THE INFLUENCE OF Cu CONCENTRATION ON OPTICAL PROPERTIES FOR THIN ZnO FILMS PREPARED BY PULSE LASER DEPOSITION

M.F.A.Alias and Kh. M. Rashid

Department of Physics, College of Science, University of Baghdad
P.O.Box 47162 Jadiriyah,Baghdad, Iraq

Abstract

In this work, thin doped ZnO films are prepared by pulse laser deposition (PLD) technique at different Cu concentration (0, 2, 4, 6, 8 and10) wt %on glass substrates .Optical properties of prepared specimens have been investigated as a function of various Cu concentration. The optical properties show that the films have energy gap decreases from 3.3 to 2.2 eV with increasing Cu concentration from 0 to 10%.The optical constants which were extinction coefficient, refractive index, real and imaginary constants were varied upon doping ZnO thin films with different Cu concentrations.

Keywords: ZnO thin film, pulse laser deposition, optical properties, Cu concentration.

I. INTRODUCTION

Zinc oxide (ZnO) is well known to scientific study. In the past 100 years, it has featured as the subject of thousands of research papers, dating back as early as 1935 [1]. It is value for its ultraviolet absorbance, chemistry, piezoelectricity and luminescence at high temperatures. ZnO has penetrated far into industry, and is one of the critical building blocks in today's modern society [2].It can be found in paints, cosmetics, plastic and rubber manufacturing, electronics and pharmaceuticals.

Recent improvements in the quality and control of conductivity in bulk and epitaxial ZnO have increased interest in the use of this material for short wavelength light emitters and transparent electronics [3, 4]. Other advantages of ZnO are the resistance to high energy radiation, which makes it suitable for space applications, as well as the stability and amenability to wet chemical etching, which can be exploited for the fabrication of small size devices [5] .Zinc oxide is a direct band gap semiconductor with 3.37 eV energy gap at room temperature. The optical properties of ZnO, which are studied using photoluminescence, absorption and photoconductivity, reflect the intrinsic direct band gap and strongly exciton binding energy (60 meV) [6].

In the present work, the pulse laser deposition method has been used to deposit pure (undoped) and Cu-doped ZnO thin films at different Cu concentrations. The effect of Cu doping on the optical properties of ZnO films has been investigated.

II. EXPERIMENTAL PROCEDURE

Pure zinc oxide powder and different doping concentrations for Cu with high purity (99.999%) were prepared by pressing them under 5 Ton to formed a target with 2.5 cm diameter and 0.4 cm thickness. It should be as dense and homogenous as possible to ensure a good quality of the deposit.Prior to deposit films, the glass substrates were cleaned in with cleaner solution, distilled water and followed by alcohol using ultrasonic bath.

ZnO:Cu thin films were prepared by using pulse laser deposition (PLD) technique (Nd: YAG (HuafeiTongda Technology—DIAMOND-288 pattern EPLS) SHG Q-switching beam) which carried out inside a vacuum chamber generally at (10^{-3}Torr).

The thickness of prepared films was about 130nm which measured by Michelson interferometer. An optical transmittance and absorptance spectra were recorded, at room temperature, in the wavelength range 300-1100nm using OPTIMA SP-3000 UV-VIS spectrophotometer.

The absorption coefficient (α) of pure and Cu-doped ZnO thin films was calculated from the optical transmittance (T) spectrum measurements for t film thickness using the formula [7]:

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

The energy gap and optical constants were calculated as a function of different Cu concentrations.

III. RESULTS AND DISCUSSION

Optical measurements for deposited ZnO films on glass substrate by pulse laser deposition with different doping concentrations with Cu (0, 2, 4, 6, 8 and 10) % is carried out in the wavelength range 300–1100 nm at room temperature (RT). Figure (1) shows the room temperature transmittance spectra for samples doped with different Cu concentrations.

All spectra show good transparency, the transmittance pattern of all deposited thin films increases with increasing of wavelength (λ). On the other hand the transmittance decreases with the increase of Cu concentration which means increase in the reflection and absorption..This result is in agreement with results shown by Singh et al.[8] and Romero et al. [9] .It is obvious from the figure that the transmittance for pure ZnO film at wavelength equal to 500nm was found to be 82.22%,while it was 16.17 for doped thin ZnO film with 10%Cu.

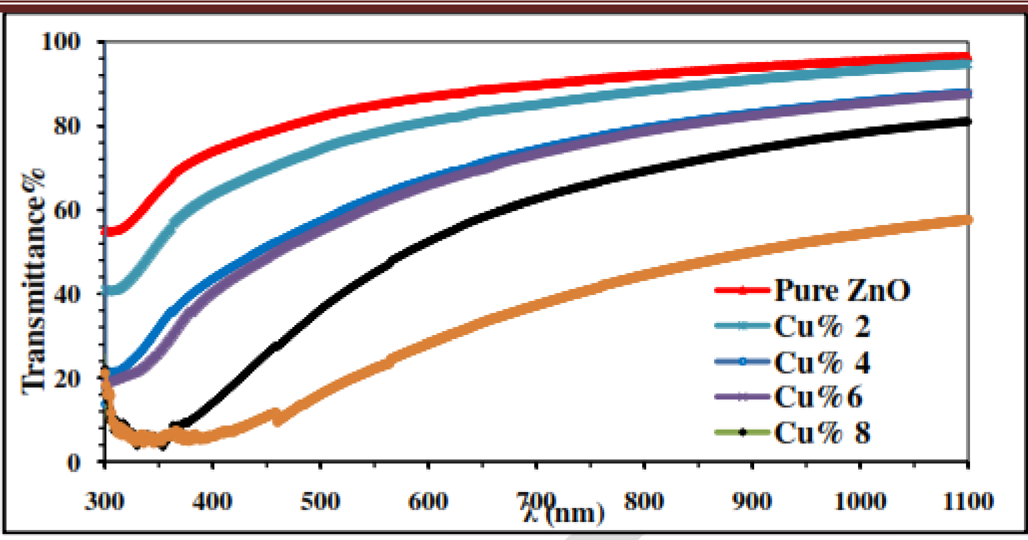

Fig. 1. Transmittance variation with the wavelength for pure ZnO films and doped with Cu at different concentrations (2, 4, 6, 8 and 10) %.

Figs.(2) illustrates the variation of absorption coefficient with wavelength for ZnO thin film at different doping Cu concentrations. All spectra illustrate absorption coefficient pattern of all deposited pure and doped thin ZnO films decrease with increasing of wavelength (λ) from 400 to 1100 nm. On the other hand the absorption coefficient increases with the increase of Cu concentration which means decrease in the reflection and transmition. Another noticeable remake is that the peaks of absorption coefficient pattern shifts to higher wavelength i.e. shorter photon energy (red shift) with increasing Cu concentrations. Table (1) illustrates all values of optical parameters.

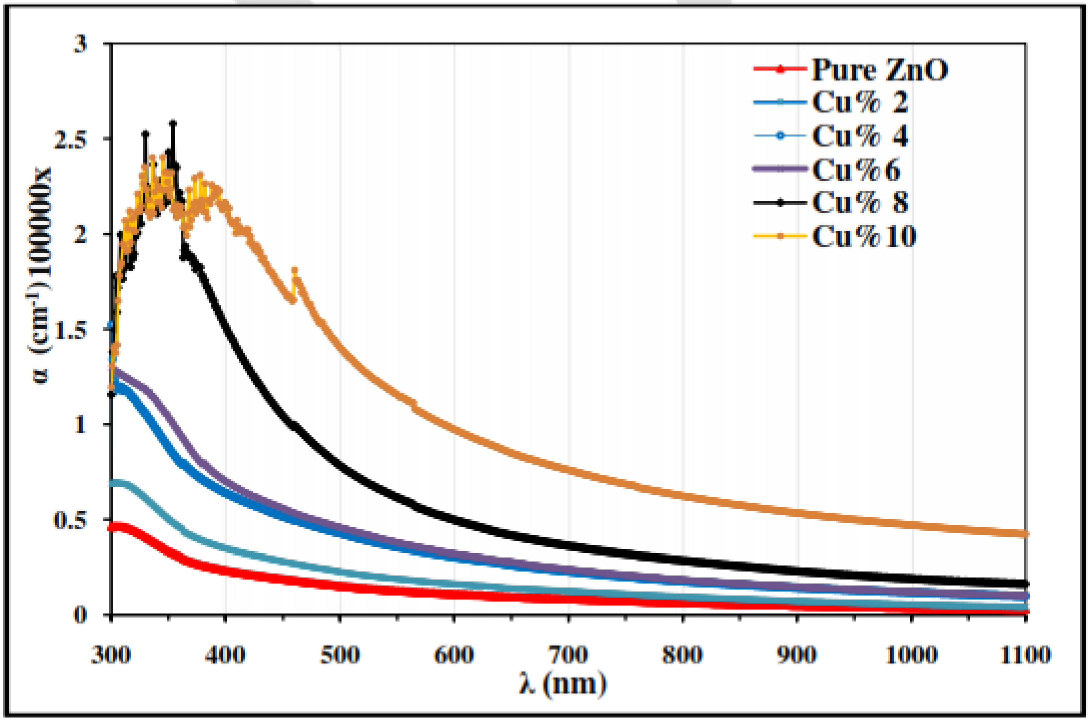

Fig.2. Variation of absorbance coefficient with the wavelength for pure ZnO films doped with Cu at different concentrations (2, 4, 6, 8 and 10) %.

The optical energy gap values (E_g) for thin ZnO films on glass have been determined by using Tauc equation [10].

$$\alpha h\upsilon = A\left(h\upsilon - E_g\right)^r$$

where hυ is the photon energy, A is inversely proportional to amorphousity and r is used to find the type of the optical transition by plotting the relations $(\alpha h\upsilon)^{1/2}$,$(\alpha h\upsilon)^{1/3}$,$(\alpha h\upsilon)^{2/3}$,and $(\alpha h\upsilon)^2$ versus photon energy (hυ).The energy gap is then determined by the extrapolation of the linear portion at $(\alpha h\upsilon)^2 = 0$. It is found that the relation for r=1/2 yields linear dependence part at which the absorption coefficient $\alpha \geq 10^4 cm^{-1}$, which describes that thin ZnO film has the allowed direct transition. This result is in agreement with result had shown by Alias et al. [4].

The variation of $(\alpha h\upsilon)^2$ as a function of photon energy for pure and Cu doping thin ZnO film at different of Cu concentration has been plotted in Fig. (3).This figure reveals that the increasing of Cu concentrations from 0 to 10% leads to decrease the energy gap from approximately 3.3 eV to 2.2 eV respectively. This can be attributed to increase the mineral content .This result is in agreement with Bouhssira et al.[11].This decrease in E_g value after doping with Cu is attributed to that Cu introduces interband energy levels in the band gap of thin ZnO films which were responsible for the shift of optical E_g to lower band gap energy.

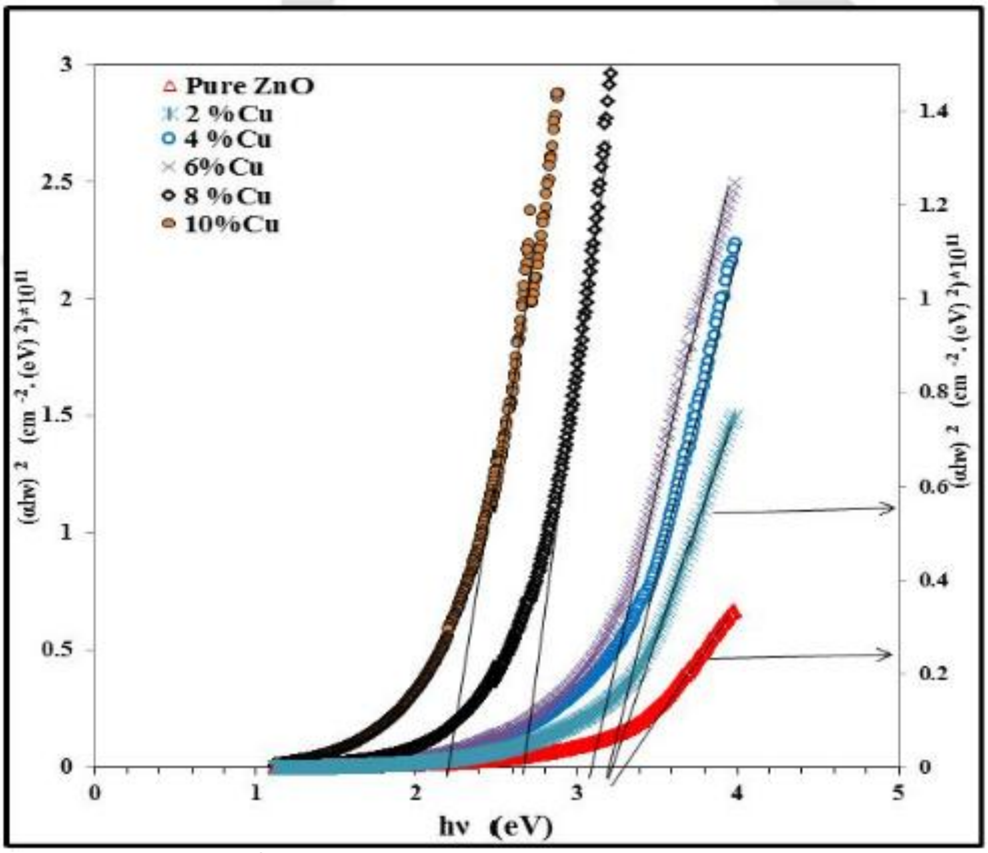

Fig.3. The variation of $(\alpha h\upsilon)^2$ versus photon energy for pure ZnO films doped with Cu at different concentrations (2, 4, 6, 8 and 10) %.

It is important to determine the optical constants of thin films such as refractive index (n), extinction coefficient (k), and the real (ε_r) and imaginary (ε_i) parts of dielectric constant.

Fig.(4) shows the variation of extinction coefficient (k= α λ/4π) with wavelength at different Cu doping ratio. The extinction coefficient depends mainly on absorption coefficient; for this reason, the behavior of it is similar for absorption coefficient i.e., the increasing of extinction coefficient with increasing photon energy because the absorption is increased and the peak shift to higher wavelength (red shift) with increasing Cu doping concentration.

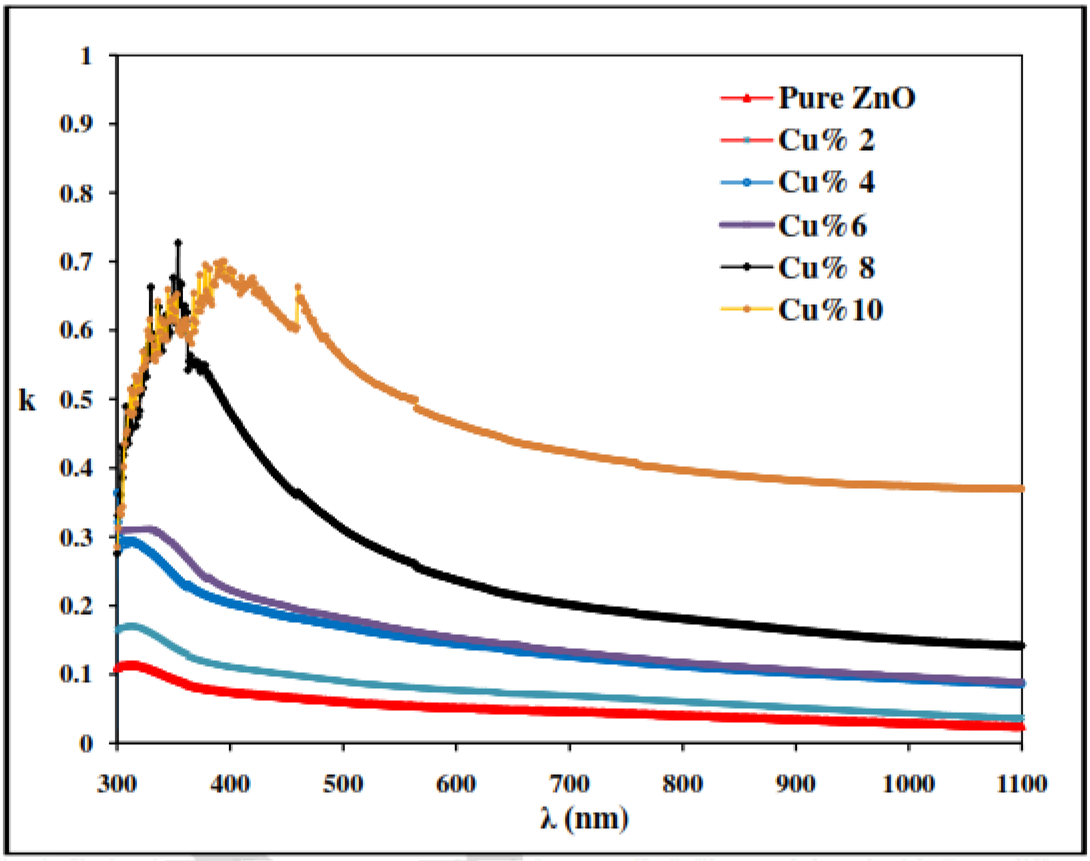

Fig. 4. Extinction coefficient versus wavelength for pure ZnO films and doped with Cu at different concentrations (2, 4, 6, 8 and 10) %.

The index of refraction of pure and Cu doped thin CdTe films was estimated from the reflectance (R) data using the relation [12]:

$$n = \sqrt{\frac{4R}{(1-R)^2} - k^2} - \frac{R+1}{R-1}$$

The variation of the refractive index versus wavelength in the range 300–1100 nm, for deposited thin ZnO films on glass with different Cu doping ratio has been shown in Fig. (5). It is clear from this figure that the refractive index in general increases with increasing of doping concentration with Cu . This behavior is due to the decrement in energy gap. Another noticeable remark is that the peak of curves is shifted to shorter photon energy (red shift).

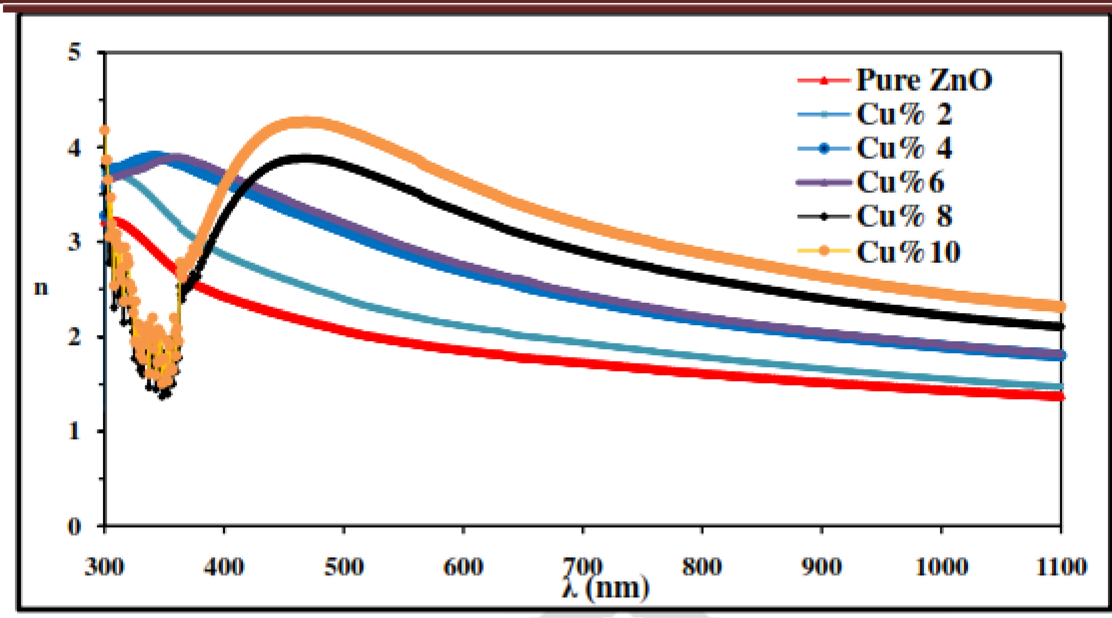

Fig. 5. The variation of refractive index with the wavelength for pure ZnO films and doped with Cu at different concentrations (2, 4, 6, 8 and 10) %.

The real and imaginary parts of dielectric constant were evaluated using the formulas [13]:

$\varepsilon_r = n^2 - k^2$

$\varepsilon_i = 2nk$

The variation of the real and imaginary parts of the dielectric constants values versus wavelength have been shown in figures (6 and 7) for deposited pure and Cu doped thin ZnO films on glass with different doping concentrations. Their value are decreased with wavelength more than 500nm.The variation of the dielectric constant depends on the value of the refractive index. By contrast, the dielectric loss depends mainly on the extinction coefficient values which are related to the variation of absorption.

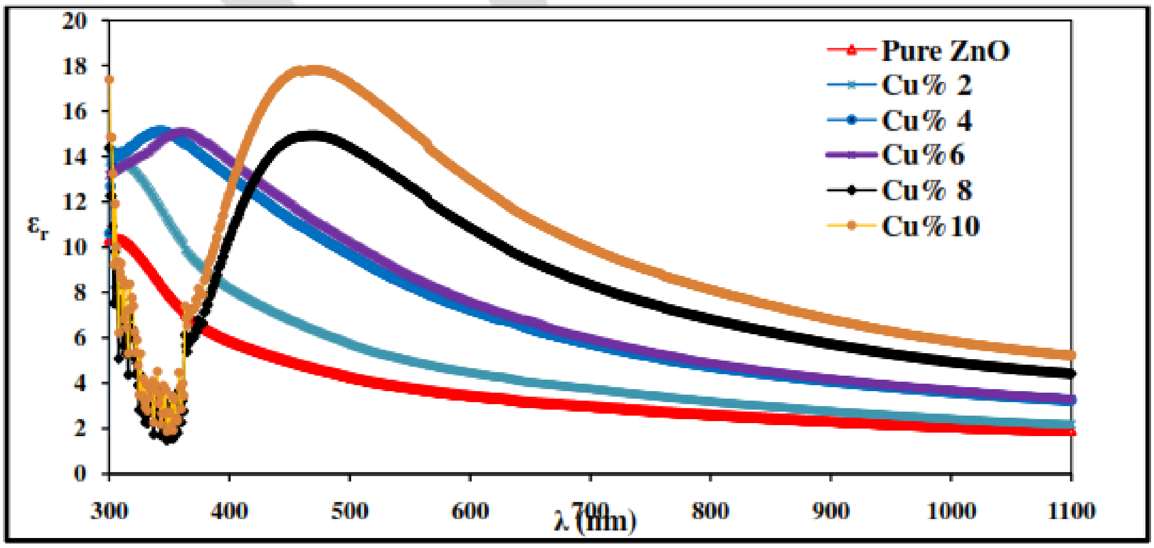

Fig.6. The variation of ε_r with the wavelength for pure ZnO films and doped with Cu at different concentrations (2, 4, 6, 8 and 10) %.

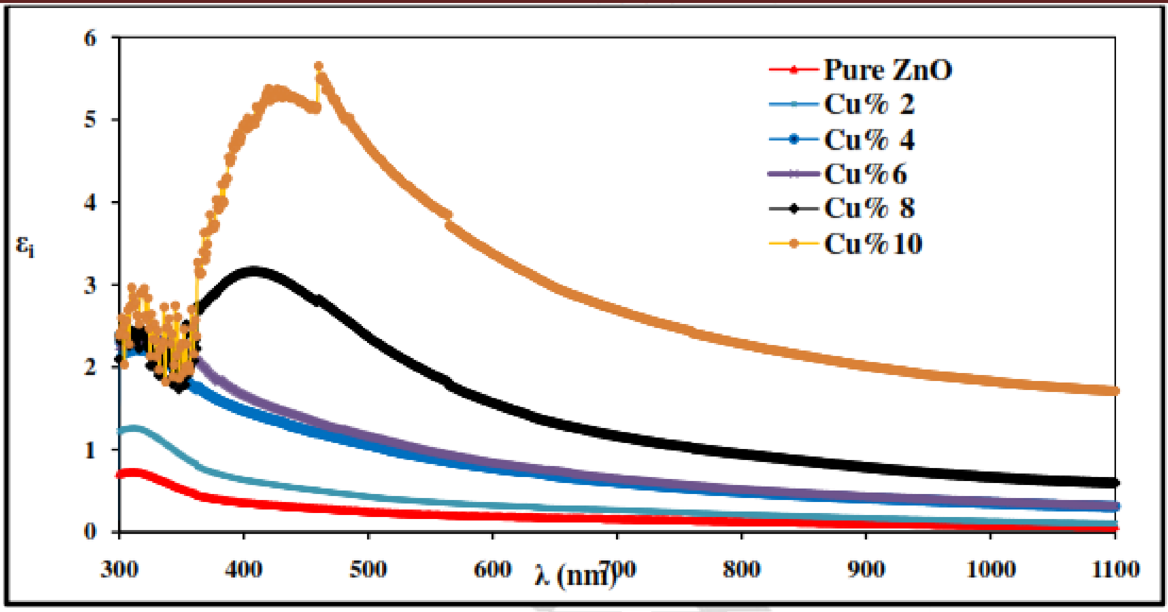

Fig.7. The variation of ε_r with the wavelength for pure ZnO films and doped with Cu at different concentrations (2, 4, 6, 8 and 10) %.

Table (1) shows the optical constants for deposited pure and Cu doped thin ZnO films on glass with different doping concentrations(0, 2, 4, 6, 8 and 10%) at λ = 500 nm and the optical parameters values for these prepared samples. This Table illustrates that the values of α, k, n, ε_r and ε_i increase with increasing Cu dopant concentrations, whereas the behavior of T and E_g are opposite i.e., they decrease with increasing Cu doping concentrations.

Table .1 The optical parameters for pure and doped ZnO films at different Cu doping concentrations.

doping %		T% at λ = 500 nm	α (cm^{-1})*10^5 at λ = 500 nm	E_g^{opt} (eV)	k at λ = 500 nm	n at λ = 500 nm	ε_r at λ = 500 nm	ε_i at λ = 500 nm
Cu	0	82.22	0.151	3.30	0.060	2.065	4.261	0.248
	2	74.56	0.226	3.20	0.090	2.395	5.728	0.431
	4	57.40	0.427	3.15	0.170	3.114	9.667	1.059
	6	55.27	0.456	3.10	0.182	3.199	10.202	1.162
	8	36.23	0.781	2.65	0.311	3.807	14.397	2.368
	10	16.17	1.402	2.20	0.558	4.188	17.226	4.673

IV. CONCLUSIONS

Optical properties of pure and Cu doped thin ZnO films deposited by pulse laser deposition technique have been studied as a function of different Cu dopant concentrations. The outcome of this investigation can be summarized as follows:

- The transmittance increases with increasing wavelength while it decreases with increasing Cu doping concentrations.

- The energy gap decreases from 3.3 to 2.2 eV with the increase of Cu doping concentrations from 0 to 10 wt%
- The optical constants values(α, k, n, ε_r and ε_i) increase with increasing Cu dopant concentrations,

References

[1] C. W. Bunn, "The lattice-dimensions of zinc oxide," Proc. Phys. Soc. London, 835, 1935,47.

[2] D. R. Lide (editor), "CRC Handbook of Chemistry and Physics", CRC Press, New York, 73rd edition, 1992.

[3] D. Look, "Recent advances in ZnO materials and devices". Materials Science and Engineering B, 80, 2001, 383.

[4] M.F.A.Alias, R.M.Aljarrah ,H.Kh.Al-Lamy and K.A.W.Adam ,"Investigation the Effect of Thickness on the Structural and Optical Properties of Nano ZnO Films Prepared by d.c Magnetron Sputtering", International Journal of Application or Innovation in Engineering & Management (IJAIEM) ,2,7, 2013, 198.

[5] W.P. Shen and H.S. Kwok , " Crystalline Phases of II-VI Compound Semiconductors Grown By Pulsed Laser Deposition ", Appl. Phys. Lett., 65,17,1994,2161.

[6] D. Norton, Y. Heo, M.P. Ivill, S. Pearton, M. Chrisholm, and T. Steiner., "Zinc-oxide: Growth, doping and processing", Materials Today, Review Feature, 2004, 34

[7] Z. Rizwan, A. Zakaria, M. Ghazali, A. Jafari, F. Ud Din, and R. Zamiri, Int. J. Mol. Sci., 12 , 2011, 1293.

[8] A. Singh, M. Kumar, R. Mehra, A. Wakahara and A. Yoshida, J. Indian Inst , "Al-doped Zinc Oxide (ZnO:Al) Thin Films by Pulsed Laser Ablation". Sci. Sept., 81, 2001, 527.

[9] R. Romero, M. Lopez, D. Leinen, F. Martin and J. Ramos, Material Scince and Engineering, B 110, 2004,87.

[10] J. Tauc, "Amorphous and Liquid Semiconductors", Plenum Press, London and New York (1974).

[11] N.Bouhssira, S.Abed, E.Tomassella, J.Cllier M. Aida and M. Jecquet, Applied Surface Science,252,2006,5594.

[12] S. Aksoy, Y. Caglar, S. Ilican, and M. Caglar, Optica Applicata, XL,1 ,2010,7

[13] L. Kazmerski, "Polycrystalline and Amorphous Thin Films and Devices", Academic Press 1980.