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Optical characteristics of ZnO:Al thin films prepared by magnetron sputtering

الخصائص البصرية لأغشيةZnO:Alالمحضرة بطريقة الترذيذ المغناطيسي

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Abstract :-

Undoped and Al doped ZnO samples with 1.05 wt% of Al were synthesized by magnetron sputtering method. We have studied optical properties of the samples in spectral range (300 – 900)nm.The XRD spectra shows that the films have polycrystalline structure with hexagonal phase. Al impurities do not causes observable action on structure of the films , but it reduce the optical transmittance of ZnO and reduce also optical band gap (E_g) from 3.2 eV to 2.8607 eV . Reflectance, Extinction Coefficient (K_0), Absorption Coefficient (α) and Refractive index (n) have higher values for ZnO:Al compared with that for ZnO.

الخلاصـــة :-

حضرت اغشيةZnO غير المشوبة والمشوبة بالالمنيوم بتركيز(1.05 wt%) بطريقة الترذيذ المغناطيسي.
وتمت دراسة الخصائص البصرية في المدى الطيفيnm(300-900). و بينت فحوصات الاشعة السينية
2.8607ان للاغشية تركيب متعدد التبلوروبطور سداسي وان التشويب لم يؤثر على التركيب البلوري وانه .
ادى الى نقصان في النفاذية البصرية للمادة وتقليل قيمة فجوة الطاقة من 3.2 eVالى eV
وكانت قيم كل من الانعكاسية ، معامل الخمود ، معامل الامتصاص ، معامل الانكسار للمادة المشوبة اكبر من تلك لغير المشوبة.

Introduction :-

Zinc oxide (ZnO) is a n-type wide band gap (Eg~3.3eV at 300K) semiconductor with optical transparency in the visible range. ZnO is used as transparent conducting electrode material for various applications such as solar cells, organic light-emitting diodes, flat panel displays, blue and ultraviolet light emitters, gas sensors. ZnO transparent conducting films have been investigated by magnetron sputtering, thermal evaporation, low temperature chemical bath method, pulsed laser deposition, molecular beam epitaxy, sol-gel etc **[1]** .

Recently, the doping of different elements has been attempted to induce new interesting properties, such as for transparent electrodes . In particular, transparent conductive oxide (TCO) electrodes using Al-doped ZnO have attracted much attention as powerful candidate materials for ITO transparent electrodes **[2]** . One of the most perspective materials for wide zone «windows» for the solar cell are ZnO:Al films , obtained by magnetron sputtering method **[3]**. The purpose of this work is to study the optical properties (which include optical energy gap and optical constants) for ZnO & ZnO:Al .

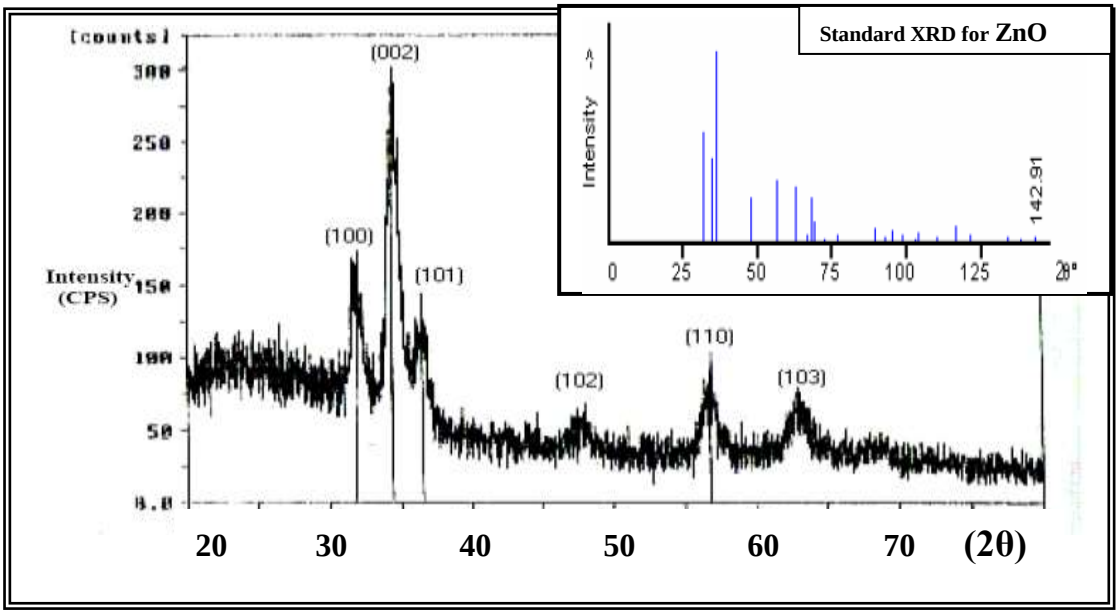
Experimental Part :-

ZnO:Al films were prepared by dc magnetron sputtering , sintered disc composed of a mixture of ZnO powder with 1.05 wt% Al_2O_3 (purity 99.98%) doping, calcined at $900^{o}C$ in an air atmosphere for 5 hours to be used as the targets. Argon gas 99.9998 % is used as sputter gas in pressure 6×10^{-2} Torr.

Substrate temperature equals to 200°C, and deposition time 1.5 hours. Target-anode distance (30 mm) .The film was deposited on (glass) with thickness (0.85μm). The data of the experiment and the specifications for X-ray test were as follows: Tube anode: Cu, Wavelength [Å]: 1.54060, Divergence slit : 1°. The optical transmittance of the undoped ZnO and ZnO:Al thin films was determined by the spectrophotometer within the wavelength range of 200-900nm.

Results and discussion :-

From figure(1) , it is clear that the film has polycrystalline structure with hexagonal phase. The little concentration of Al impurities does not causes observable action on XRD of ZnO, because there is no peak belongs to Al ,this can be deduced easily by comparing XDR in figure (1) with that of standard XRD for Al in figure (2) **[4]** .



Figure(1) Diffraction pattern of ZnO:Al with 1.05% Al, 200°C substrate temperature, and standard XRD for ZnO [5].

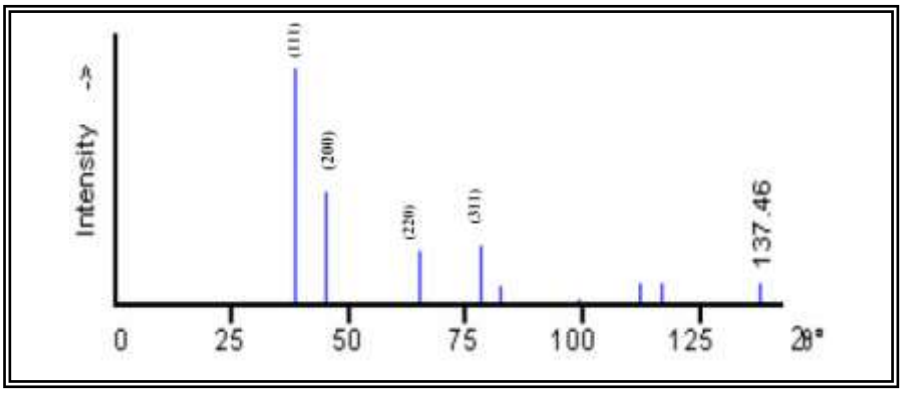


Figure (2) Standard XRD for Aluminum element.

Figure (3) shows that, the optical transmittance in the range (400-800) nm is in the range of (49-95 %) for undoped ZnO, in comparison with the transmittance of ZnO:Al (31-87 %) .The decreasing of transmission for ZnO:Al might be due to increase scattering of photons by crystal defects , and the free carrier absorption of photons contributed to the reduction in optical transmittance **[6]** . The peak

oscillation in the curve might be due to the irregular surface of the film **[2]** . From this figure it is observed that the transmittance decreases at the low wavelength region, which is the spectral region of fundamental absorption, in this region the incoming photons have sufficient energy to excite electrons from the valence band to the conduction band and thus these photons are absorbed within the material to decrease the transmittance. For this reason, this region carries the information of the band gap of the material **[7]**.

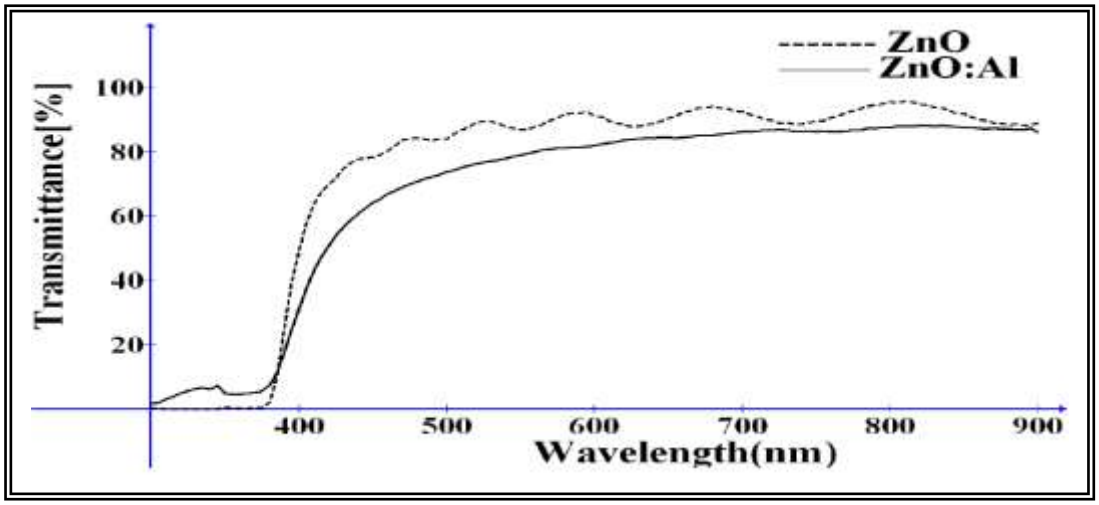


Figure (3) Transmittance against Wavelength for ZnO & ZnO:Al.

Also Reflectance depends on the doping of ZnO film; this is clear in figure (4). In visible region reflectance of ZnO:Al is higher than that for ZnO.

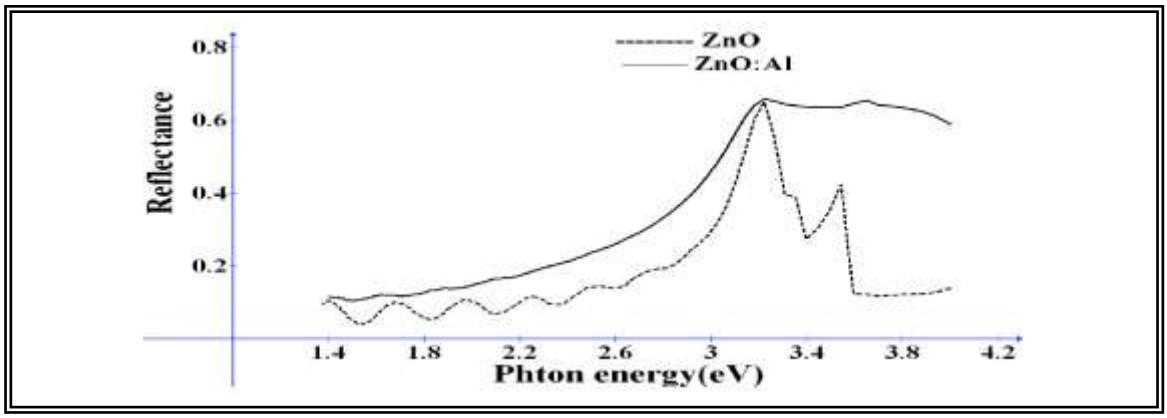
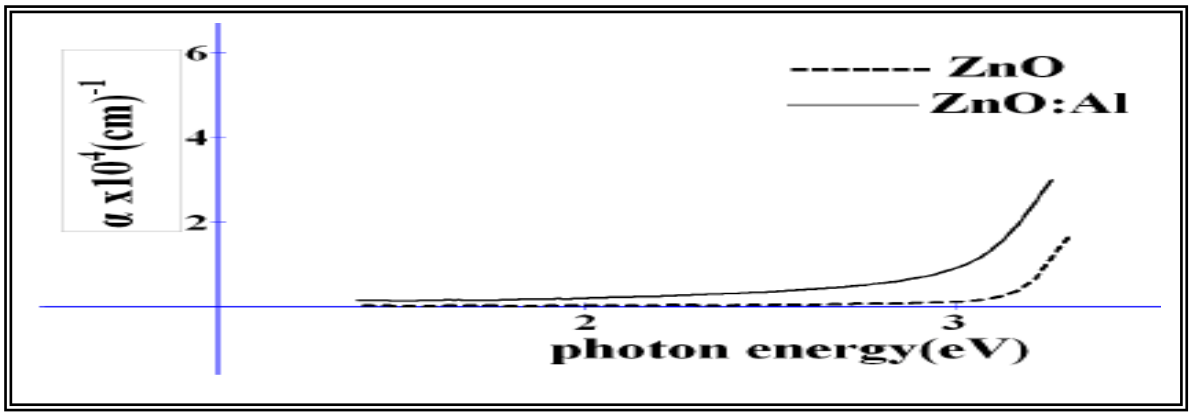


Figure (4) Reflectance as a function of Photon energy (eV).

The behavior of Absorption Coefficient (α) is illustrated in figure (5), at large photon energy α takes higher values ($\alpha \geq 10^4$) and then decreases with decreasing photon energy, this is attributed to the electronic transitions through the defect centers such as impurities **[8]** .



Figure(5) Absorption Coefficient as a function of Photon energy(eV).

Because Al-doped ZnO film is a direct transition-type semiconductors **[9] ,** the optical band gap (E_g) – for direct allowed transition- can be obtained by plotting α^2 vs. hν (α is the absorption coefficient and hν is the photon energy). The photon energy at the point where $\alpha^2 = 0$ is E_g. The E_g value was determined by the extrapolation method. Figure (6) shows the results of the E_g values for both, ZnO and Al-doped ZnO , they are 3.2 eV and 2.8607 eV respectively.

It is important to mention that, P. SAGAR, et.al. reported that both the average transmittance and band gap are found to increase with increasing Al doping concentrations from 0 to 0.8 at. % **[10]**.

Cut-off wavelength refers to the absorption edge, it can be calculated from the energy gap as in relation: $\lambda_{(cut\ off)} = 1240/E_{g(eV)}$. In this study, $\lambda(ZnO)_{cut\text{-}off}$ =387.5 nm , $\lambda(ZnO{:}Al)_{cut\text{-}off}$ = 433.4 nm.

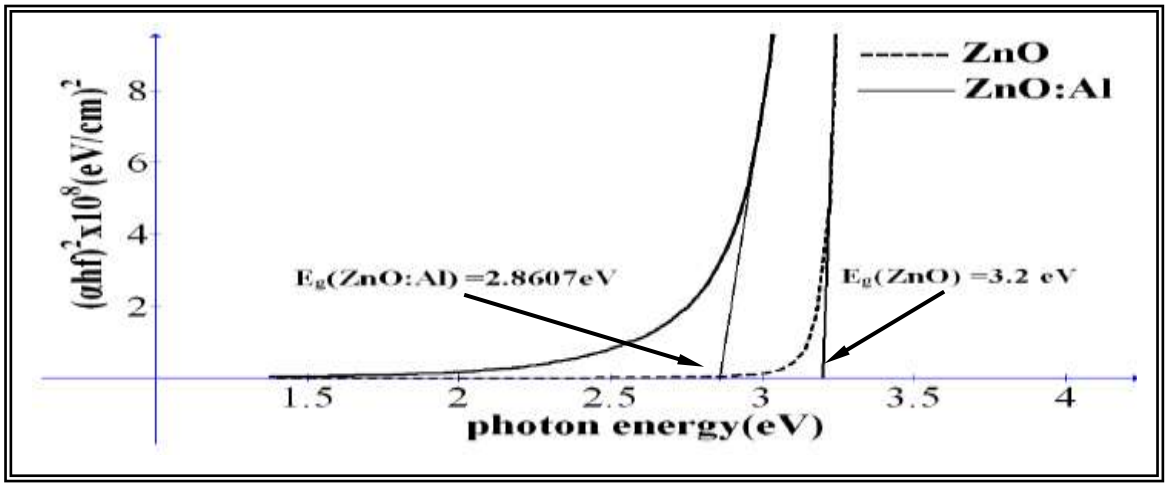
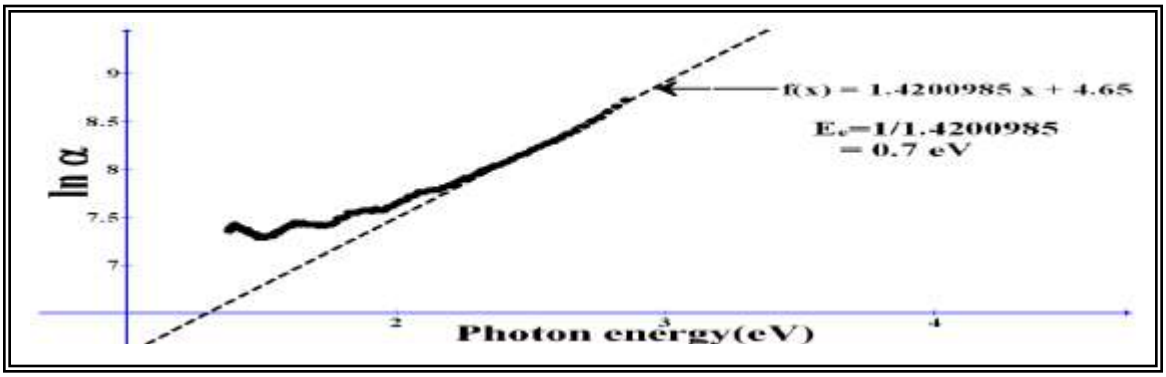


Figure (6) Band gap E_g estimation for ZnO & Zn0:Al films.

The shift to lower energy due doping in the films, seem to be related to presence of localized donor levels (E_e) in the band gap. The absorption coefficient α(f) in the low energy range follows the well knows exponential law, i.e. the Urbach law tail which it is expressed by:**[11]**

$$\alpha(f) = \alpha_{\eta} \exp(\hbar f/E_e)$$

where E_e is interpreted as the width of the localized states in the band gap. E_e is estimated from the inverse slope of the linear plot between ln(α) vs. hf (eV) as in figure(7) . In this present study, E_e = 0.7eV, the value of E_e obtained for undoped ZnO is reported to be in the range of (0.07–0.10) eV **[12].** Hence, the higher values of E_e obtained in this work indicates large number of localized donor levels in the band gap.



Figure(7) ln α as a function of Photon energy.

Extinction Coefficient (K_0) represents the imaginary part of complex refractive index and it can be defined as the amount of energy losing as a result of interaction between the light and the charge of medium .**[13]**

The relation between (K_0) and photon energy is illustrated in figure (8). (K_0) for ZnO is smaller than that for ZnO:Al, because it has smaller absorption coefficient and due to increase the structure defects with doping .

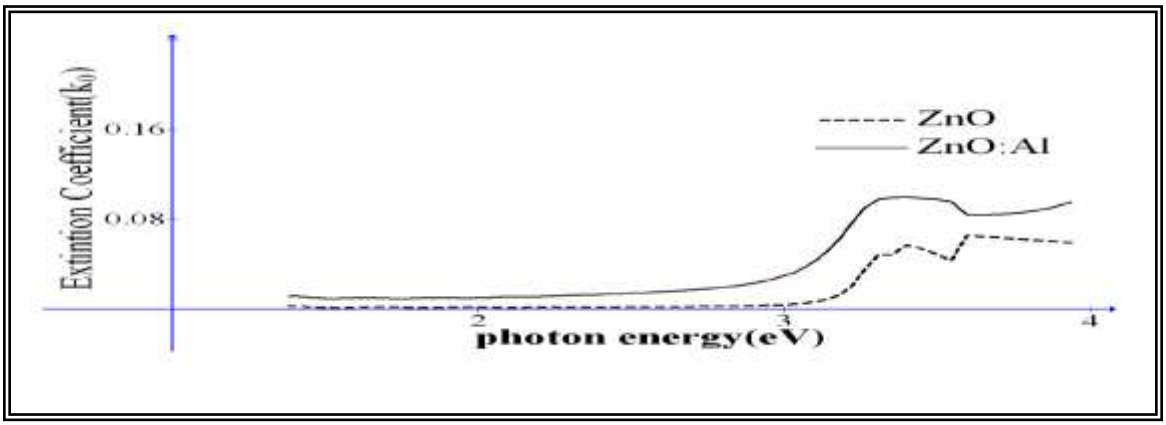


Figure (8) Extinction Coefficient as a function of photon energy

The behavior or refractive index in figure (9) likes that of reflectance R , because it is calculated depending on it as in following equation:

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

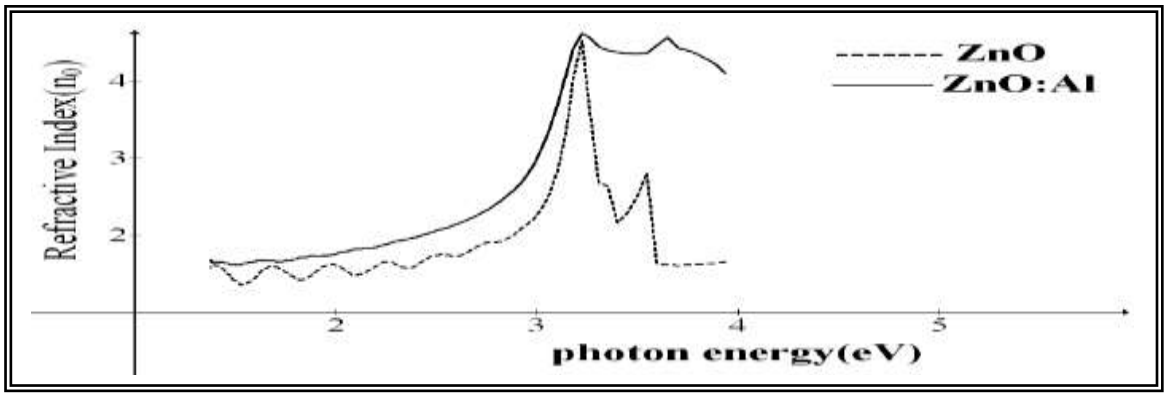


Figure (9) Refractive Index as a function of photon energy

The electromagnetic wave will have its amplitude reduced by a factor 'e' after traversing a thickness (called the skin depth) χ such that:

$$\chi = \lambda / 2\pi k_0$$

which may be the order of 100 to several thousand angstroms , depending on the material **[14]** . **F**igure (10) shows the variation of skin depth as a function of wavelength for ZnO & ZnO:Al thin film, from this figure one can conclude **[15]** :

- At short wavelengths close to the ($\lambda_{cut\text{-}off}$) , the probability of absorption highly increase and the amplitude of the incident photons will be reduced by a factor 'e' through the short distance within the film thickness , then the skin depth was small .
- At wavelengths greater than the ($\lambda_{cut\text{-}off}$) within the visible region, the absorption effect vanishes and the reduction in amplitude occurs after passing a larger distance, then the skin depth will be large.

As it was mentioned above , the peak oscillation in the curve might be due to the irregular surface of ZnO film.

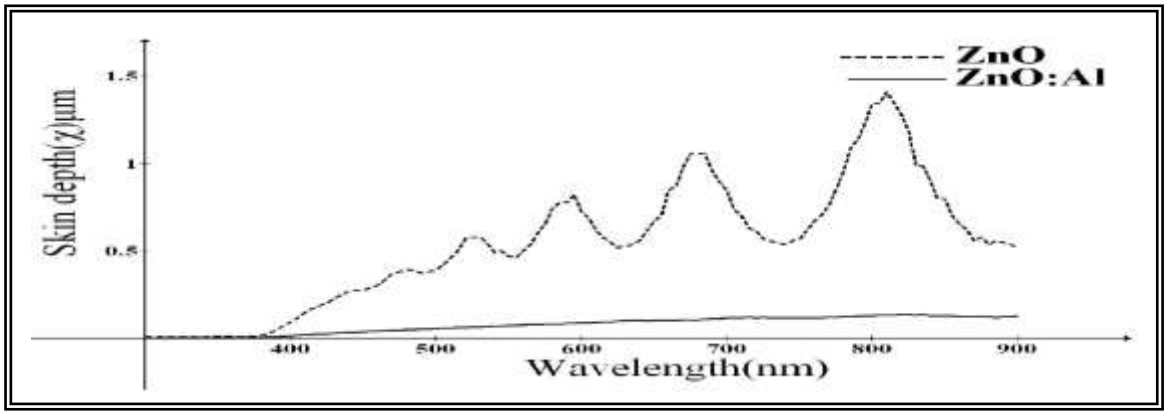


Figure (10) variation of skin depth as a function of wavelength.

Conclusions

The little concentration of Al impurities does not causes observable action on XRD of ZnO,but it reduce the optical transmittance for ZnO from (49-95 %) to (31-87 %) in visible region with $\lambda(ZnO)_{cut\text{-}off}$ =387.5 nm , $\lambda(ZnO{:}Al)_{cut\text{-}off}$ = 433.4 nm. Optical properties (Reflectance, Extinction Coefficient (K_0), Absorption Coefficient (α) and refractive index (n)) have higher values for ZnO:Al compared with that for ZnO.

The optical band gap (E_g) –direct allowed transition- for both, ZnO and Al-doped ZnO, are 3.2 eV and 2.8607 eV respectively. The width of localized states inside energy gap for ZnO:Al is E_e=0.7eV indicating to large number of localized donor levels in the band gap.

References :-

1- J. Yoo, J. Lee, S. Kim, K. Yoon, I. Jun Park, S.K. Dhungel, B. Karunararan, D. Mangalaraj, J. Yi, Thin Solid Films 480 (2005) 213.

2- Jong Moon Shin, Su-Young Cha, Jin Woo Park and Se-Young Jeong. Journal of the Korean Physical Society, Vol. 49, December 2006, pp. S584_S588

3- European Photovoltaic Solar Energy Conference and Exibition, Barselona, Spain, 1997, p. 2089-2093.

4- Bur.Stand.(U.S.),Circ.539,1,11,(1953).

5- Mc.Murdie,H.et.al. Powder diffraction.1,76 ,1986.

6- J. P. Upadhyay , S. R. Vishwakarma , and H. C. Prasad , Thin Solid Films , 109 , (1989) , 195 .

7- A.N. Banerjee1, C.K. Ghosh, S. Das, K.K. Chattopadhyay .Physica B 370 (2005) 264–276.

8- A.F.Gibson,Proceeding of Phys.Soc.,B63,(1950)pp.756-767.

9-. Luis Manuel Angelats Silva **,** thesis , University of Puerto Rico,2006.

10- P. SAGAR Materials Science-Poland, Vol. 23, No. 3, 2005.

11- F. Urbach, Phys. Rev 92(1953)1324.

12- S.B. Majumder, M. Jain, P.S. Dobal and R.S. Katiyar, Mat. Scienc and Eng, B103 (2003) 16-25.

13- Thesis**,** Firas Hashem Ahmed AL-Mustansiriay University,2003.

14- J. F. Eloy , " Power Lasers " , National School of Physics, Grenoble , France , John Wiley & Sons , 1984 , 59 .

15- Ali Jasim AL-Jabiry **,** thesis , University of Technology,Baghdad,2007.