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Electronic Transitions And Optical Properties Of ZNO:In Thin Films

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***Abstract*—Undoped Zinc Oxide and Indium doped Zinc Oxide with different doping percentage (1 - 7 step 2) % have been deposited on a glass substrates at a substrate temperature of (400 ˚C) . The thickness of the deposited films found to around (300±25) nm. The optical properties were achieved by recording absorbance and transmittance in the wavelengths range (400 – 900) nm. The optical energy gaps for the allowed direct transitions was calculated , and the value was increased with increasing in doping percentage (3.14 – 3.20) eV . the absorbance that decrease with the increase in doping percentage . The transmittance increased to (95%) when the doping percentage was 7% and (reflectance , extinction coefficient , refractive index , real and imaginary parts of dielectric constant) were decreased by increasing in the doping percentage .**

Keywords—Optical properties , ZnO:In thin films , Chemical Spray Pyrolysis , direct allowed transition

Introduction:

Zinc oxide is a transparent conducting oxide with broad uses non-toxic material , low solubility in water , has a high permeability , reflectivity of light in the IR region abundance in nature in addition for being and high chemical stability [1-4]. There are several techniques used for the deposition of thin films , including the method of thermal evaporation , of Sol- gel method, Chemical Spray Pyrolysis**.** The most appropriate method for the fabrication of thin-film is the method of chemical spray pyrolysis [5]. It is simple technique low cost and can be obtained for a large area . The study of nature of these films membranes through by the knowledge of it optical properties and through the study of absorption spectrum in visible region .The electronic transition from of the highest peak in the valence package to lower valley in the valence band are deduced from the study of absorption spectrum in the fundamental absorption region .Which gives an idea about the value of the absorption coefficient and the optical energy gap and the energy gap of Zinc oxide is (3.2 eV) ,which in turn lead to weak transmission in the short wavelengths region but doping gives the possibility to control the characteristics of this material and make it more convenient when it used in the applications of solar cell and thermal mirrors [6-8].

Experimental work:-

Thin films of Zinc oxide and Indium doped Zinc oxide were prepared using the method of chemical spray pyrolysis by using zinc chloride ($ZnCl_2$) and (0.1M) was dissolved in (100ml) of distilled water by using mixer glass under normal atmospheric pressure, Then the solution was sprayed on the glass Substrates of films was heated at a temperature of (400° C) . Thickness of (300 ± 25) nm , The indium was used as a doping agent with a volumetric concentration of (1,3,5,7)%. The thickness of the membrane of the equation: -

$$t=\frac{\Delta m}{\rho A_s} \qquad \text{-----------} \ (1)$$

Transmittance and absorbance were recorded using a spectrophotometer type (Shimadzu UV-1650 PC) in the wavelength range (400- 900) nm . All readings were recorded at room temperature.

Results and discussion:-

Figure 1 shows a relationship between the absorbance (A) and the incident wavelength for undoped Zinc oxide films and doped by Indium of different doping ratios. It was noted that the values of absorbance decrease by the increasing of wavelength , To explain this phenoma , that is related the incident photon energy is less than , the value of the forbidden gap . We can notice also that the absorption shift to word the short wavelength leading to an increase in the value of optical energy gap with the increasing of doping concentration.

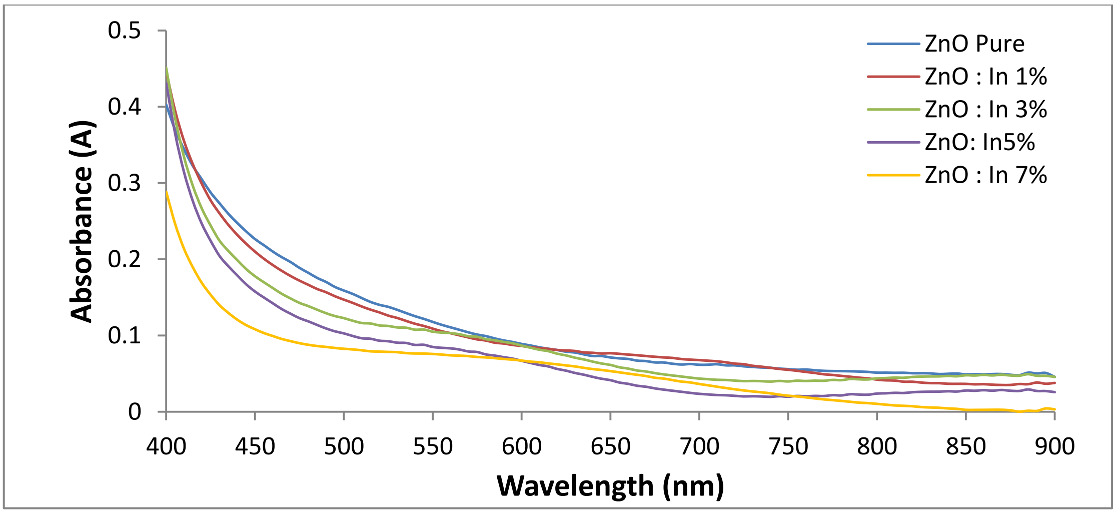


Figure (1) absorbance as a function of wavelength for zinc oxide films is undoped and doped Indium and different rates doping.

Figure (2) represents the relationship between transmittance (T) and wavelength of undoped Zinc oxide films and doped Indium , transmittance increased with increasing wavelength and also transmittance increase by doping ratio. This could be attributed to the decrease in surface roughness . Which was increased by indium doped (ZnO: In) . The surface roughness reduces dispersion of light and this improves the transmittance [9].

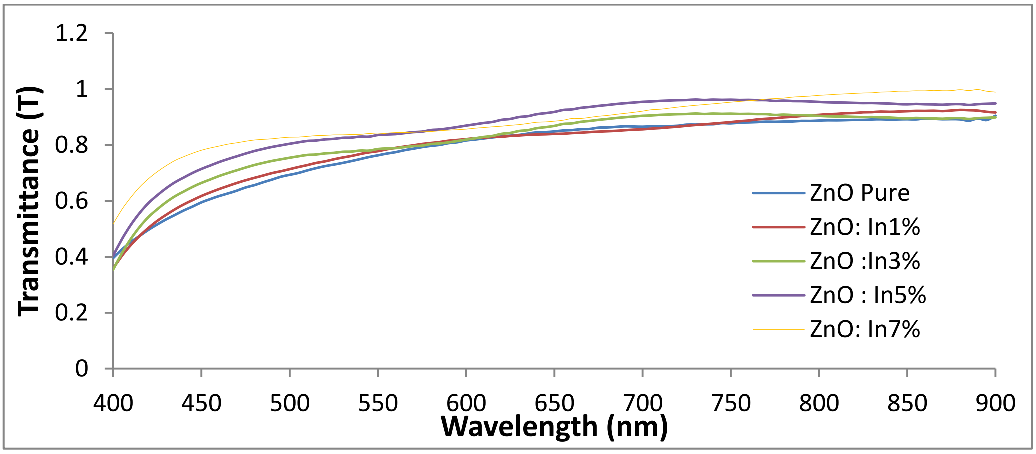


Figure (2) transmittance as a function of wavelength for zinc oxide films is undoped and doped Indium and different rates doping.

The absorption coefficient (α) in the main absorption region using the relationship [10]:-

$$\alpha = 2.303A/d \text{ ----------- } (2)$$

d - the thickness of the films . A- absorbance.

When the value ($\alpha > 10^4$ cm^{-1}) this suggest the occurrence of direct allowed transitions [11].

Figure (3) shows the change in absorption coefficient via photon energy for undoped and doped ZnO. The absorption coefficient increase with increase photon energy, and that the absorption coefficient decreases with increasing of doping ratios, which is in good agreement with Sumati [12].

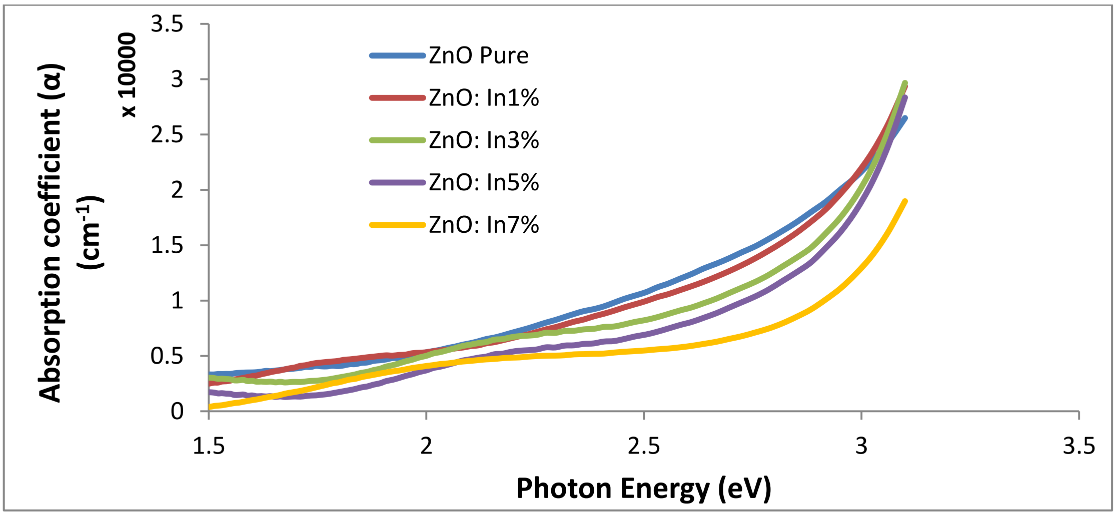


Figure (3) absorption coefficient as a function of photon energy of zinc oxide films undoped and doped Indium and different rates doping.

The optical energy gap calculation (E_g^{opt}) for direct allowed transition through the following relationship [13]:-

α(hv) = p (hv – E_g^{opt})^r ------------- (3)

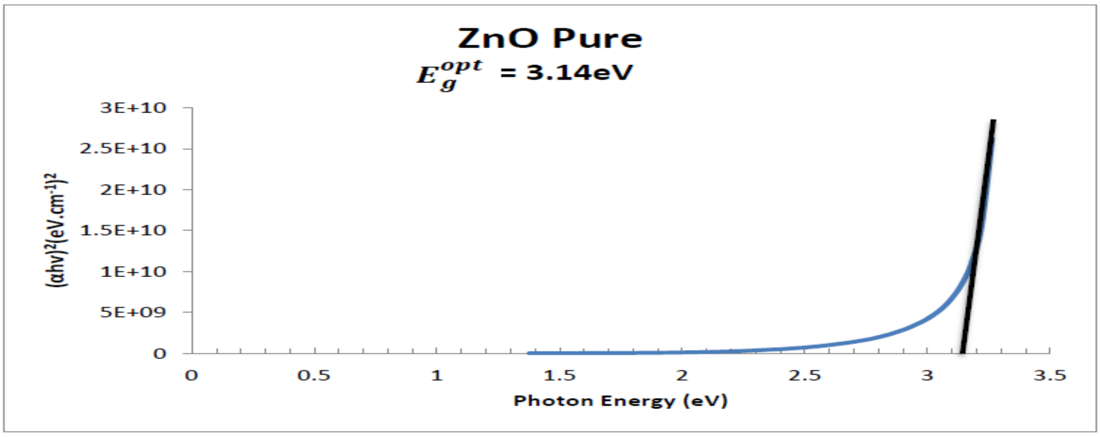
P- constant depends on the nature of the type of material. E_g^{opt}- optical energy gap.

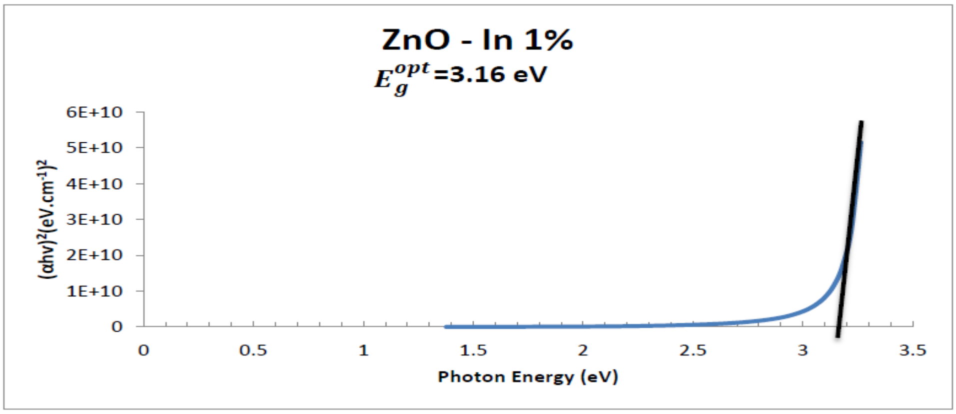
r = 1/2 value.

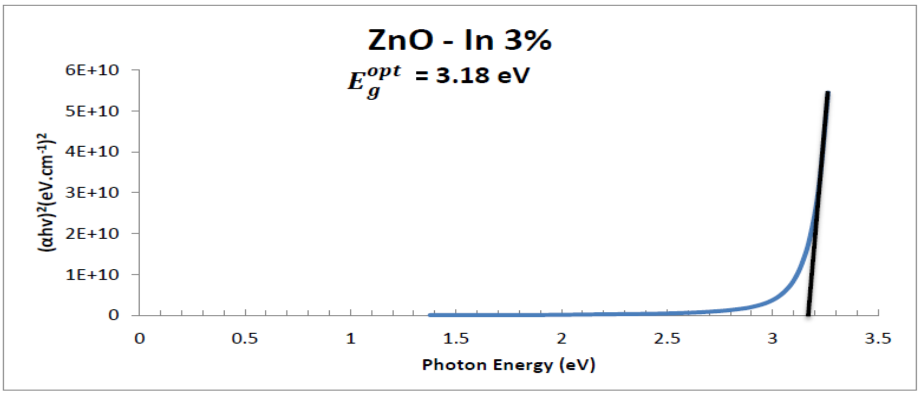
Figure (4) represents the relationship between the (αhv)^2 and photon energy of Zinc oxide for as deposited. Thin film of different concentration. The optical energy gap was increasing up on doping ratio. This can be explained by the shifting in Fermi level toward the conduction band leading to occupy all levels confined in the bottom of the conduction electrons and thereby blocking the electronic transitions to these levels there leading to increase the optical energy gap.

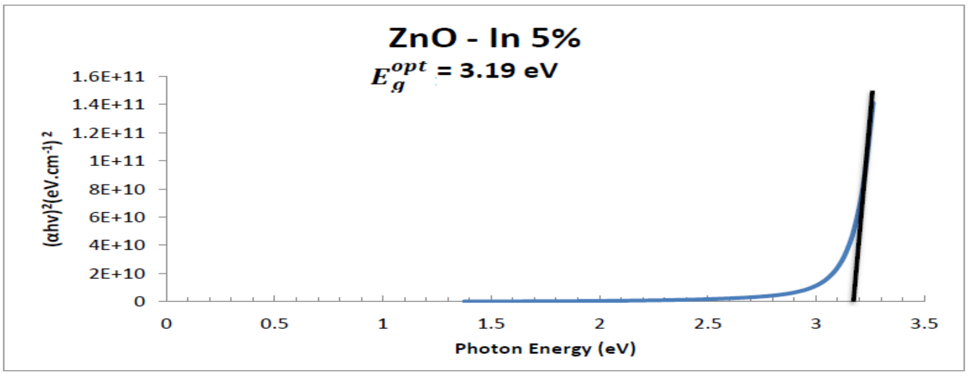
Table (1) Optical energy gap for direct transitions allowed values for zinc oxide films undoped and doped Indium and all doping ratios.

Sample	Optical energy gap values (E_g^{opt}) for direct transmission Allowed (eV)
ZnO Pure	3.14
ZnO : In (1%)	3.16
ZnO : In (3%)	3.18
ZnO : In(5%)	3.19
ZnO : In (7%)	3.20









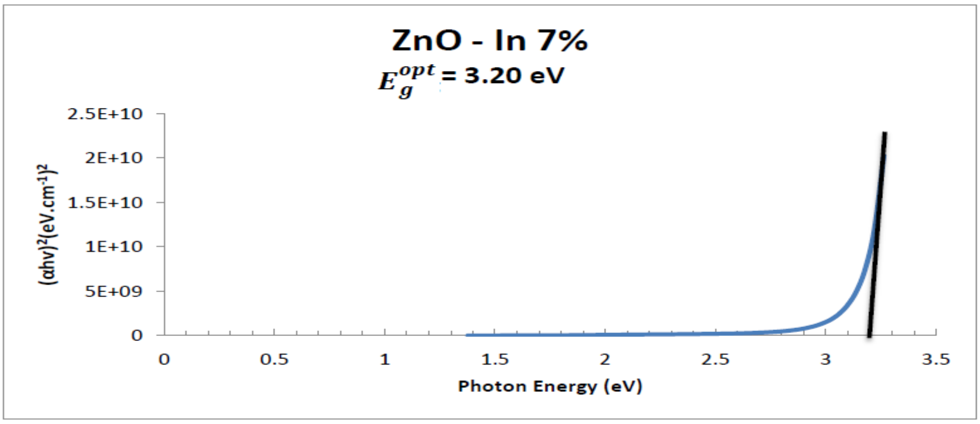


Figure (4) optical energy gap for direct transmission allowed zinc oxide films is undoped and doped Indium and different rates doping values.

Reflectance (R) can be calculated using the following relationship [14]:

A + R + T = 1------------- (3)

Figure (5) represents the relationship between the reflectance and the wavelength of the undoped and indium doped Zinc oxide for different ratios, We can notice that the reflectance decrease with the increase in wavelength for the undoped one, the reflectance of the doping thin films were decreasing as the doping ratios thus might be due to the increase in doping concentration which affects, the crystal structure and change the value of film surface.

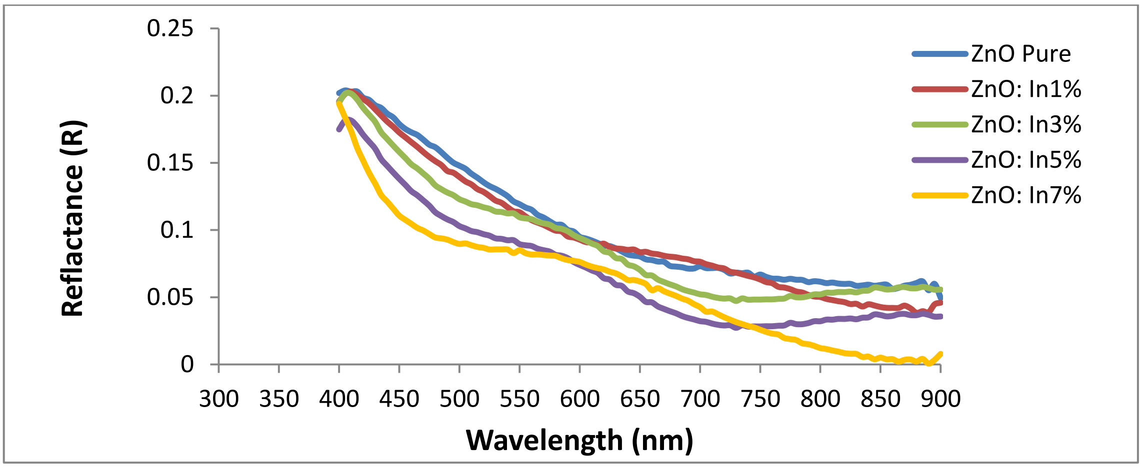


Figure (5) reflectivity as a function of wavelength for zinc oxide films is undoped and doped Indium and different rates doping.

The refractive index (n_o) can be calculated according to the following relationship [15]: -

$$n_o = \left[\left[\frac{1+R}{1-R}\right]^2 - (k_o^2 + 1)\right]^{\frac{1}{2}} + \frac{1+R}{1-R} - - - - (4)$$

Figure (6) represents the relationship between the refractive index and wavelength of the undoped and indium doped Zinc oxide different ratios, we can notice that the refractive index decrease with the increase in wavelength for the undoped one , the refractive index of the doping thin films were decreasing as the doping ratio increase. This might be due to the increase in doping concentration which affects, the crystal structure and change the value of film surface . The graph of refractive index is similar to the graph of reflectance.

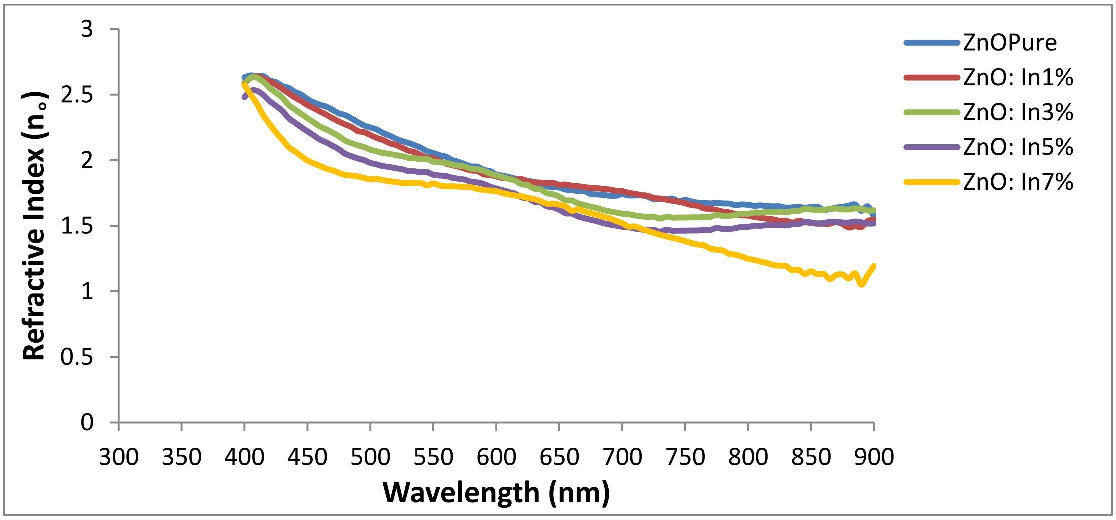


Figure (6) refractive index as a function of wavelength for zinc oxide films is undoped and doped Indium and different rates doping.

Extinction coefficient ($K_\circ$) can be calculated using of the following relationship [16]:

$K_\circ = \alpha\lambda / 4\pi$----------- (5)

Figure (7) represents the relationship between the Extinction coefficient and the wavelength of the undoped and indium doped Zinc oxide for different ratios, we can notice that the extinction coefficient decrease with the increase in wavelength for the undoped one, the extinction coefficient of the doping thin films were decreased as the doping ratio increase and they are similar to the extinction coefficient and absorption coefficient have a same behavior, this similarity results from the dependence of the values of extinction coefficient on the values of absorption coefficient.

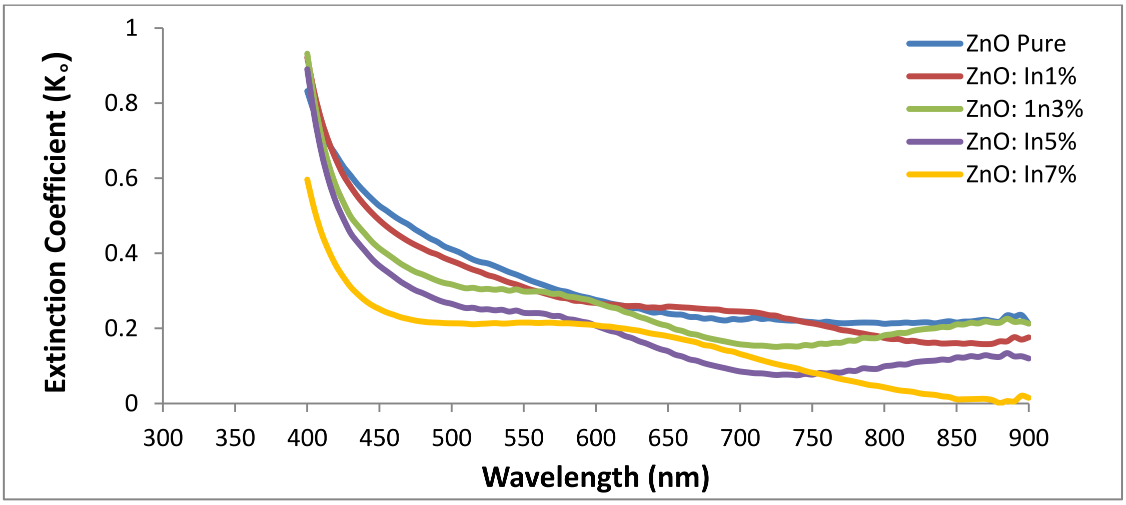


Figure (7) Extinction coefficient as a function of wavelength for zinc oxide films is undoped and doped Indium and different doping rates.

Real part (ε_1) and imaginary part(ε_2) of dielectric constant can be estimated according to the following [17]:-

$\varepsilon_1 = n_o^2 - k_o^2$ --------------- (6)

$\varepsilon_2 = 2n_o k_o$ ----------------- (7)

Figure (8) and (9) represents the relationship between the real (ε_1) and imaginary (ε_2) parts of dielectric constant and the wavelength of the undoped and indium doped Zinc oxide for different ratios respectively . From these figures we can deduce that the real part of the dielectric constant which have the same behavior can be noticed with the refractive index because of the depending of real part on refractive index according to the equation (6). While the imaginary part depends on values of extinction coefficient , which were related to absorption coefficient. Also , we can see the real part values are higher than those of the imaginary part. We can notice that the real and imaginary parts decrease with the increase in wavelength for the undoped same the real and imaginary parts of the doping thin films were decreased as the doping ratio increase.

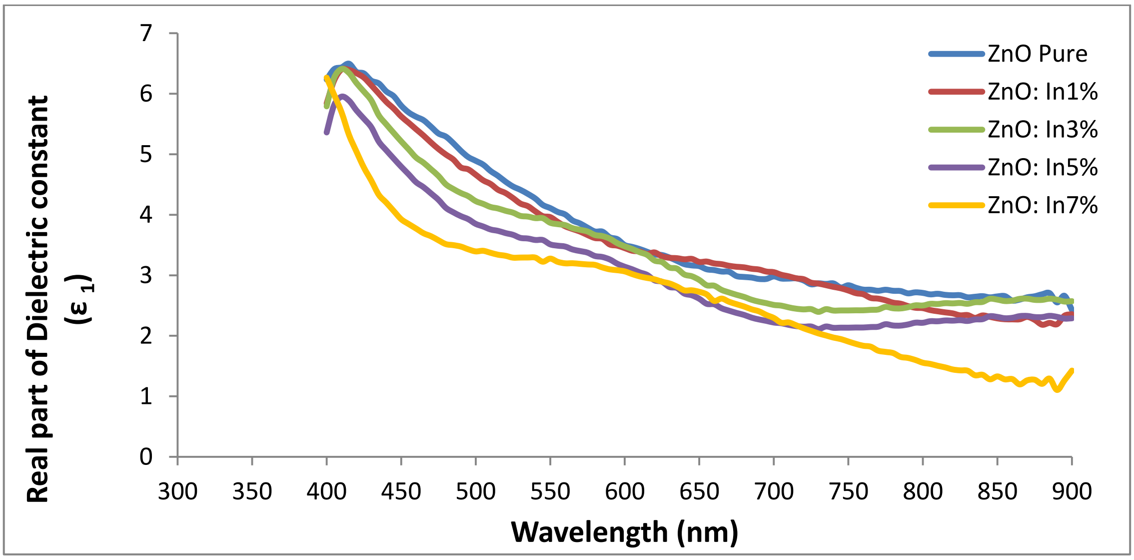


Figure (8) real part of dielectric constant as a function of wavelength for the is zinc oxide films undoped and doped Indium and different rates of doping.

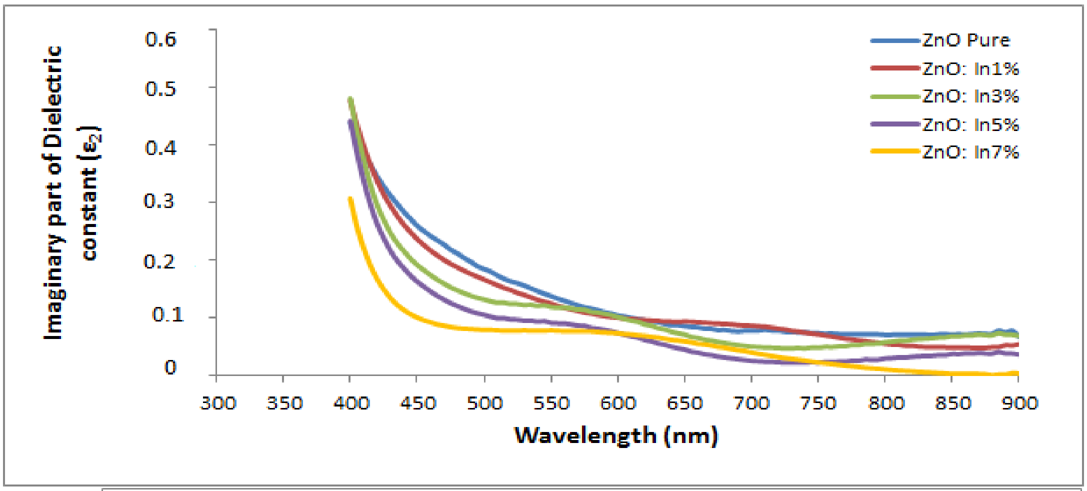


Figure (9) the imaginary part of dielectric constant as a function of wavelength for zinc oxide films is undoped and doped Indium and different rates of doping.

Conclusions: -

1- A bsorbance and the absorption coefficient and refractive index, and real and imaginary part of dielectric constant are decreased and in contrary, values of the transmittance and optical energy gap were increased with doping ratios of the thin films prepared.

2. The kind of transition observed in this work was direct allowed transition.

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