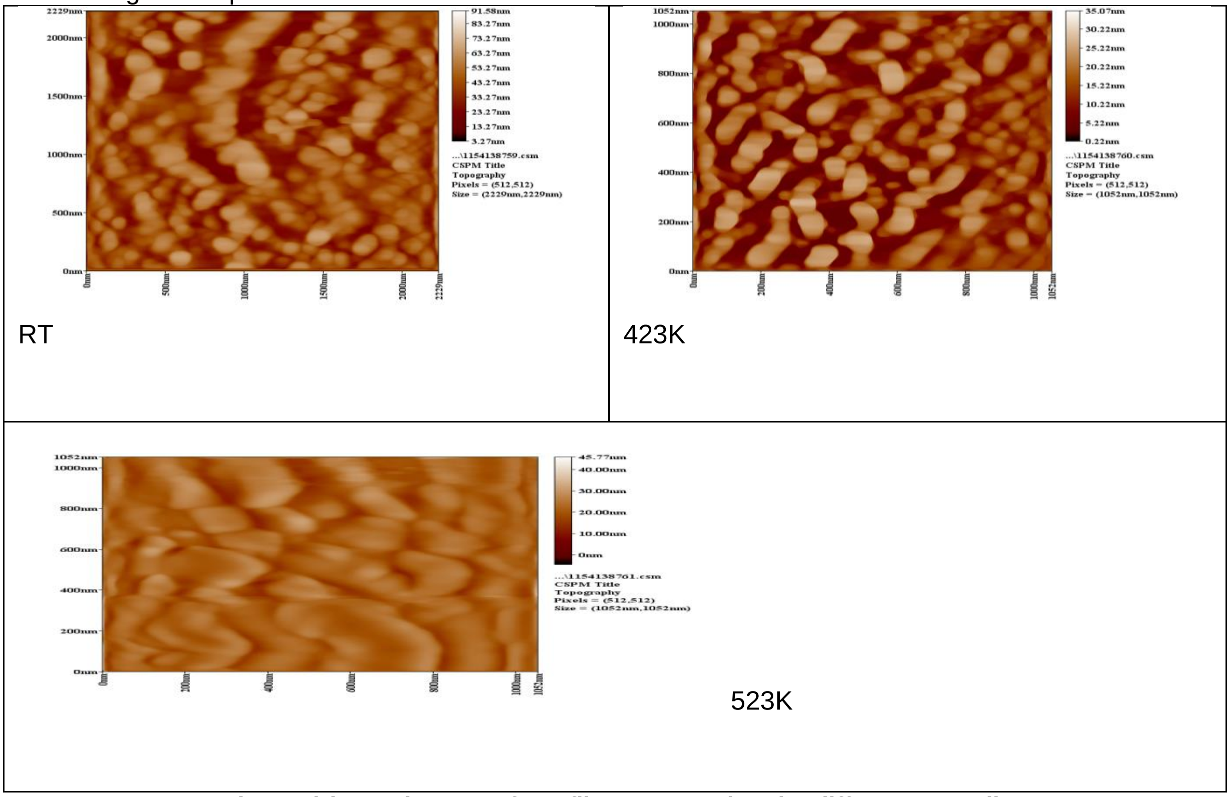



**Figure. (2) AFM images of CuI films prepared under different annealing temperatures and laser pulse energy 800mJ.**

Table(2) The AFM parameters of CuI films prepared under different annealing temperatures and laser pulse energy 800mJ.

| Temperature (K) | Average nano particle size(nm) | Average roughnes (nm) |
|---|---|---|
| RT | 36.7 | 6.5 |
| 423 | 57.88 | 5.36 |
| 523 | 90.69 | 2.57 |

The optical properties of as deposited CuI thin films have been determined by UV-VIS absorption spectroscopy in(300-1100) nm. The transmittance (T) of the prepared CuI thin films deposited at different temperature( RT,423K and 523K) ,that show in figure (3). in general, the transmittance of CuI thin films increases with increasing of λ, also transmittance decreases with increasing of annealing temperatures because increase reflection and absorption . The shifts of transmittance spectrum to the shorter wavelength higher energies compared to that of the annealed films for all CuI, may be attributed to the crystallite of film structure. It is clear from the above figure that for each analyzed thin film it has been noticed that the transmittance decreased for increasing different annealing temperature. This is probably due the improvement in the size of the Crystal and increasing roughness of the Surface of the CuI thin film with increase the scattering of light.

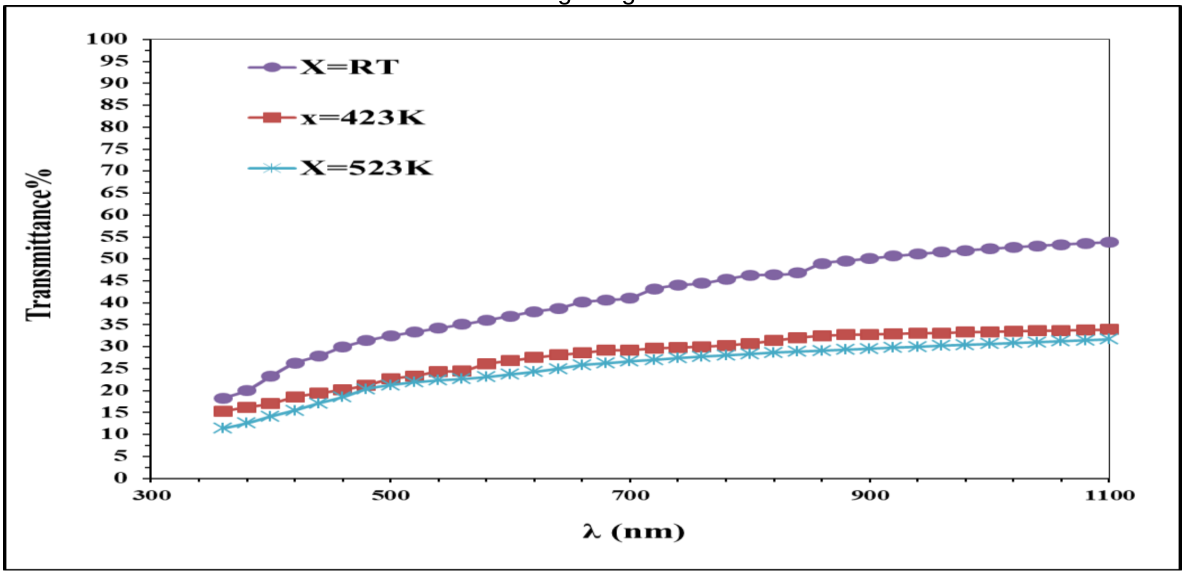



**Figure. (3) Transmittance spectrum for CuI thin film with different annealing temperatures**

The figure (4) shows that the Variation in the absorption coefficient values versus wavelength for different annealing temperatures. One can see from this figures that the absorption coefficient of the CuI thin films is characterized using strong absorption in short wavelength ( 400- 600 )nm and sharp absorption in long wavelength (600–1100)nm. The values of absorption coefficient in short wavelength takes high (α > 6.00E+04 cm-1) and then decreases Significantly with increasing wavelength. Decreasing in absorption coefficient versus wavelength belongs to the reverse proportionality with transmittance and also corresponds to the density absorption centers, such as the absorption of impurities, excitation transitions, the crystal lattice dependent on the conditions of film preparation. The explanation of the absorption edge to shorter wavelengths is refer to the disappearance the subsidiary band (tail states) which suggests from the dispersion theory that confirms the broading of an absorption edge by growth in grain size that causes increasing in the absorption coefficients and shift to longer photon energy i.e. shorter wavelengths.These results are close to the researchers [13,14]

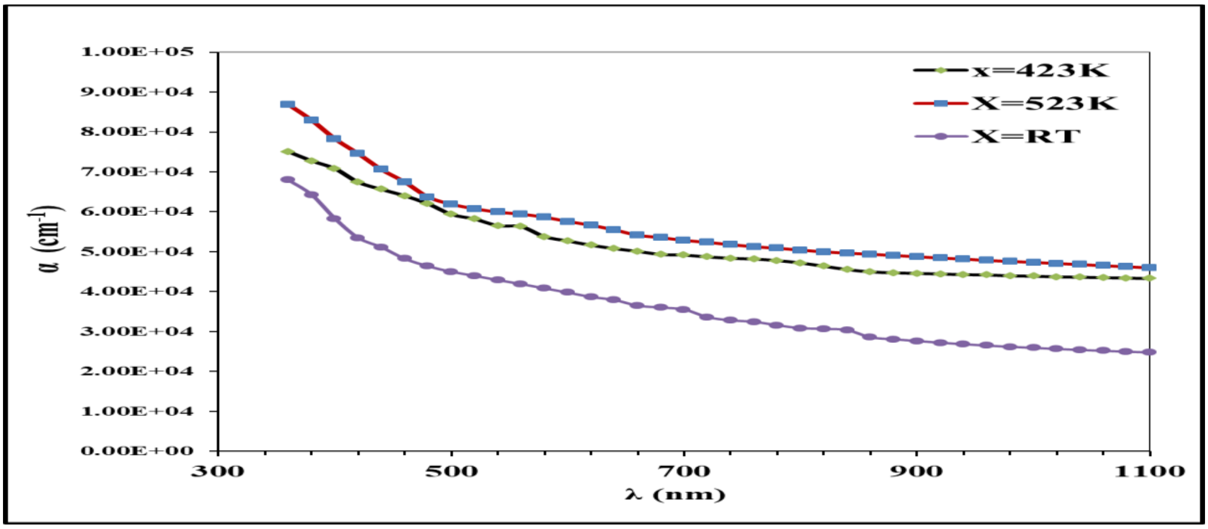



**Figure. (4) The absorption coefficient for CuI thin film with different annealing temperatures**.

Energy gap depends on the conditions and the nature of the thin film structure and method of preparation that affect the crystal structure. The variation in the characteristics of the thin film structure is the reason for these variations in the energy gap. The Variation of (αhν) 2 with (hν) for CuI films with different annealing temperature is shown in the figure (5) its refers to direct allowed transition for CuI thin films. Band gap energies values decreases with increasing annealing temperatures for each CuI film prepared by PLD technique as in table (3). Annealing leads to increase the local levels near the valence band and conduction band ,that is levels receive electrons and generate tails in the energy gap also tails works towards decrease the optical energy gap.These results are close to the researchers [13,14]

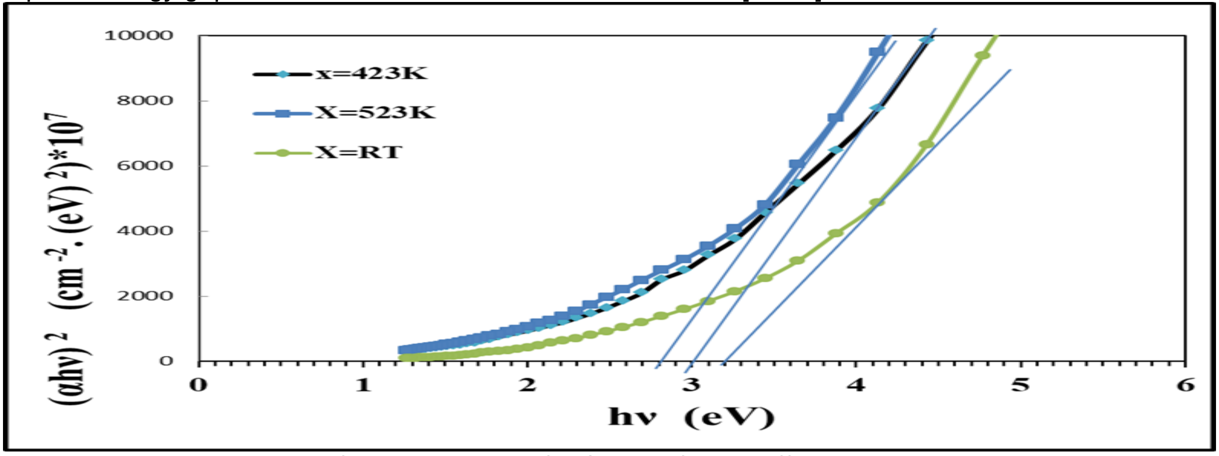



**Figure.(5) Variation of (αhv) 2 with (hv) for CuI thin film at different annealing temperature.**

Table (3):- Direct allowed band gap for CuI thin films for laser wavelength 1064nm.

| X | Eg(eV) |
|---|---|
| RT | 3.2 |
| 150 | 3 |
| 250 | 2.8 |

From the figure(6) of extinction coefficient( k) for CuI thin films with wavelength For the film at different annealing temperature .we see the extinction coefficient increase with increasing of wavelength and increases with increase of temperature. The high and low in the extinction coefficient is due to the difference in the absorbance.

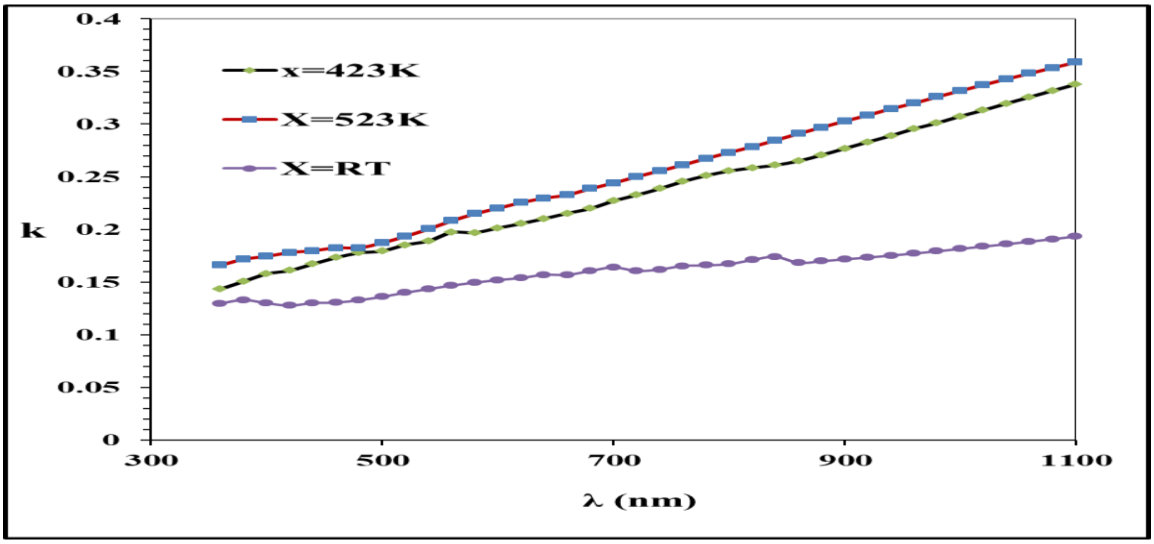



**Fig (6): The extinction coefficient for CuI thin film with different annealing temperatures.**

The CuI film samples prepared under different annealing temperature the refractive index as a function of wavelength has been represented in the figure (7) in the spectral region UV-Visible (300-1100nm), the refractive index decreases in the visible region in the shorter wavelength. decreases refractive index (n) with Increasing temperature and the reason for this, first the Compactness after heat treatment decreases along with increasing the size of the crystal. Secondly, due to the effect of different annealing temperature on the morphology thin film, breed a change in the refractive index. The values of refractive index of CuI thin film are ranging from (1.09-2.55) with the range of wavelength (300-1100nm).

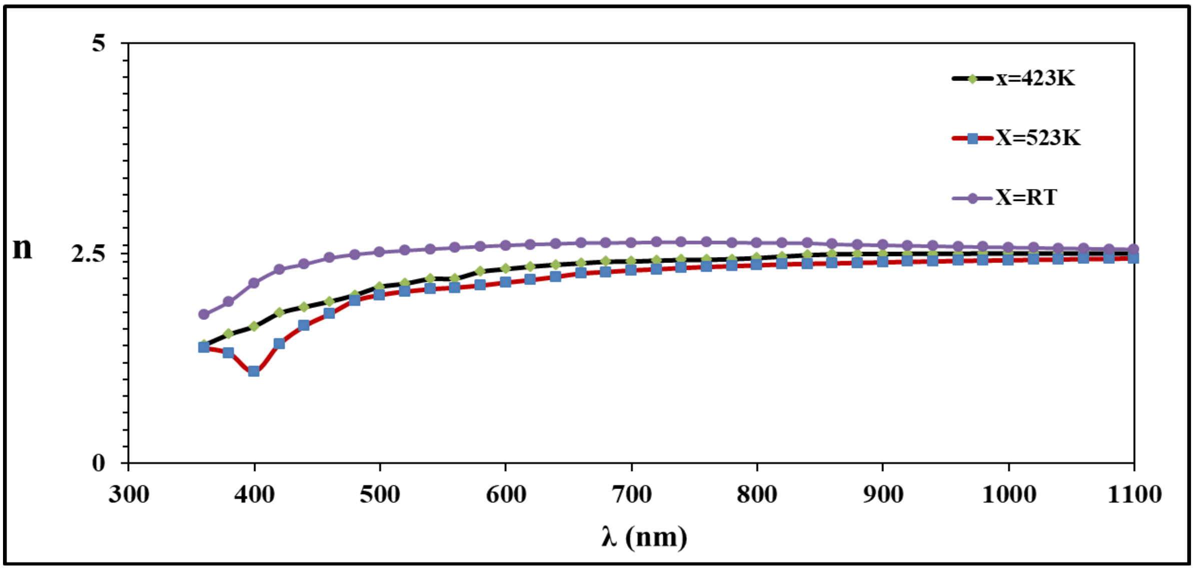


**Figure. (7)TheRefractive index for CuI thin film with at different annealing temperature.**

Figure(8) show the real parts for the dielectric constant increase monotonically with increasing wavelength, While the imaginary parts for the dielectric decreed. This can be understood on the following, the increase of εi and decrees of ofεr with wavelength can be associated with the annealing temperature .The variation indicates that at low wavelength, the dielectric constant is low.

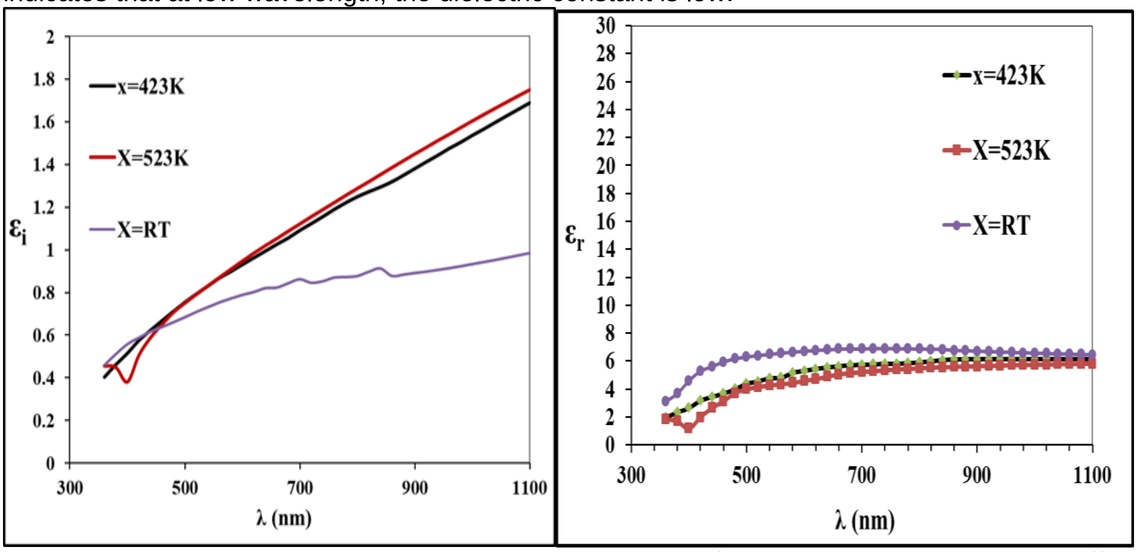
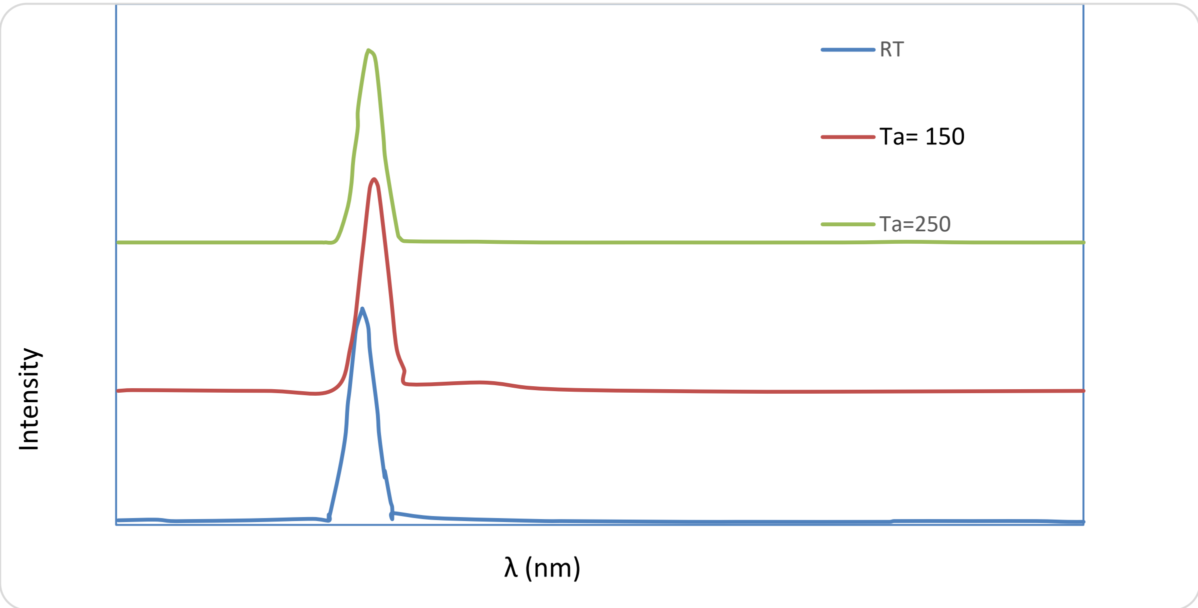


**Figure. (8) show the variation of the dielectric constant εi&εT versus wavelength with different annealing temperatures**

Figure (9) shows Photoluminescence (PL) of CuI thin film have been recorded with an excitation wavelength (220-1000) nm at different annealing temperature (RT, 423K and 523K). The characteristics of CuI films showed strong relation to the substrate temperature .The intensity of the peak increases markedly with the increase of substrate temperature, because the large exaction bending energy of CuI high energy in the short wavelength excitation photons cause more phonons to be emitted before luminescence occurs .

Fig (9): show the variation of PL versus wavelength with different annealing temperatures




**Conclusions:**

The results of structure from the x-ray diffraction show that the CuI thin films deposit on glass substrate is Polycrystalline and cubic structure. Annealing process leads to improve in the crystallization. In addition, AFM confirmed that films prepared very well. UV-Visible transmittance, found that the transmittance decreases With increasing annealing temperature. The films have allowed direct energy gap, which decreases with increasing of annealing temperatures. Also refractive index decreases and real part dielectric constant with increasing temperature, while the ExtinctionCoefficient increases. Typical luminescence behavior with two emission peaks, Photoluminescence increase with annealing temperature.

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