Structural and Optical Properties of Copper Ferrite $CuFe_2O_4$ Thin Films Prepared at different Substrate Temperature

Sumaia H. Gatia

Physics Dept. College. of Science. Basra University, Basra-Iraq

e-mail:- sumaia12@yahoo.com

Abstract

Copper Ferrite $CuFe_2O_4$ thin films have been deposited by chemical spray pyrolysis technique (CSPT) with thickness of (0.76± 0.05) µm onto glass substrates at different temperatures (300-450)℃. All samples were annealed at 500℃ for (1hr.). It was confirmed from XRD analysis that all films exhibit polycrystalline structure. In addition, XRD analysis was utilized to compute grain size (N) and dislocation density (δ). Surface morphology was characterized using SEM and photomicroscope images. The energy dispersive spectrometry data clearly states that the deposited $CuFe_2O_4$ was formed. The optical properties for all films were studied by recording the transmittance and absorbance spectrum in the range of (200-1000) nm. The optical energy gap for allowed direct electronic transition varies from (2.35-2.0) eV with increasing of the substrate temperature .The optical constants, such as extinction coefficient (K), refractive index (n), real and imaginary dielectric constants $(\in_1, \in_2)$ were calculated and discussed.

Key words: Copper ferrite; optical properties; thin films;XRD.

1. Introduction

Representing the cubic crystals of oxides that have the form of AB_2O_4 for large number of inorganic materials, which have many useful features possessed in practical applications that not appear in the binary oxides. They show synthetic, electrical, magnetic and catalyst properties, which depends on the nature, shipments and distribution of internal ions[1,2].

It is well known that magnetic phenomena is associated with a number of metals, and looking at non-metallic materials we found more of these phenomena are related to a number of ferrimagnetic, especially oxides, the origin of these oxides in these materials it is due to the magnetic iron oxide (Magnetite). This has the formula of (Fe_3O_4) or otherwise (Fe (Fe_2O_4)). Therefore, the magnetite has electrical conductivity up to ($10^4\Omega^{-1}m^{-1}$) at room temperature [1]. Magnetite is known since the ancient times and its use in electronic applications and electricity is relatively recent.

Ferrites are chemical compounds, which are composed of ceramic material and iron oxide as their main component.ferrites,has a spinel type stucture,and it is symbol ($MgOAL_2O_3$) or more ($MgAl_2O_4$)[3,4].

Ferrites cubic which form ($MeFe_2O_4$) or ($MeOFe_2O_3$) were the symbol (Me) symbolizes to any binary metal belongs transition elements in the periodic table. The cubic structure crystallizes between positive and negative charges and the oxygen ions are tightly packed with positive ions-cationic -divalent (Me^{+2}) or trivalent (Me^{+3}) which are distributed in the crystalline structure folds. Hence the name of this type of ferrite is called "ferrite spinel", Thin films of spinel ferrites MFe_2O_4 (M = Mn, Cu, Zn, Ni, Co, Cd, etc.) which exhibit excellent chemical stability and high corrosion resistivity and seem to be applicable as recording media and microwave absorbing layers. These materials are commercially important due to the magnetic properties and electrical excellence. This type of material is the subject of comprehensive studies by some physicists and chemists[5].

Nanoparticles spinel (nps) increasing utility for many applications due to their microscopic compositions this shows innovative properties that differ from those materials in their volumetric state. The difference is due to large quantity of atoms within the limits of the crystalline seeds (small and approaching atomic dimensions).

Copper ferrite crystallizes in an inverse or mixed spinel structure depending upon the preparation conditions. Under slow cooling, Cu-ferrite crystallizes in a tetragonal structure with lattice parameter ratio c/a of about 1.06. Tetragonal phase of Cu-ferrite has inverse spinel structure with almost all Cu^{2+} ions occupying octahedral sub lattice, whereas Fe^{3+} ions are divided equally between the tetrahedral and octahedral sub lattices. There is a structural phase transition from tetragonal to cubic at a temperature of 390˚C due to disorientation of Jahn–Teller distortion as a result of thermal motion of lattice at high temperatures(6).

There has been a number of studies on Copper-ferrite thin films with the objective of enhancing magnetization for application(7,8,9,10).Ferrite thin films have the potential to replace the huge external magnet in the main steam microwave devices and it can provide functions unique circuit that cannot be produced by other materials(4).

In this work, we report the result on an investigation of the structure and optical of chemical spraying pyrolysis $CuFe_2O_4$ thin films under different substrate temperature. The study shows the role-played by the substrate temperature on the properties of the prepared films.

2. Experimental Process

Copper Ferrite $CuFe_2O_4$ under investigation is prepared using the chemical spray pyrolysis technique (CSPT). The spray set up and experimental details was mentioned closely in previous investigation(11,12).

The sprayed solution is prepared by mixing (0.05M) aqueous solutions of Cu $(NO_3)_2.3H_2O$,$Fe(NO_3)_3.9H_2O$. The Cu/Fe ratio in the solution was 1:2 .The compound solutions are sprayed onto heated glass substrates using air as a carrier gas, the substrate pre- heated at the required temperature for 20 min before spray process. The spraying was carried out on and off periodically (10sec on and 20sec off).The vertical distance between the glass substrate and the end of the spray tube is 29cm. The spray rate is 1ml/min. The substrate temperature was varied in the range (300-450) ˚C. Thickness of the prepared samples is estimated by weighing method was around (0.76± 0.05) μm. All samples were annealed at 500˚C for 1 hr. The films obtained were clear,transparent,and brownish in color, exhibit smooth surfaces, and free pinholes.

The structural properties of the films were analyzes by X-Pentpro MPD. A filtered Cu Kα radiation (λ=1.548 A°) at 40 KV and 40 mA was used for x-ray diffract meter (XRD).Also a Photomicroscope image scanning electron microscope (SEM) and EDX were used to observe surface morphology of thin films.

Optical absorb measurements are carried out using SP-1800 UV/VIS Double beam spectra photometer; it covers the range from (200-1000) nm. All measurements were carried out at room temperature.

3. Results and discussion

3.1 Structural properties

X-ray diffraction analysis were carried out on $CuFe_2O_4$ thin films prepared for different substrate temperature in range (300-450)˚C.fig.1 (a,b,c,d) show the XRD patterns of copper Ferrite samples with diffraction angle between (20-60) . The optimum films was found at temperature 450˚C. This figure show the characteristic peaks of monocrystal peak positions observed which agree with cubic structure of $CuFe_2O_4$ and represented by miller indices of (003),(202),(131), and(213),. Planes of cubic observed at diffraction angles of (2θ=8, 30, 35.38°, , 43.92°,) respectively.

This results are in agreement with the previous studies [13, 14]. Which corresponds to copper Ferrite phase standard, (JCPDS files $CuFe_2O_4$: 25.283). The average diameter (D_{av}) of grain size was calculated using Scherer's formula[15]:

$$D_{av} = 0.9\lambda/\beta \cos\theta$$

Where β is the instrumental effect, corrected full width at half maximum of the peak measured in radian. θ is Bragg angle and λ is the wavelength of X- ray. As observed from fig.1 (a, b, c, d) the broadening intensity of 3 peaks arises due small crystalline grain size, and the value of grain size was increasing with substrate temperature. Using the grain size in the relation below[16]:

$$\delta = 1/D_{av}^2$$

We obtain the value of dislocation (δ) as it appears at different substrate temperature see Tabl.1. As observed, the density of dislocation decreases with increasing substrate temperature which indicates homogeneity and the increase of proportion of crystalline.

The number of crystals (N) per unit area is calculated using the following equation[17]:

$$N=t/D_{av}^3$$

Where t is the thickness of thin films. It is found that the number of crystals decreases with increasing the substrate temperature as shown in table.1.

Table .1 Values of grain size, dislocation, number of crystals, and energy gap of $CuFe_2O_4$thin films.

(T)˚C	(D_{av}) nm	(δ) nm^{-2}	(N)nm^2	(Eg)eV
300	8.15	0.015	$3.24*10^{-19}$	2.35
350	23.693	0.0017	$1.323*10^{-20}$	2.2
400	34.48	0.00084	$4.29*10^{-21}$	2.1
450	38.64	0.00067	$3.04*10^{-21}$	2.0

3.2 Surface Morphology

Optical microscope images in fig.2 show a globular structure composite of nano-crystals. This relearns homogeneity of material on substrate surface and the average crystallite size that increase with increasing substrate temperature. Fig.3 shows SEM images for samples that consist of spherical shape grains closely peaked to each other indicating good adhesiveness of the film with substrate. The (SEM) micrographs shows that the films have nano-crystalline structure, It is observed that the grains of the $CuFe_2O_4$ films are more densed and uniform when increasing substrate temperature. EDX investigation of $CuFe_2O_4$ thin films carried out on the atomic abundance of copper iron and oxygen species present at the surface of thin films. It is well known that EDX technique supplies an accurate determination of relative atomic concentration of different elements that are present on their surfaces. EDX spectrum in fig.4 supports the presence of Cu, Fe, O element in the find $CuFe_2O_4$ and observed extra peaks of other elements Si, Mg, Cl and C are due to glass substrate.

3.3 Optical properties:

Optical measurements include the transmittance, absorbance and reflectivity as function of wavelength values were make. Also the forbidden energy gap account for the direct transmission of photon energy as visual tests such as the refraction index (n), Extinction coefficient (k) and dielectric constant (ε). Optical measurements has been carried out at room temperature for all samples, the optical absorbance and transmittance in UV-VIS-NIR regions. FiG.5 shows the spectrum transmittance of $CuFe_2O_4$ indicating that transmittances increases with the wavelength, which is similar to the behavior of the spectrum of $CuFe_2O_4$ thin films prepared in other ways and recorded in previous studies (18). However, we noticed a decreasing transmittance with increasing temperature, that due to the increase in surface roughness of the thin films with increasing temperature while in FiG.6 the absorbance of spectrum as a function of wavelength is introduced and it is clear that the behavior of the absorbance spectrum has the opposite behavior to the behavior of the transmittances. And it is gradually lessens with increasing wavelength. This means that the photon incident cannot irritate the electron and remove it from the valence to conduction bund that have less than the value of the energy gap. While the figure shows that, the absorbance increases with increasing substrate temperature, causally there are a lot of atoms with energy levels are there to absorb photon; and hence absorbance depends on the type and nature of chemical composition, crystal and the thickness of the films.(17)

FiG.7 refers to the reflectivity spectra. Through the shape we notice that the reflectivity increases rapidly at low energies, and then the peak at energies corresponding to the values of energy gap forbidden and interpreted on the basis that the absorption is negligible or very little at photonic energies smaller than the capacity of the gap concomitant by an increase in the reflectance on the surface film. The note of the shape also increase the reflectivity values for $CuFe_2O_4$ thin films with increasing substrate temperature, the reason for this behavior is the reducing crystalline defects and regularity of atoms.

The absorption coefficient (α) was calculated using the relation(19): $\alpha=2.303A/t$

Where (t) is the thickness of the films. The photon energy at each wavelength is calculated from the relation $h\nu = 1.240/\lambda$ .The FiG.8 shows that the absorption coefficient increases with increase of photon energy and the values of absorption coefficient are greater than(10^4 cm^{-1}) at low wavelengths (high photon energy),which is likely to occur in direct electronic transitions. The results showed that the coefficient of absorption increases by increasing the temperature of the substrate. The absorption data manipulated for the determination of the band gap energy.

Fig.9 shows the expected values of energy gap as determined from the following relation[20]:

$$\propto hv = A(hv - Eg)^n$$

Where A is the constant in dependent of photon energy [21], and (n) is assumed (½) for allowed direct transitions. The optical energy gap which ranged between(2.35-2.0)eV, is decreasing with increasing the substrate temperature, the decrease in (Eg) is due to the increases of average grain size because of the increasing substrate temperature.

Measurement of the fraction of light lost scattering and the absorption per unit distance known as extinction coefficient, (k) which can be determined by using the relation [22]:

$$K=\alpha\lambda/4\pi$$

We notice that the relationship associated with absorption coefficient, from the plot of the values of (K) as a function of photon energy, fig.10 shows that (K) increases with photon energy. In addition, we found similarities in the nature of curve (k) with absorption coefficient curved.

Refractive index (n) is regarded as one of the essential properties of optical materials due to its correlation with the electronic polarization of ions and local field inside the material. The refractive index account for $CuFe_2O_4$ thin films with different substrate temperature using the following formula [23]:

$$n= (1+R^{1/2})/ (1-R^{1/2})$$

A plot of refractive index as a function of photon energy is shown in fig.11. The index (n) increases as photo energy increases. In addition, it increases with increases substrate temperature, which is due to the increase in grain size. We also calculated real and imaginary parts of the dielectric constant using the relation[24,25]:

$$\epsilon_1=n^2-k^2,\ \epsilon_2=2nK$$

Where (ϵ_1) the real part and (ϵ_2) is the imaginary part of dielectric constant

It has been noticed that ϵ_1 behaves similarly to that of refractive index because of the small value of K^2 compared to n^2, while ϵ_2 depends mainly on K values, which can be seen from figs. (12, 13). These results showed that the (ϵ_1, ϵ_2) increase with the photon energy and with increase substrate temperature

Conclusion

In this study, $CuFe_2O_4$ thin films are formed on glass substrate by chemical spray pyrolysis technique (CSPT) with different temperature ranging from (300-450) ℃. XRD,AISO XRD analysis showed that $CuFe_2O_4$ thin films have a cubic structure with predominant (131) orientation.

The optical properties was investigated ,and it has been found there was a decrease in the transmittance spectra with increasing substrate temperature , this due to the increased dispersion of light resulting from the increased surface roughness with high temperature .Absorption coefficient increases with substrate temperature. It is observed that the photon energies are higher than $10^4 m^{-1}$ that leads to the conclusion that the energy gap is due to the direct in transmission of the photon, and the energy gap decreases with increase substrate temperature due to formation of new levels within the gap. The extinction coefficient increases with increase substrate temperature as well as increasing both the real and imaginary dielectric constants with substrate temperature

Acknowledgements

The author would like to thank physics departments in Basra University for providing us the materials.

Reference

1- S.D.Sartale, C.D.Lokhande, M.muller, mater.chem.phys. 80(2003) p.120-128.

2-S.Roy, and J,Ghose, J.magn. Mater; 307 (2006) , p. 32-37

3- G.F.Goya, H.R.Rechenberg , J.Z.Jiang Jing J.appl . phys.;84(1998

4- Z.Sun, L.Liu, D.Z.Jia and W.Pan, Sens. Aetuators, B.chem 125(2007), p.144-148.

5- K.S.Kang , C.H .Kim ,W.C.Cho K.K.Bae , S.W,Woo, C.S. park Int.j.Hydrogen Energy ,33(2008) ,p4560-4568

6- C.Baubet, ph.tailhades , C.Bonning ue ,A.Rousset and Z.simsa , J .Phy. Chem. Solids; 61(2000) 863-867.

7- M.Kucera ,V.Kolinsky,S.Visnovsky , D.Chvostova ,N. Venkataramani, S.Prasad, P.D.Kulkarni and R.Krishnan , J. Magn.Magn. Mater. 316(2007) NS.prasad e688-e691

8- G.Srinivatan ,B.V.M.Rao , J.Zhao , M.S.Seehra ,APPly .phys .lett.59 (1991)372 – 347 .

- 9- M.Desai, S.Prased , N. Venkatar- amani , I.Samajdar , 246(2002) 269. 266

10 – A..Yang ,Z.Chen ,X.Zuo ,D.Aren ,J.Kirleland , C.Vittoria and V.G.Harris , APPL.PYYS.lett 86 (2005) 252510 .

11 – L.Bahadur , M.Hamdan , J.Fekoening and P.Chartier , solar energy mater. , vol. 14,(1986) 107 .

12 – C.Belleccl and A.Bonanno , J.APPL .Phy. ; vol.15 ,(1982) 112 .

13- Douaa.B.fahad,"Structural, Electrical and Optical properties of ferrite system" Athesis, College of Science, University of Baghdad, Iraq .2014

14- E.Mugnier, A.Barnabe, L.persmanes, and Ph.Tailades, thin solid films, 516(2008)1453-1456.

15- G. Willeke, R.Dasbach, Sailer, B., Bucher, E.E, Thin Solid Films, 271(1992).

16- MG.Sridharan, Sa.K, Narayanclass, D.Mangalaraj and H.Chuellee, Journal of optoelectronics and Advanced Materials, Vol.8, (2005).12

17- GM.Yousuf,"Solid state physics", Part11, Baghdad University press (1989).

18- A.Sabah, S.alman, Asaad .A.Kamil, sahar .J. Abed,J.Chem.Bio.Phy. C, Vol.6, No.1, (2015)124-134.

19- K.L.Chopra,"Thin film phenomena",Mc.Graw-Hill,New York ,(1985)

20-Y.Jayasree, V.chalapathi, P.Uday Bhaskar, V.Sundara Raja, Applied. Surface science, 258(2012).2732-274

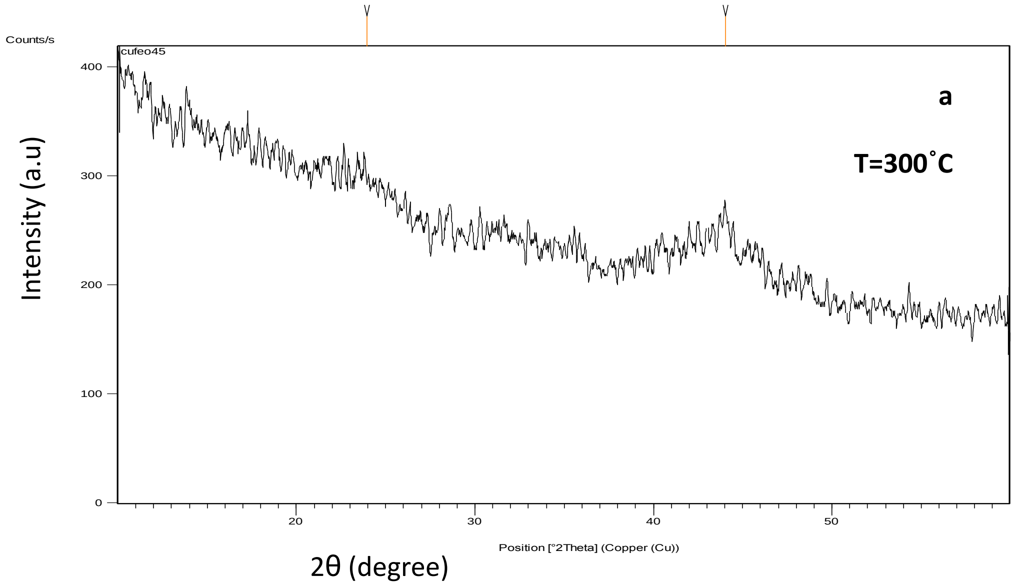
21- H.Neumann, B.perit, N.A.K.Abdul. Hussein and R.D.Tomlinson, Cryst. Res.Technol. 17,469(1982).

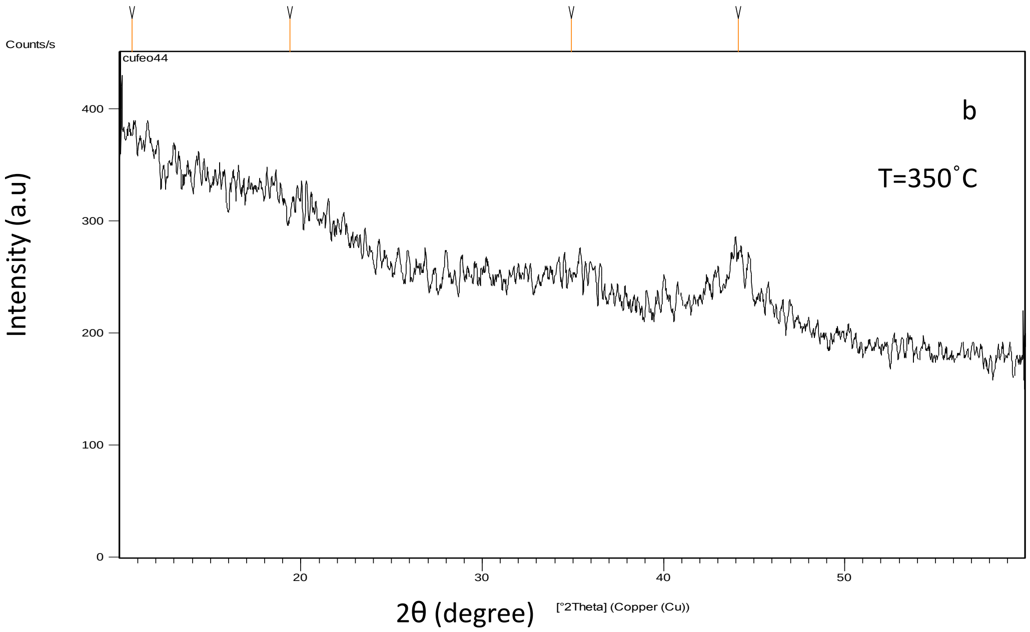
22- S.W.Xue, X.T.Zu, W.L.Zhou, H.X.Deng\, X.Xiang and H.Deng, Journal of Alloys and Compounds, (2008), 448, 21-26

23- D. L. Greenway, G. Harbeke, Optical properties and band
24- structure semiconductor (Pergamon Press, UK, 1970).
D.L.Greenway,Opt.Pro.in additione,band strucr.of semiconductor(1977).

25- Guneri, E. and Kariper, A., J. of Alloys and compounds, 516(2012).20

,


Counts/s
cufeo45
400
300
200
100
0
a
T=300˚C
Intensity (a.u)
20
30
40
50
Position [°2Theta] (Copper (Cu))
2θ (degree)


Counts/s
cufeo44
400
300
200
100
0
b
T=350˚C
Intensity (a.u)
20
30
40
50
2θ (degree)
[°2Theta] (Copper (Cu))

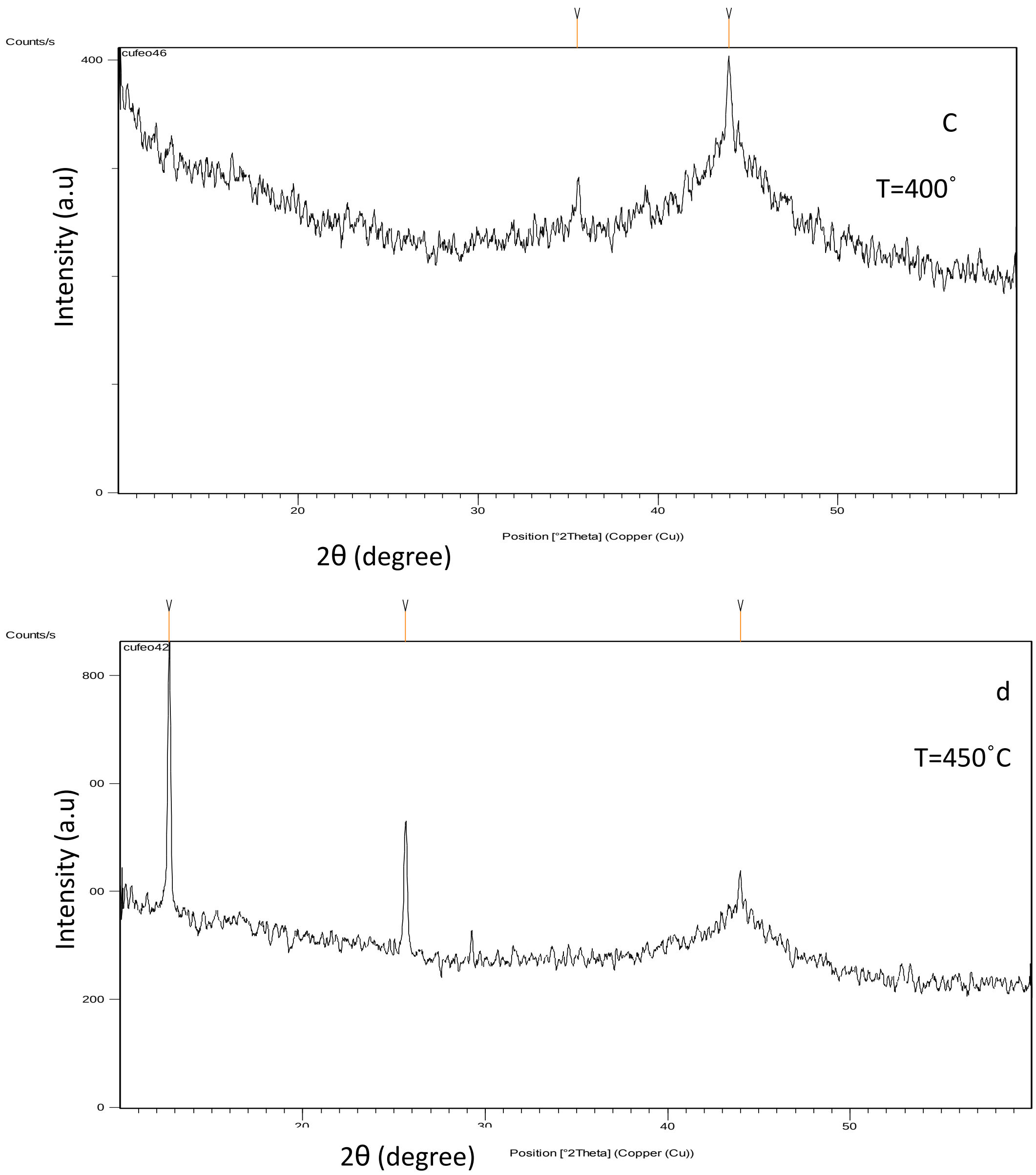
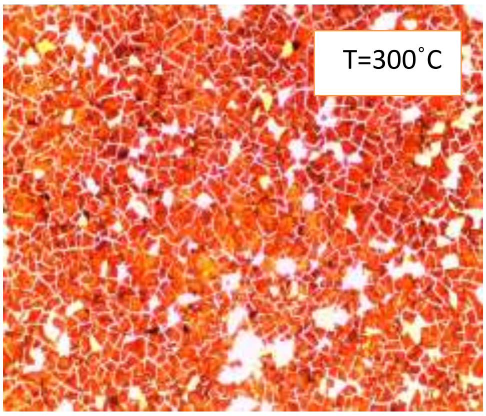
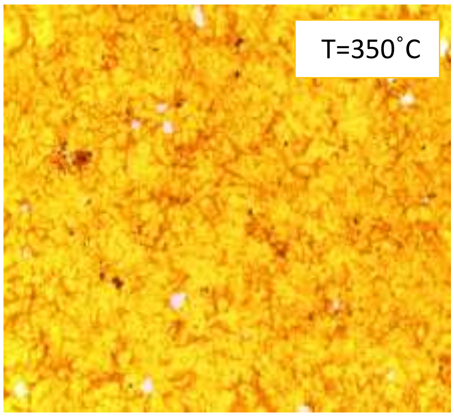


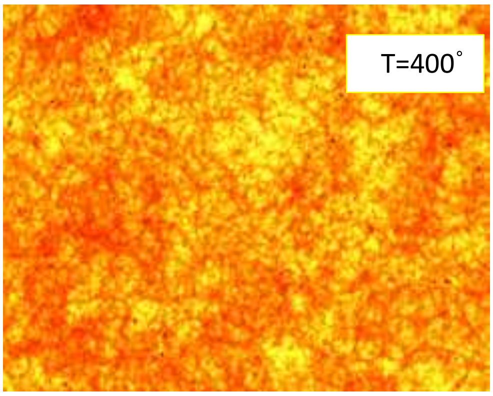
FIG.1.X-ray diffraction of $CuFe_2O_4$ thin films at (a) 300˚C (b) 350˚C (c) 400˚C, and (d) 450˚C.



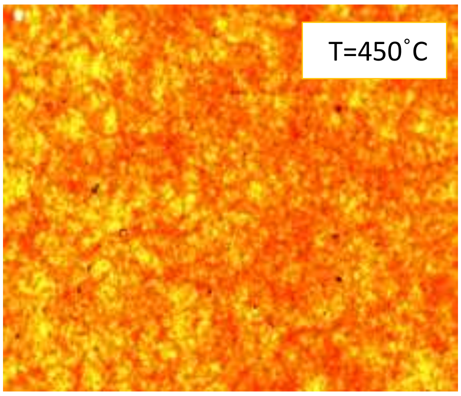
(a)



(b)



(c)



(d)

FiG.2. Photomicroscope image of $CuFe_2O_4$; 400x.

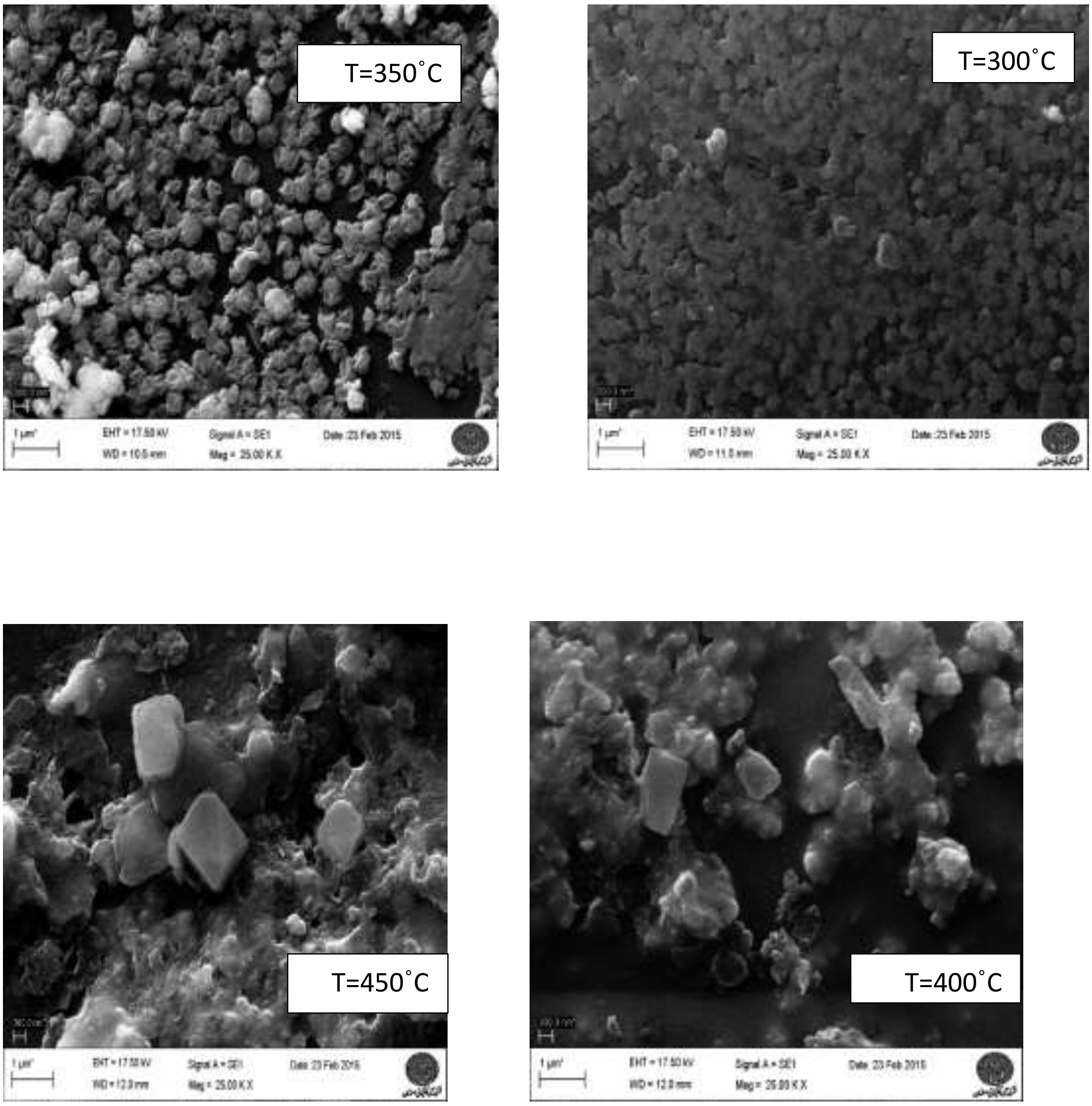


FIG.3. ESM of $CuFe_2O_4$ thin films prepared at different substrate temperature.

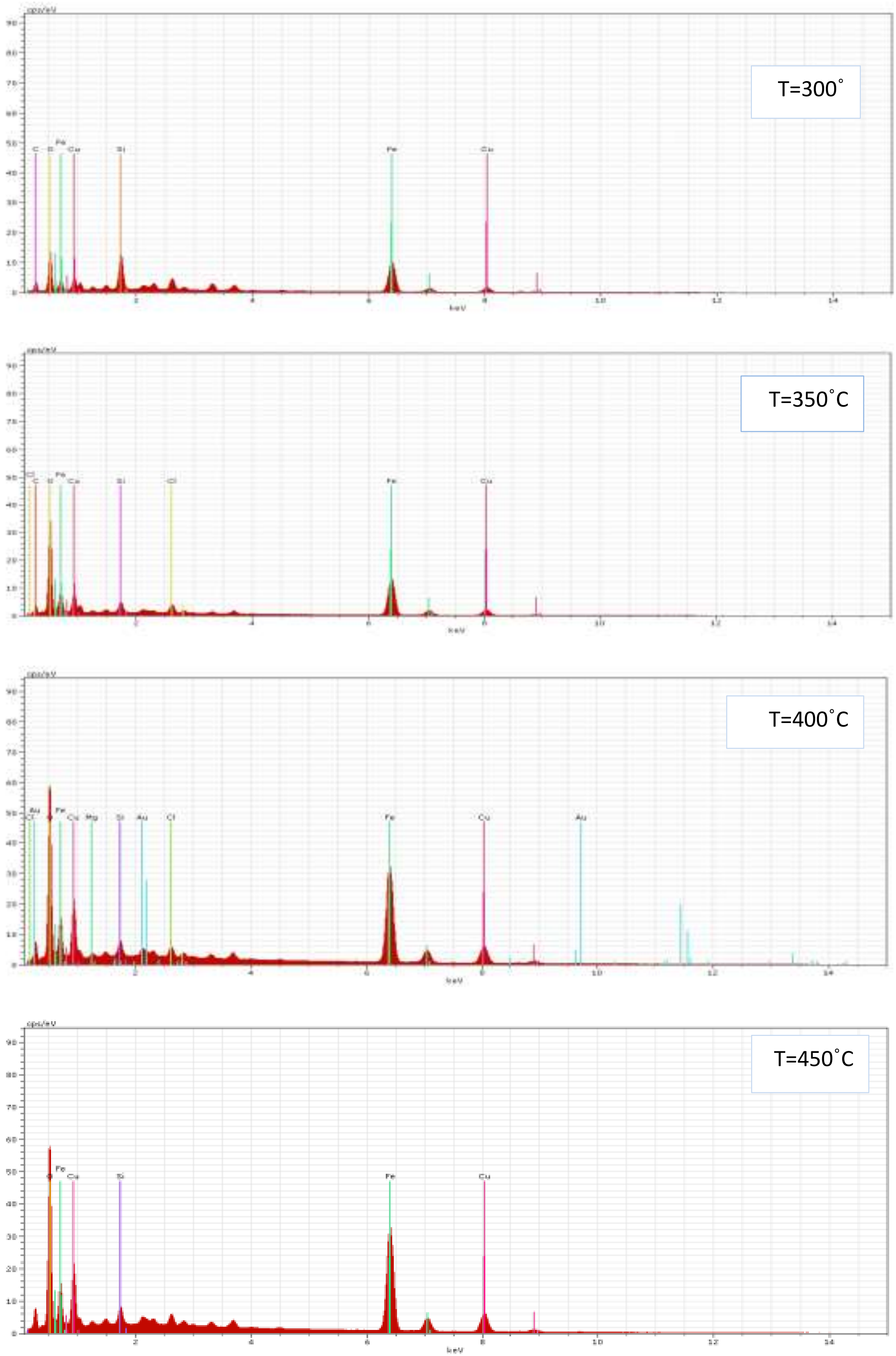


FIG.4. EXD spectrum of cufe2o4 thin films.

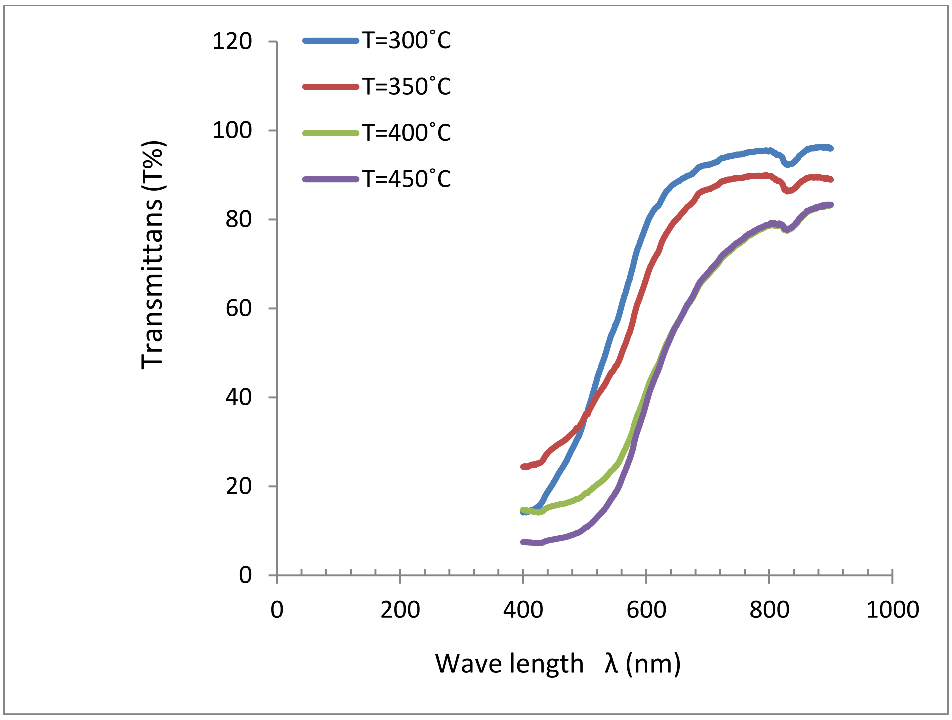


FIG.5. Transmittance spectra of $CuFe_2O_4$ thin films.

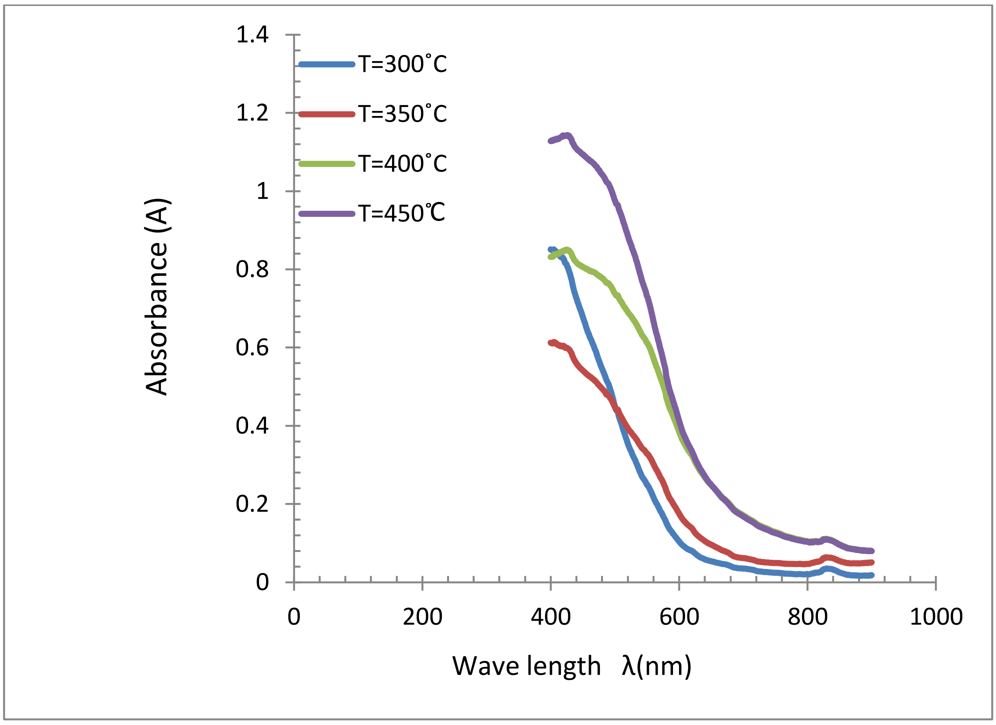


FIG.6. Absorption spectra of $CuFe_2O_4$ thin films

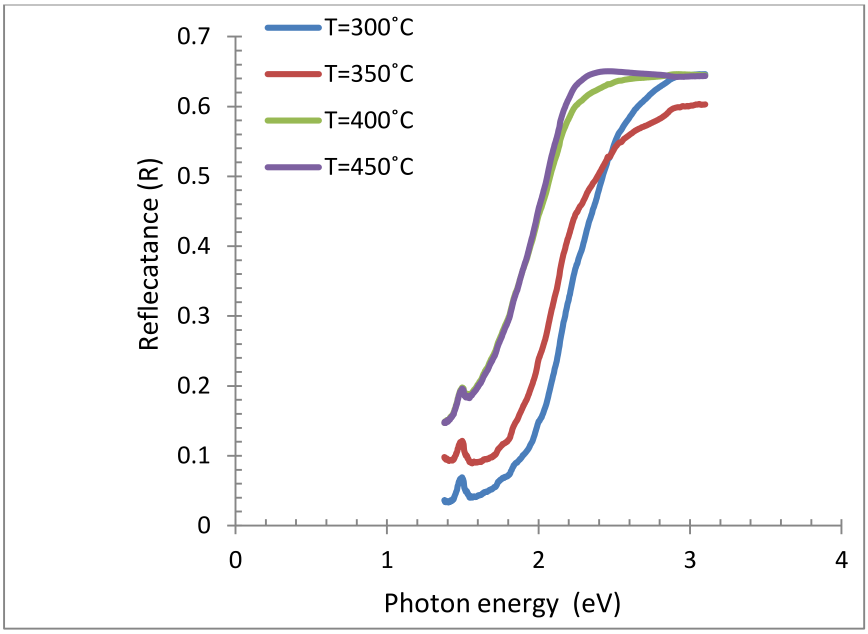


FIG.7. Reflection spectra of the $CuFe_2O_4$thin films

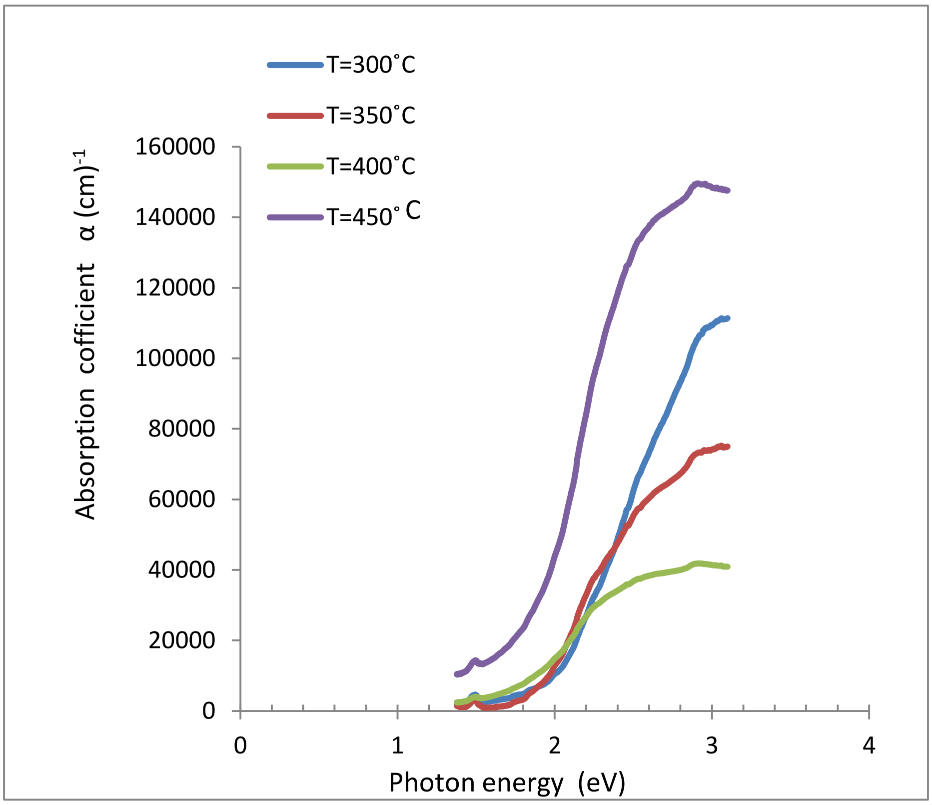


FIG.8. Absorption coefficient of $CuFe_2O_4$thin films.

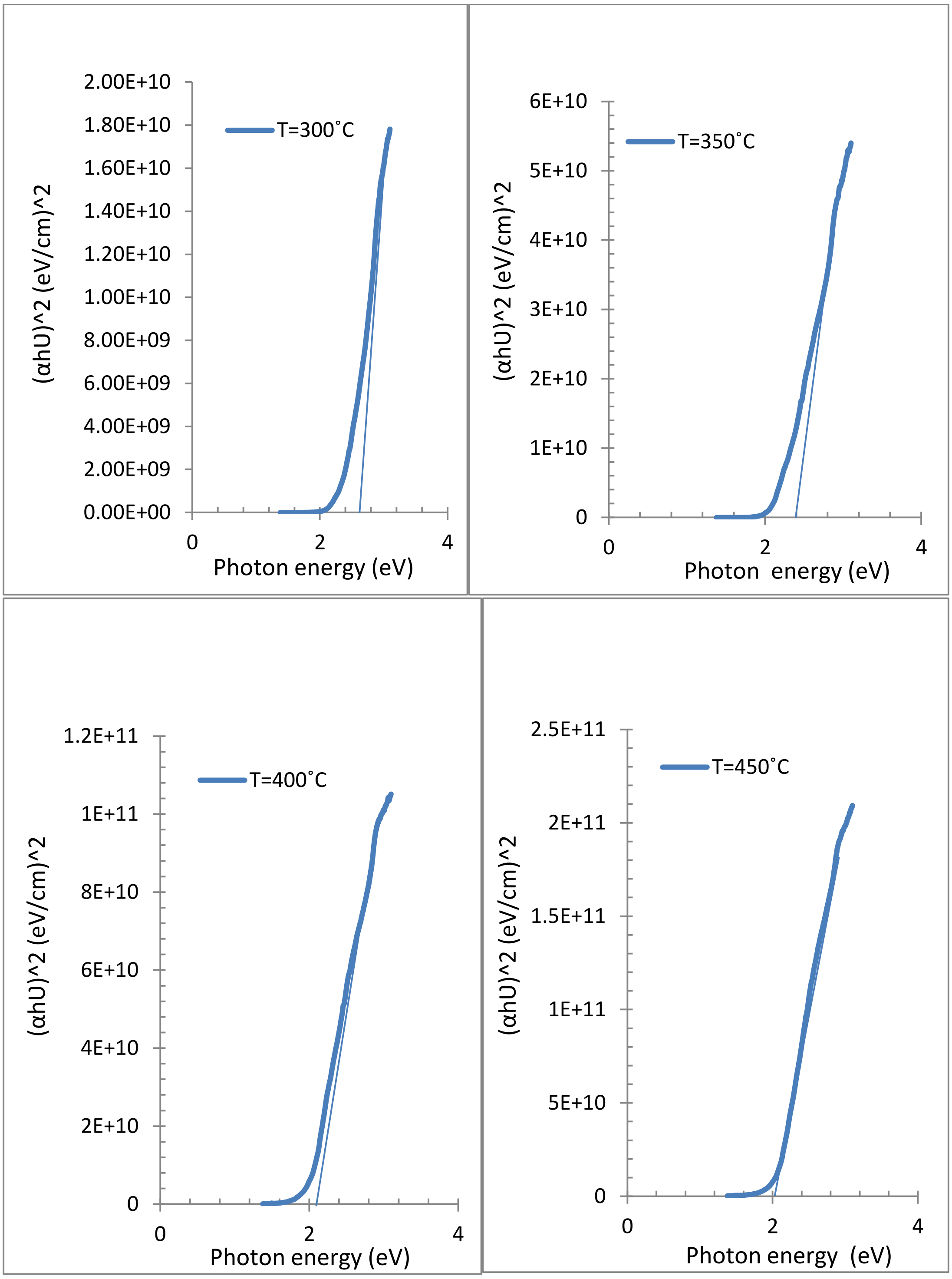


FIG.9. Energy gap of $cufe_2o_4$ thin films.

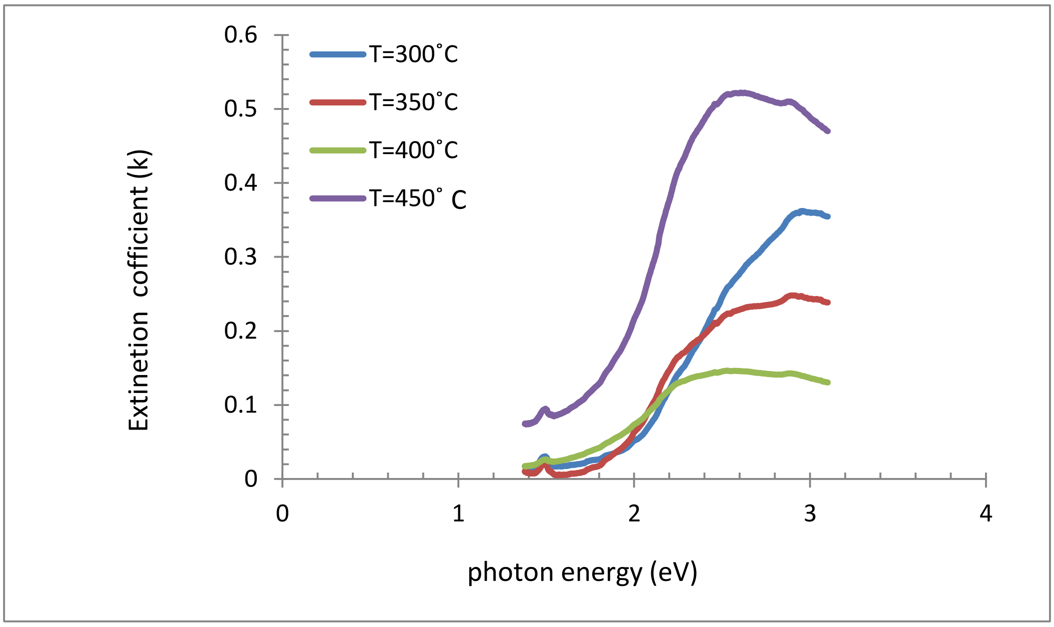


FIG.10. Extinction coefficient of the$CuFe_2oO_4$ thin films.

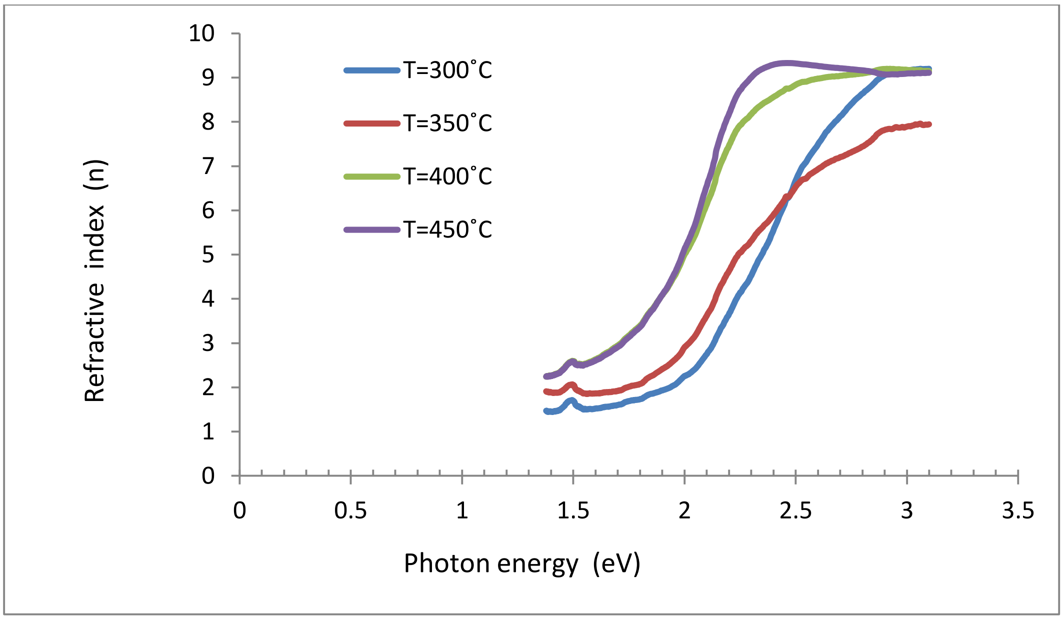


FIG.11. Refractive Index (n) of the $CuFe_2O_4$ thin films

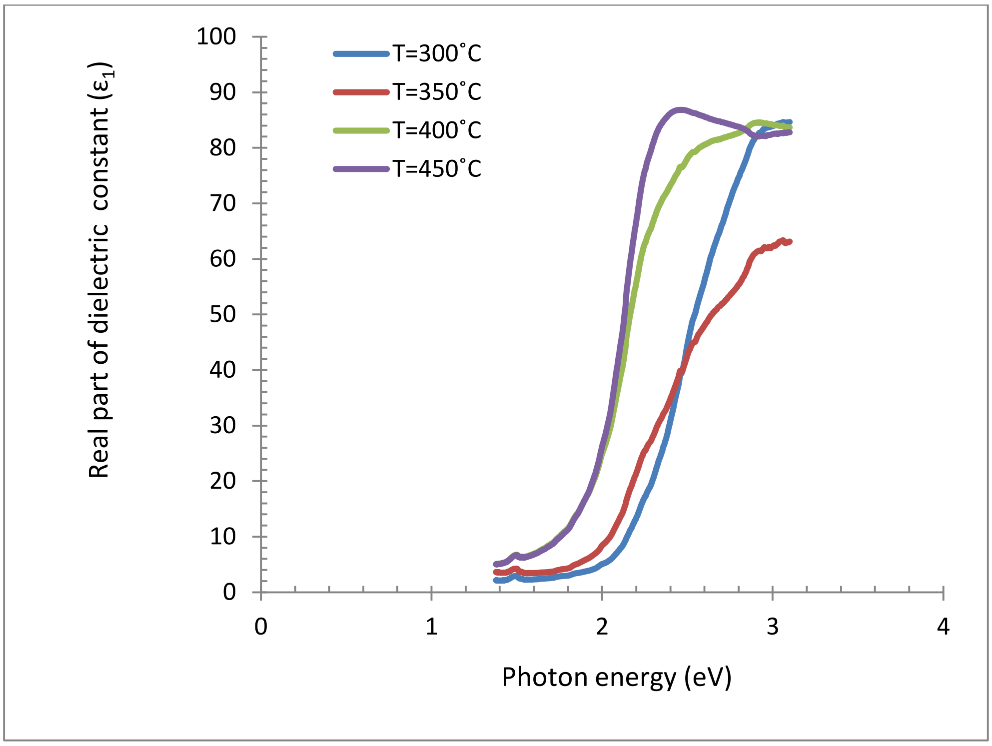


FIG.12. Real part of dielectric constant (ε_1) of $CuFe_2O_4$ thin films.

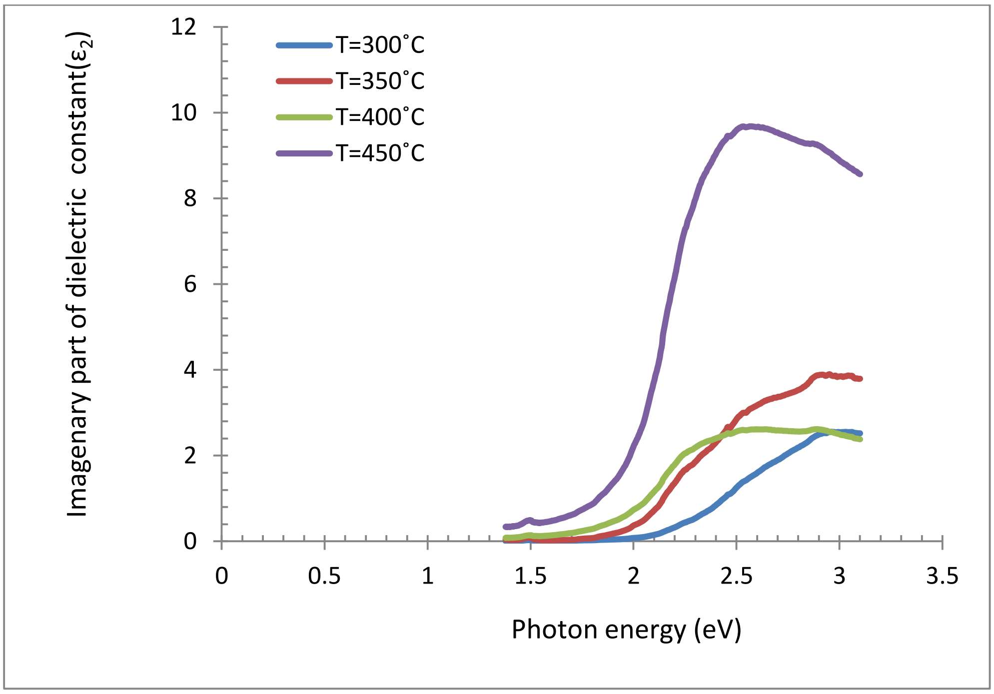


FIG.13. Imaginary part of dielectric constant (ε_2) of the $CuFe_2O_4$ thin films.

الخواص التركيبية والبصرية لأغشية فرأيت النحاس الرقيقة $CuFe_2O_4$ المحضرة بدرجات حرارية مختلفة

سمية حسن كاطع

قسم الفيزياء ،كلية العلوم، جامعة البصرة ، بصرة، عراق

e-mail:- sumaia12@yahoo.com

الخلاصة

حضرت أغشية رقيقة من فرأيت النحاس $CuFe_2O_4$ بتقنية الرش الكيميائي الحراري (Chemical Spray Pyrolysis Technique) وبسمك μm (0.76± 0.05).وعلى قواعد زجاجية بدرجات حرارة C˚(300-450) .جميع النماذج تم معالجتها حراريا بدرجة 500˚C ولمدة ساعة واحدة .من تحليل الأشعة السينية (XRD) وجد ان الأغشية متعددة التبلور . و تم حساب حجم الحبيبات (N) وكثافة الانخلاع (δ).و تم دراسة سطح الأغشية بواسطة المجهر الضوئي والمجهر الماسح الإلكتروني SEM.وقد بين طيف تشتت الطاقة(EDX) تكوين المركب $CuFe_2O_4$على القواعد الزجاجية. درست الخواص البصرية من خلال تسجيل طيف النفاذية والامتصاصية ولمدى الأطوال الموجية nm(200-1000) .ووجد ان نوع الانتقالات البصرية هي من النوع المباشر المسموح وتناقصت قيم فجوة الطاقة من eV (2.0 -2.35) مع ارتفاع درجة حرارة القاعدة .وقد وتم حساب ومناقشة الثوابت البصرية مثل معامل الانكسار (n) ومعامل الخمود(K) وكل من الجزء الحقيقي والخيالي ($\varepsilon_1, \varepsilon_2$) لثابت العزل.