Effect of Doping with Cobber on Optical Properties of Zinc Oxide Thin Films Prepared by Sol-Gel Method

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Abstract:
Thin films of cobber doped ZnO have been prepared on glass substrate using the Sol–Gel spin coating technique. The effect of doping percentage of Cu to ZnO thin films on the optical properties and optical constants are concluded from absorption and transmission measurements, which are obtained by using double beam UV-Visible 1800 spectrophotometer in the wavelength (300-800)nm. It was found that the transmittance increases with increasing the doping percentage (0.01, 0.02, 0.03 and 0.04)mol%, while the Absorbance is decreased. The optical energy band gaps have been evaluated and their values seem to be decreased by increasing the doping concentration level in the range(0.01, 0.02, 0.03)mol% followed by a rise with increasing the doping level to 0.04mol%.

Keywords: Sol-Gel, semiconductor, doping, optical energy band gap, optical properties

Introduction

The research concentrated on ZnO semiconductor material for many decades, due to its convenient properties and prospects in optoelectronic applications. The availability of high-quality ZnO thin film and a largeexciton binding energy (60meV),besides its simple crystal-growth technology[1], has made it one of the most candidates for many applications.

Although research focusing on ZnO goes back many decades, it gained more interest after recent work has predicted that ZnO-based semiconductors can present ferromagnetic behavior besides p-type conduction at room temperature when doped with transition metals such as Mn[2,3]. In addition, by controlling the doping level electrical properties can be changed from insulator through n-type semiconductor to metal while maintaining optical transparency that makes it useful for transparent electrodes in flat-panel displays and solar cells. There have been a number of publications which appear to confirm these predictions[1].
Applied ZnO materials should be stable in hostile environment containing acidic and alkali solutions, oxidizing and reducing atmos-pheres and elevated temperature.These properties are strongly related to the methods of elaboration. High quality ZnO thin films can be grown at relatively low temperature less than 700^{o}C[1], by a number of methods including; pulsed laser deposition, dc reactive magnetron sputtering, atomic layerdeposition, sol–gel spin coating, RF magnetron sputtering, metal organic chemical vapor deposition and chemical spray pyrolysis [4-8]. Among these methods, the Sol-Gel method with spin coating technique has applied in this work.
This study is focused on the growth of cobber doped ZnO thin films of different doping concentration levels deposited on glass substrate by sol-gel process spin coating. In addition, studying Cu doping concentration level on the optical properties.

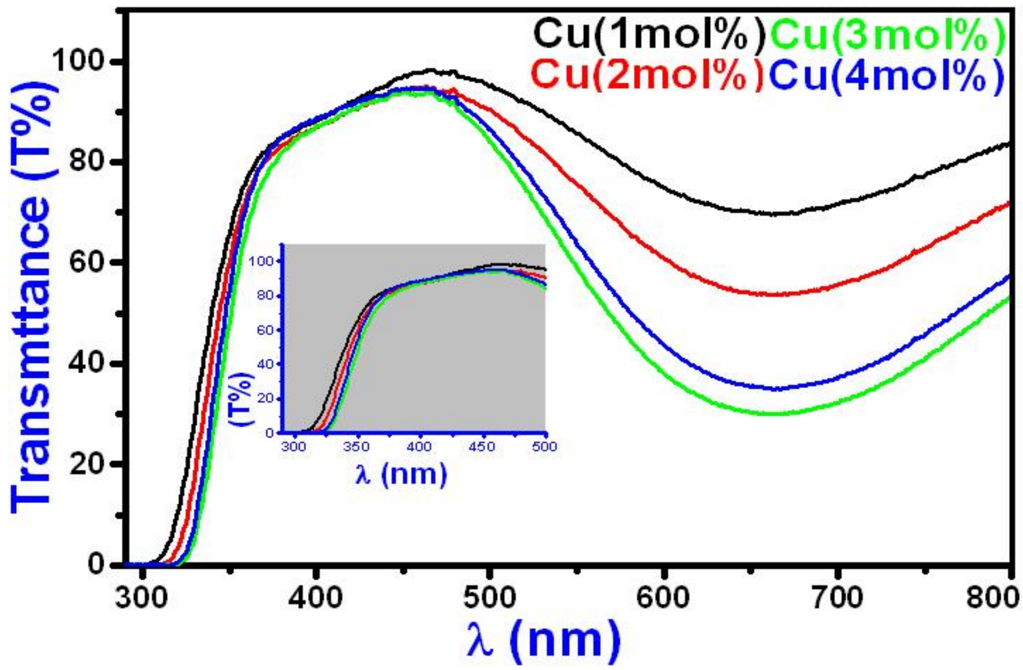
Material and Methods

Samples preparation:

Cobber doped ZnO thin films were fabricated using the Sol–Gel spin coating technique. The initial stock solution was prepared from Zinc Acetate Dehydrate Zn(CH3OO)2.2H2Oof purity 99.5% and IsopropanoleCH3CH(OH)CH3, at 0.1 M concentration at room temperature. The solution was stirred on a magnetic stirrer with a hot plate for an hour. Some drops of Diethanol amine (DEA) C2H5-OH were added drop by drop to obtain a clear transparent solution with continues rotating for two hours. The doping was achieved by adding cobber nitrate Cu(NO3)2.The growthwas performed with a slow spray rate on a circular well cleaned glass substrate of 10mm diameter and 1mmthickness.The thickness of the obtained films was measured by the Gravimetric methodof about (300±20)nm. The optical properties of ZnO films were carriedout with a double beam UV–Visible 1800 spectrophotometer.

RESULTS AND DISCUSSION

The prepared samples have been loaded into the spectrophotometer, the transmittance and absorbance spectra have been collected. Figures (1) and (2) are showing changes in transmittance and absorbance spectrums of doped ZnO:Cu thin films of different doping concentration levels (0.1,0.2,0.3,0.4)mol%, as afunction of photon wavelength. Figure(1) indicates that;in the visible light range(290-500)nm, all ZnO:Cu thin films show high transmittance exceeds 95% and a reduction in transmittance with increasing doping level. This behavior appears more clearly in the range(450-800)nm.



Figure(1) The transmittance of the deposited ZnO:Cu thin film versus wavelengthfor different doping concentration levels.

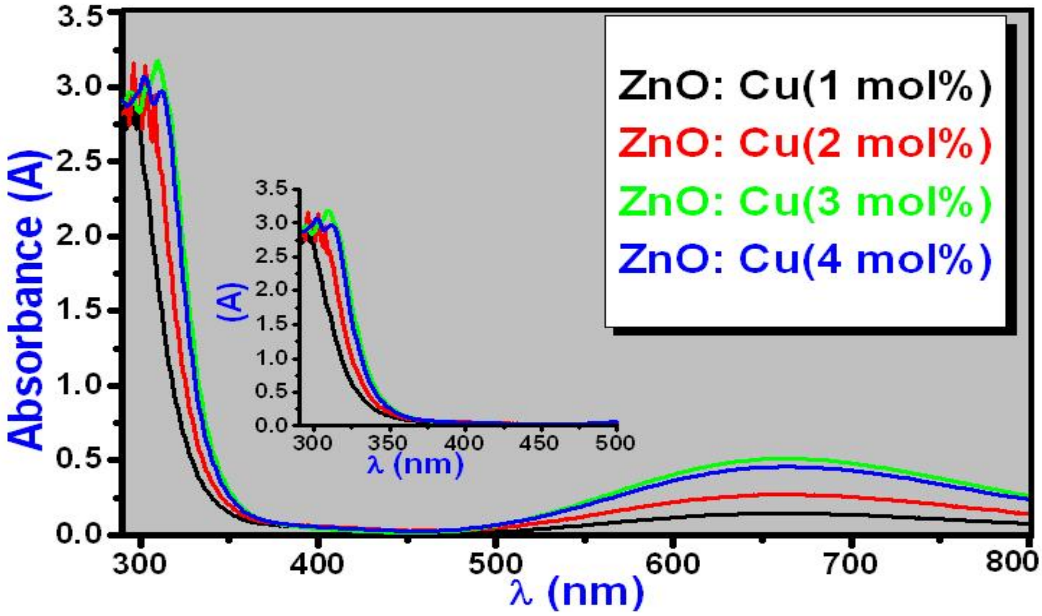
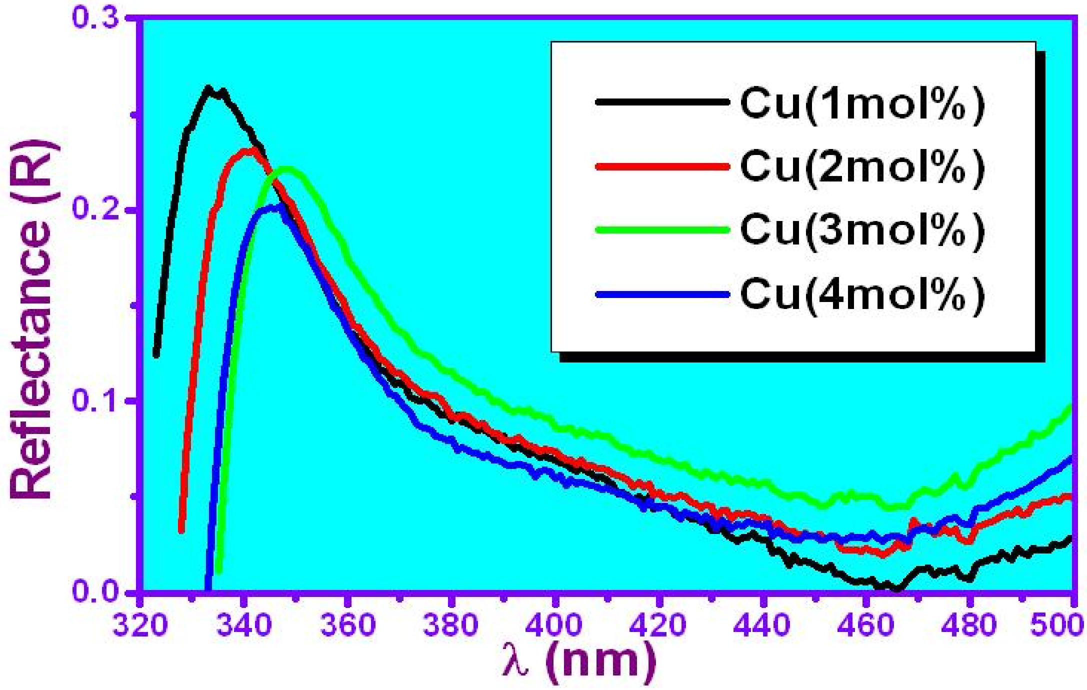


Figure (2) The absorbance spectrum of the deposited ZnO:Cu thin film versus wavelength for different doping concentration levels.

However, figure(2) indicates absorbance increase with rising doping percentage. These interesting changes can be attributed to enrolling of Cu atoms in the ZnO structure and may point to an increase in the localized impurity levels in the energy band gap of ZnO as the concentration of Cu is raised, the same behavior was also observed by Choi and Kim [9] and Bacaksizet al. [10] .

Although the doping increase causes rise in absorbance, the highest value observed at doping level of 0.3mol%. In addition, the lowest transmittance noticed of thesame film, which means that there is anirregular behavior obtained with increasing doping concentration level to 0.4mol%. This behavior can be explained according to Burstien -Moss effect[11].

The reflectance as a function of the wavelength has been calculated. The obtained spectrum is shown in figure(3). It shows a reduction in the reflectance with increasing the photon wavelength. The maximum reflectance can be observed at low wavelengths which equivalent to fundamental absorption edge. In addition, reflectance decreases with increasing Cu doping concentration level and a clear shift of the fundamental absorption edgeto lower energy can be observed with rising concentration level of Cu(0.1, 0.2, 0.3)mol%. However, this behavior is inverted by increasing doping level to 0.4mol%.

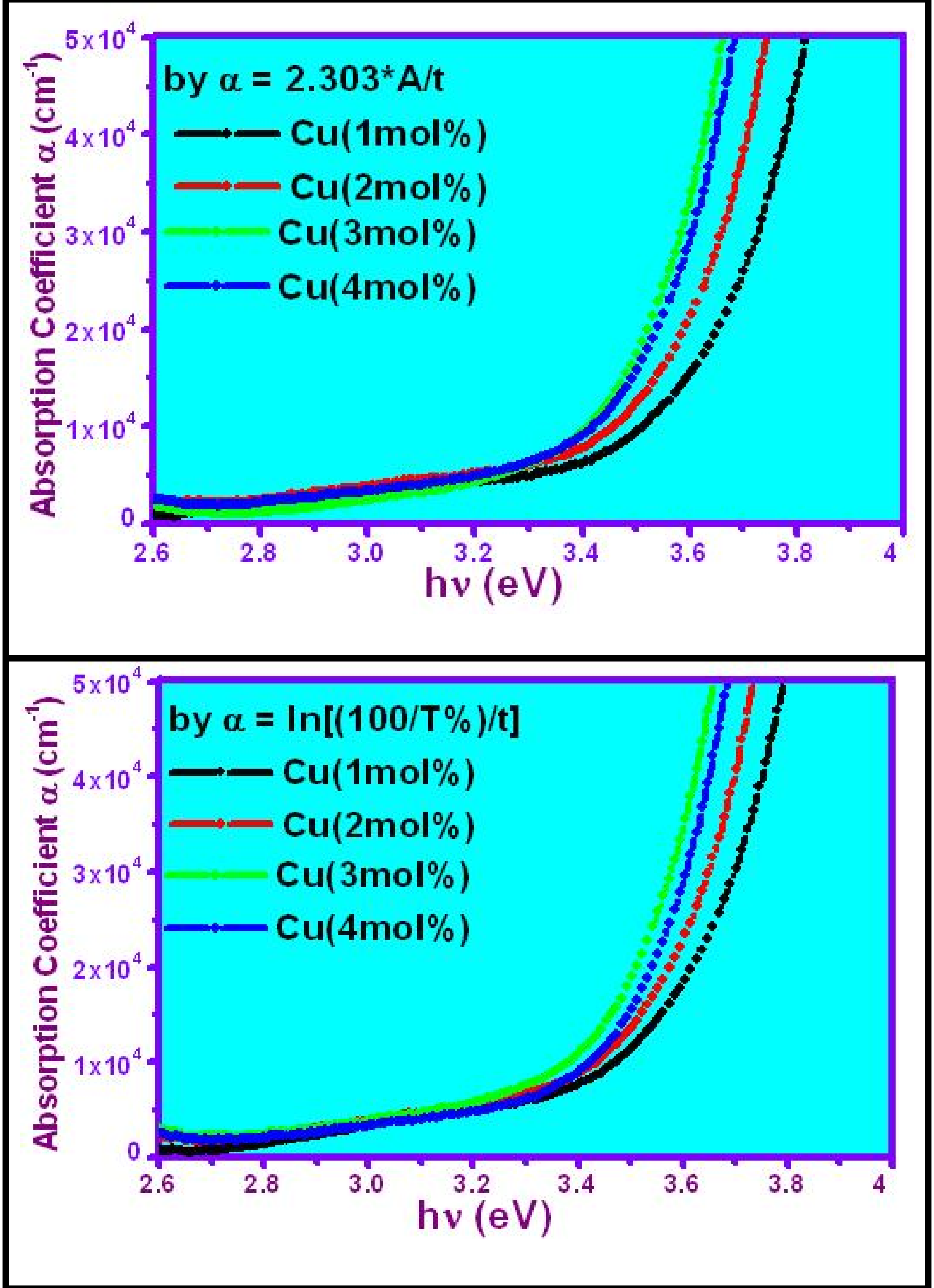


Figure(3) Reflectance versus wavelength of the incident photon for different doping concentration level of Cu.

The absorption coefficient has been calculated using the relation [α=2.303A/t] and Bouger-Lambert law [α = ln(100/T%)/t]. Absoption coefficient spectrum as a function of photon energy is indicated in figure(4(a,b)). The spectra are showing a slight rise of α with increasing photon energy up to 3.1eV followed by an exponential increase of α with increasing photon energy which is called Urbachtail.The spectral dependence of the absorption coefficient(α) and photon energy(hν) is known as Urbach empirical rule, which is given by the following equation:[$\alpha = \alpha_o e^{\frac{h\vartheta}{E_u}}$], where α_0 is a constant and E_u denotes the energy of the band tailor Urbach energy.

It can be seen from figure (4) that the film of 3mol% has the highest absorption coefficient.

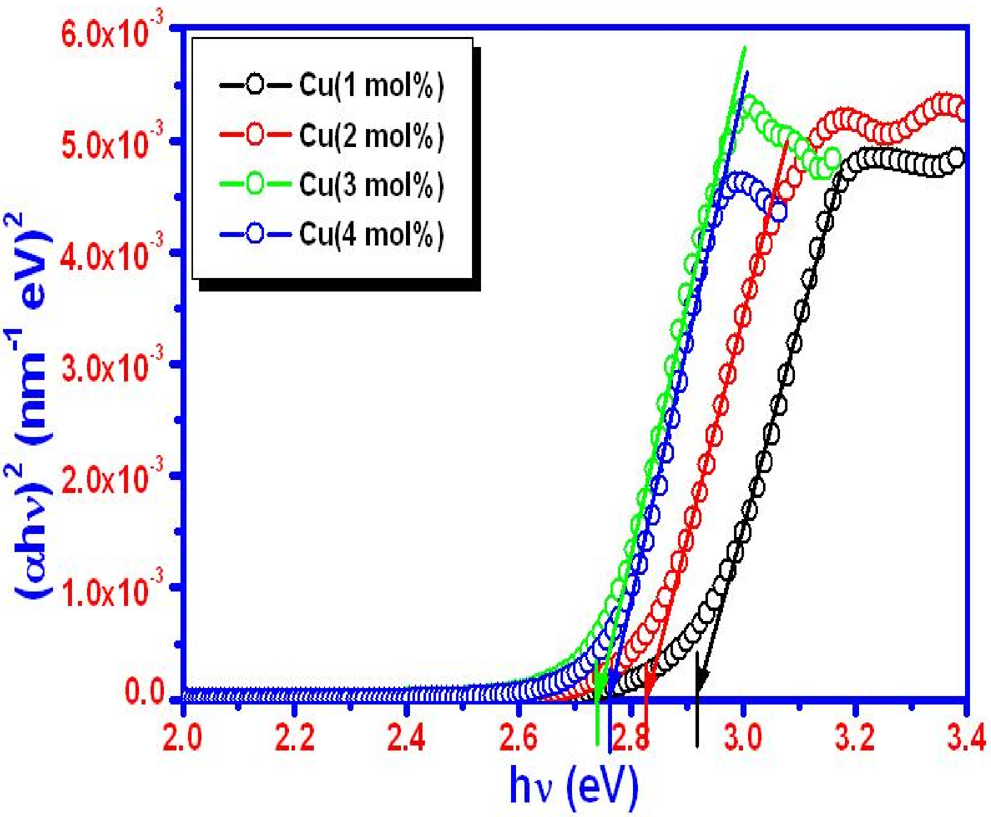
The fundamental absorption edge, which corresponds to the electron excitation fromvalence band top to conduction band bottom is usually used to determine the value of directoptical band gap using the Tauc relationship [11] ; $(\alpha h\nu)$ 2=A $[h\nu - Eg]$
Where A is a constant which is inversely propostionaltoamorphousity.Figure(5) shows the plot of (αhυ)2versus photon energy of the films under investigation.
The calculated optical energy band gap valuesof doped ZnO:Cu thin films are showing in figure(4) and table(1). They indicate that increasing Cu doping concentration level (0.1, 0.2, 0.3)mol% leads to a reduction in the optical energy band gap which can be explained due to



Figure(4,a-b) Absorption coefficient versus photon energy for different doping concentration level of Cu.

inserting localized energy states below conduction band. These states can be occupied by moving electrons from valence band. However, further increase in the Cu to 0.4mol% results in aslight rise in the optical energy band gapand this variation could be attributed to Burstein–

Moss shift[11,12]. Whereby, conduction band bottom is filled with electrons of donor atoms at room temperature. Therefore, moving electrons from valence band require a slight higher energy to be settled in the conduction band.



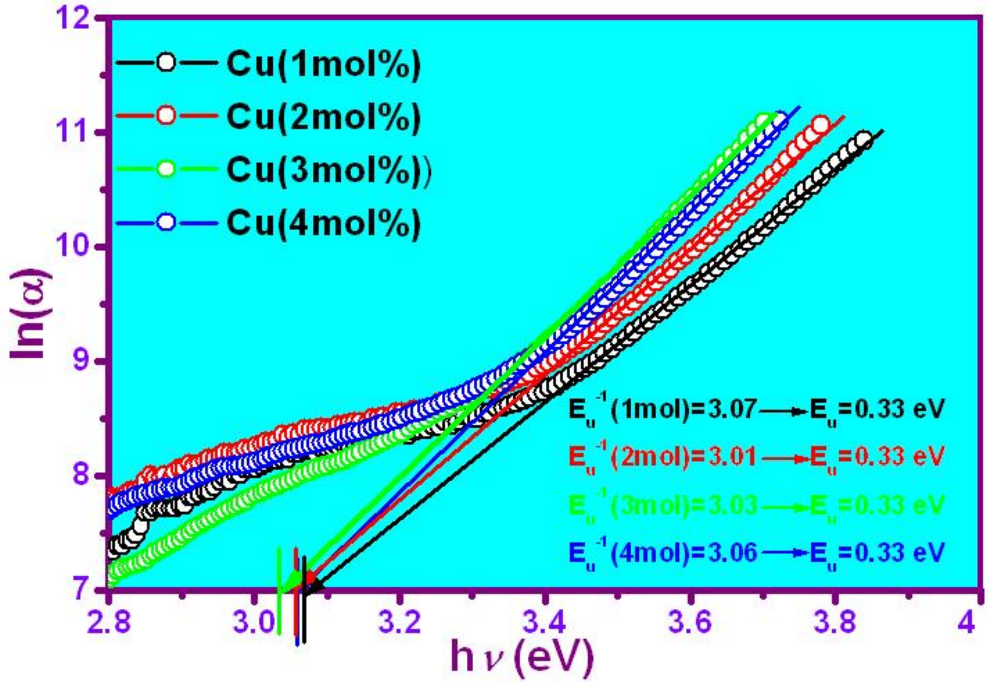
Figure(5) Dependence of $(\alpha h\upsilon)^2$on the photon energy of doped ZnO:Cuthin films.

According to the evaluated values of optical energy band gap, it is obvious that the film of 3mol% has the lowest energy band gap. Therefore, the highest absorption coefficientof this film which is shown in figure(4) can be explained.

Table(1) Evaluated optical energy band gap of different concentration levels ZnO:Cu thin films.

Cu doping level	1mol%	2mol%	3mol%	4mol%
Optical energy gap Eg (eV)	2.92	2.83	2.74	2.76

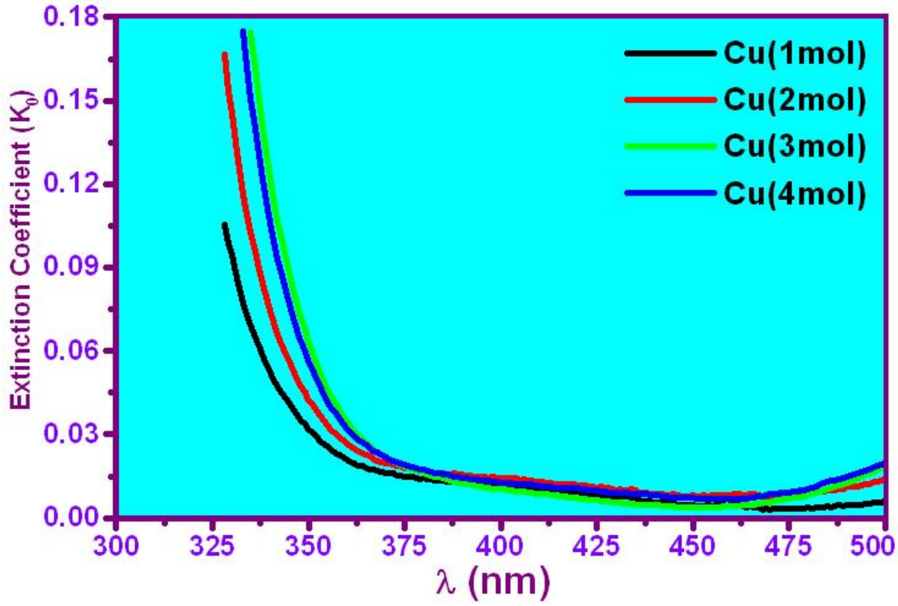
Urbach energy is one of the important parameters in thin films which indicates the degree of crystalline in the structure(amorphous or disorder) due to the formation of localized states with energies at the boundaries of the energy band gap.
According to the equation $ln\,\alpha = ln\,\alpha_0 + (\frac{h\vartheta}{E_u})$, the Urbach energy can be obtained from the slope of the straight line of plotting ln(α) against the incident photon energy.
As shown in figure(6) Urbach energy values of doped ZnO thin films of different concentration levels of Cu are almost having the same value E_u~0.33eV.



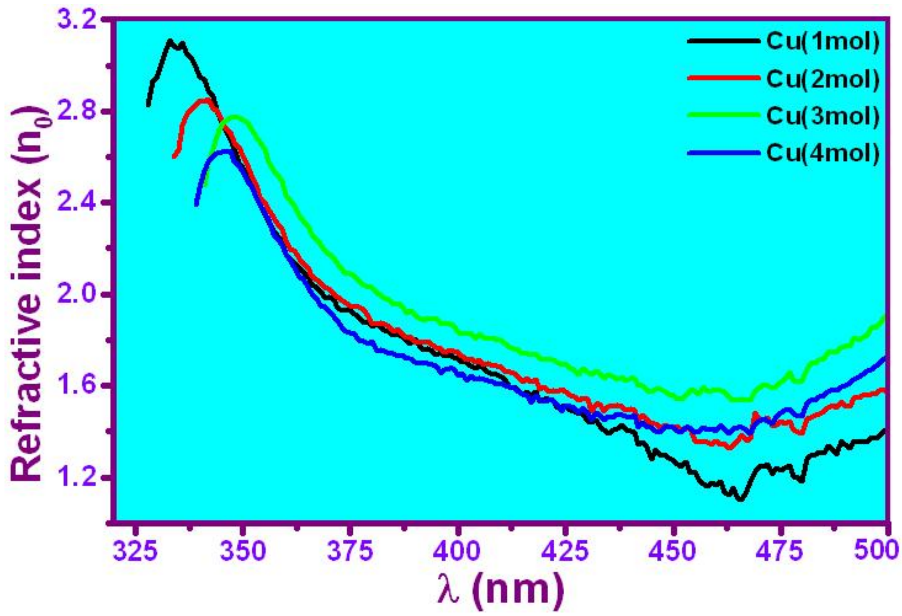
Figure(6) Urbachenergyversus photon energy for different doping concentration level of Cu.

The extinction coefficient(K_0) (the imaginary part of the refractive index[14]) of the thin films-has been calculated by the relation[13]: $K_0 = \frac{\alpha\lambda}{4\pi}$. Figure(7) displays the extinction coefficient as a function of wavelength for whole Cu doped ZnOthin films. The extinction coefficient of whole samples have a peak at low λ , which decrease with increasing wavelength. In addition, the maximum values of $K_0$are obtained by the film of 3mol%, which is having the narrowest energy band gap.
Refractive index(n_0) has been calculated by using the equation[13];

$n_0 = \left[\left(\frac{(1+R)}{(1-R)}\right)^2 - (K_0^2 + 1)\right]^{1/2} + \frac{1+R}{1-R}$,Figure(8) represents refractive index variations as a function of wavelength of doped ZnO:Cuthin films of different concentration levels. It can be noticed that $n_0$is having a peak at low wavelength and decreases with rising λ and n_0 curve is similar to the reflectance curve.



Figure(7) Extiction coefficient as a function of wavelength for Cu doped ZnO of different concentration levels.

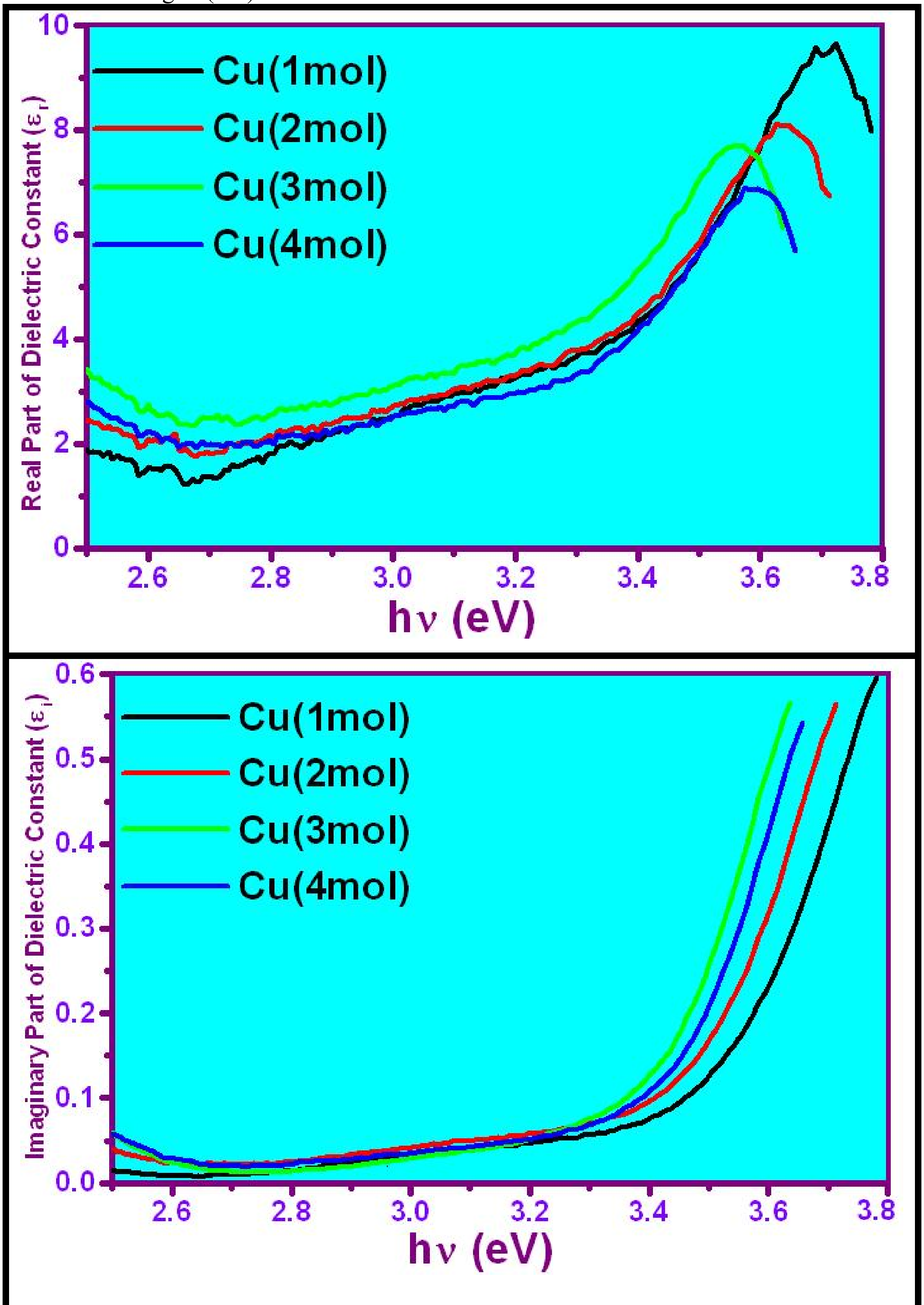


Figure(8) Refractive index as a function of wavelength for doped ZnO:Cuof different concentration levels.

Photon interactionwithmaterial may causes charge polarization. The polarization normally described by the complexdielectric Constant(ε), whereby $\varepsilon = \varepsilon_r + \varepsilon_i$.Both real part ($\varepsilon_r$)and imaginary part($\varepsilon_i$)have been calculated according to the following equations respectively; $\varepsilon_{r=}n_0^2 - K_0^2$, $\varepsilon_i = 2n_0K$, for every concentration level. Whereas,ε_r represents the measure of polarizibilty and ε_r represents value of the loosing energy due to movement of polarized dipoles as a heat.

Figures(9-a,b) show changes in real part and imaginary part values of dielectric constant as a function of photon energy of Cu doped thin film of different concentration levels.Whereas both $\varepsilon_r$andε_i of the prepared thin films increase with rising hν. In addition, the figure(9-a) is showing that doped thin film polarizibilty is decreased with increasing doping concentration level. Whereby, the lowest concentration level thin film is having the highest polaroizibilty.

On the other hand, this film is loosing the minimum energy as a heat compared with other films as shown in figure(9-b).



Figure(9) Dielectric constant as a function of wavelength for doped ZnO:Cu of different concentration levels(a) real part, (b) imaginary part.

Conclusion:

Doped ZnO:Cu thin films of different percentages have been prepared by Sol-Gel spin coating technique. The analysis of UV-visible spectra have shown that the transmission of the Cu doped films were very high and exceeds 95% in the wavelength range (350-500)nm. Increasing doping level leads to a reduction in transmittance. On the other, it causes a rise in absorbance. In addition, it causes a shift of the fundamental absorption edge to higher wavelength values.As a result a reduction in optical energy band gaps is observed. The results show that all the deposited thin films have direct optical energy band gaps lying inthe range of (2.74-2.94)eV. In addition, data obtained from absorption and transmittance spectra are used to determine some other optical parameters.

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