J.Basrah Researches (Sciences) Vol. 33. No.2 .((1- 6)) Jun. (2007)

Optical properties of Aluminum-Zinc oxide thin films Prepared by spray pyrolysis technique

G.M.Shebeeb
Department of physics. College of Education.
University of Basrah,Basrah-Iraq

ISSN –1817 –2695
(Accepted 13/1/1998)

Abstract:

Thin films of ZnO:Al about one μm were deposited on glass substrates using spray pyrolysis technique . The optimum spray conditions were identified to obtain good compatible between optical and film homogeneously properties. The optical parameters were calculated depending on transmission spectrum in the range (0.3-0.85) µm. The fundamental absorption in the band to band transition was also investigated and energy gap of 3.25 eV was recognized in term of the imaginary part of the dielectric constant.

Introduction

Extensive research on transparent metal oxides have been carried on at different places around the world They include. mainly thin oxide films with various proper dopants. The distinguished properties of these films can be summarized by its n- type semi conducting properties due to the existence of ionization donor energy level below the conduction band. ZnO thin film has many applications in technology, it used in microwave transmission lines [1], gas sensor equipments and has a widely used in multilayers solar cells. The transparency for these films has a broad band width for visible light because of its relatively large energy gap (3.0-3.3) eV, and it has electrical mechanical couple coefficient larger than that of electrically unploarizcd materials [2,3] .There are many reports concerning the methods of preparation. The most commonly used methods are vacuum evaporation [4], sputtering [5] and spraying pyrolysis method [6] . The first two methods can be used to prepare films with high transmittance and low electrical resistively but characterized with a high cost and in addition a high working temperature is required during preparation process. The third method is characterized with a low cost and provides films with desired properties. moreover high quality thin films can be obtained by satisfying the optimum spraying conditions. The optical properties of' transparent conducting zinc oxide films prepared by spraying pyrolysis method were studied in the u.v-visble region [7]. It was observed that pure ZnO films has high resistively about 1.5×10^{-1} Ω.m which is decreases by doping with Indium and reached a saturated value 10^{5} Ω.m[8].
In this study zincoxide thin films doped with Al were prepared by spraying pyrolysis technique. The optical parameters comprise absorption coefficient , refractive index. And extinction coefficient are evaluated in the optical spectra region .The fundamanted absorption in the band to band transition was also investigated in terms of the imaginary part of the dielectric constant .

Experimental details

ZnO films has been prepared by spray pyrolysis method .A mixture solution (0.7)M from desolving ZnO into Hcl was sprayed on a quartz substrate heated to 400°c .
Doping with Al was carried out by desolving Al (0.7)M into Hcl with doping ratio (1:1000). The spraying parameters were kept unchanged during preparation process ,the sprayed period was kept at 15 seconds followed by 45 second stop to avoid excessive cooling . The distance between substrate and spray nozzle was 33 cm . the spray rate was 15 cm3 /min.
In order to obtain uniform and homogenous films , the substrate were kept under constant rotation during spraying process . It was found that a change in the spraying rate will caused defects such as stacking faults and vacancies in the film which may increase the internal stress.

Optical studies were carried out by measuring the transmission spectrum of the thin film using pye-unicam Sp8-100 . Spectrophotometer, were the film spectrum was normalized with quartz as a reference substrate.

Results and discussion

The optical properties of ZnO:Al films have been studied by recording the ratio transmission Spectrum of films having different thicknesses . the transmittance of the thin film deposited on transparent substrates given by [9].

$$T=\frac{B}{2R_{af}R_{fg}\cos\psi+R^2{}_{af}R^2{}_{fg}e^{-\alpha t}+e^{\alpha t}}\quad\text{----------(1)}$$

Where:
$B=16n^2{}_f\, n_g\,(n_f+1)^{-2}\,(n_f+n_g)^{-2}$
And
$\psi=\frac{4\pi t}{\lambda}$
R_{af} , R_{fg}, n_f, n_g, α. And t are air –film & film substrate reflections, film&
Substrates refractive index absorption coefficient, and film thickness respectively .In the region of band to band transition the absorption is so large that made exp(αt)>> $R^2{}_{af}\,R^2{}_{fg}$ exp(-αt) and the interference term is very small ,therefore equ.(1)can be written as:
$T=Be^{-\alpha t}$ ---------(2)
The transmission ratio for two films with different thickness is given by:
$T_{1/2}=\exp(-\alpha\Delta d)$ ------(3)
Where Δd is the thickness difference of two films. The thickness difference can be considered as a thickness of a hypothetical film that is resulted from putting the thicker sample in the sample beam and the other one in the reference of the spectrophotometer.
Figure(1)shows the spectral dependence of the spectral transmittance in the wave lengths range (300-900)nm
Where sharp absorption edge can be seen in the fundamental absorption region . All prepared films exhibit a high transmittance (about 80%)in the visible region , which is nearly similar to that observed for ZnO and ZnO:Al
Prepared by RF sputtering method [10] .
It was observed that a blue shift in the absorption edge was associated with doping with AL[7-11]. Moreover the absorption edge in polycrystalline ZnO thin films was dependent on the details of preparation conditions.
The absorption coefficient of the films can be calculated from the ration transmission according to this relation .
$\alpha=(2.303 / (\Delta d)\log 1/T_{1/2}$ --------(4)
The extinction coefficient k Was calculated from knowing the absorption coefficient where;
$\alpha=\frac{4\pi k}{\lambda}$
Figure (2) shows the variation of α and K with hν . The drastic behavior of K can be noticed in the low energies due to the onset of the electron transitions to the conduction band .
The refractive index n is related to the k and R in the normal incidence by the relation:

$$R=\frac{(n-1)^2+k^2}{(n+1)^2+k^2}\quad\text{---------------(5)}$$

The spectral variation on of the refractive index is shown in figure(3) . It was also observed that the behavior of n has qualitative similarity to that of the single crystal ZnO [12].It is well known that calculated energy gap depending on optical absorption data provides an accurate way than other methods where this method summarized by plotting the $(\alpha\Delta d)^{1/n}$ with hν according to the relationship of α with has in the equation :

$\alpha=\alpha^{\circ}(h\nu-\Delta E)^{n}$ --------(6)

Where n is a number has a definite value as ½ , 3/2 , 2 ,or 3 depending on the transition type that occurred through the energy gap (direct or indirect transition) [13] . Since according to this method a value of energy gap is nearly 3 .25 and 3 .20 eV has been calculated for pure and doped films respectively .Further more the optical transition was also investigated depending on the relationship between the optical and electrical indices , following Maxwell equation , where the refractive index and the extinction coefficient is related to the dielectric constant according to :

$\varepsilon_1=n^2-k^2$ --------------------(7)

$\varepsilon_2=2nk$ ---------------------(8)

Where ε_1 and ε_2 are the real and the imaginary part of the dielectric constant .

Figure (4) shows the spectral variation of ε_1 and ε_2 with hν .

The fundamental transition in the band to band transition in the term of imaginary part of dielectric constant is given by [14].

$(h\nu)^4\,\varepsilon^2_2=c(h\nu-\Delta E)$ $h\nu\geq E$

$\varepsilon_2=0$ $h\nu\leq E$

Where c is a constant almost independent on the photon energy .

Figure (5) show the relationship between $(h\nu)^4\ \varepsilon^2_2$ versus hν .At high photon energy the extrapolation of the straight line to $(h\nu)^4\,\varepsilon^2_{2=0}$

gives a value of band gap about 3.21 eV for doped films . The reduction of the energy gap can be explained as the result of comparison between two main parameters [15] . First is the Burstein – Moss band filling effect which has a positive effect on increasing band gap with increasing the carriers concentration and second the characteristic nature and strength of interaction potentials between donors and the host crystal which lead to shrinkage the band gap , which was observed to be the prevailing one .

The gap shrinkage does not depend on the method of sample preparation but it represents a fundamental property of the semiconductor . According to the prevailing optical properties of these films , they can be used as antireflection coating on solar cell with a value of refractive index satisfying the mismatch behavior between the silicon and air refractive index.

Conclusion

Thin film of ZnO doped with Al has been prepared by spraying pyrolysis technique. The optical properties involved energy gap, absorption coefficient , index and extinction coefficient have been investigated .The value of energy gap of the films was found to serve as a window reflection film .The shrinkage in the energy gap was explained due to the prevailing of interaction potentials between donors and the host crystal.

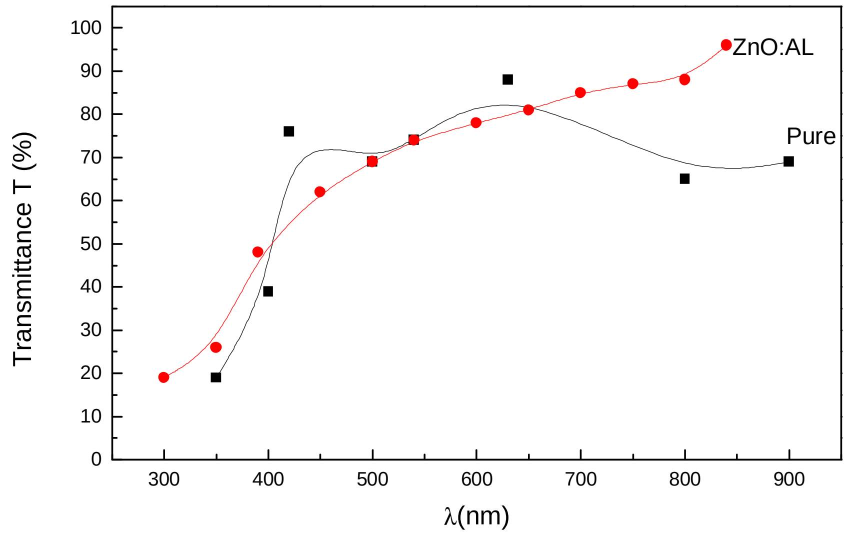

Figure (1) the relationship between the transmittance and tile wavelength.

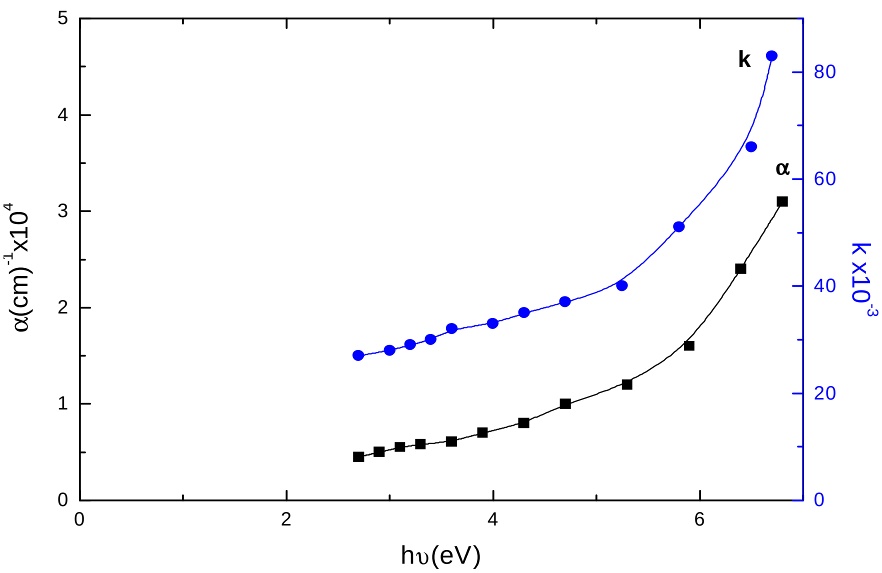

Figure (2) the variation of α and k with hv.

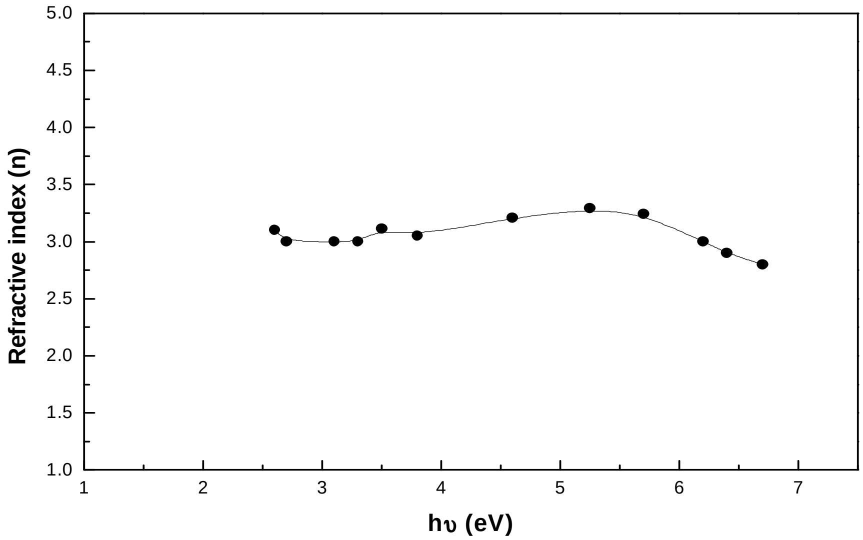

Figure (3) the variation of n with hv.

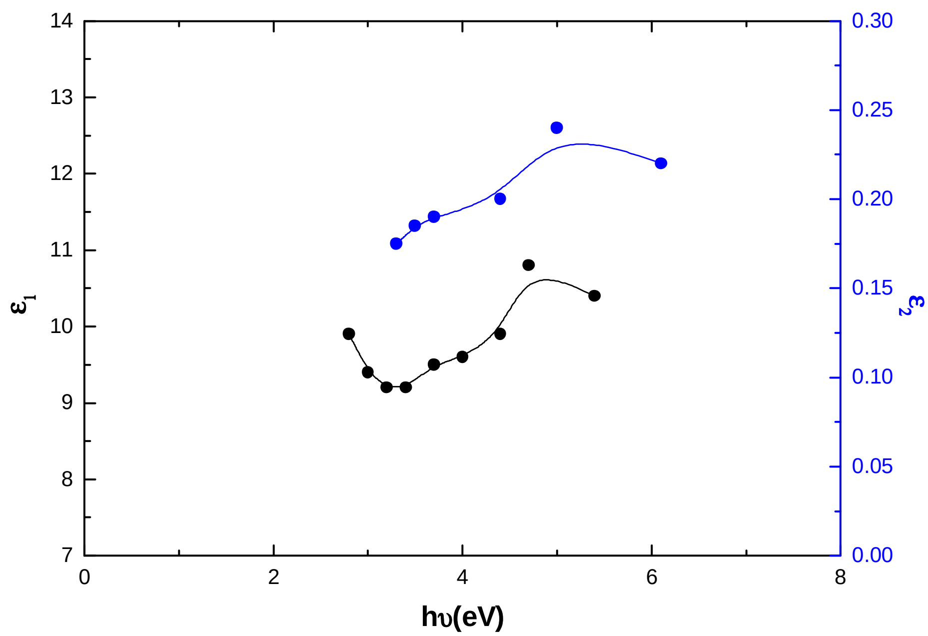

Figure (4) the spectral variation of ε_1 and ε_2 with hv.

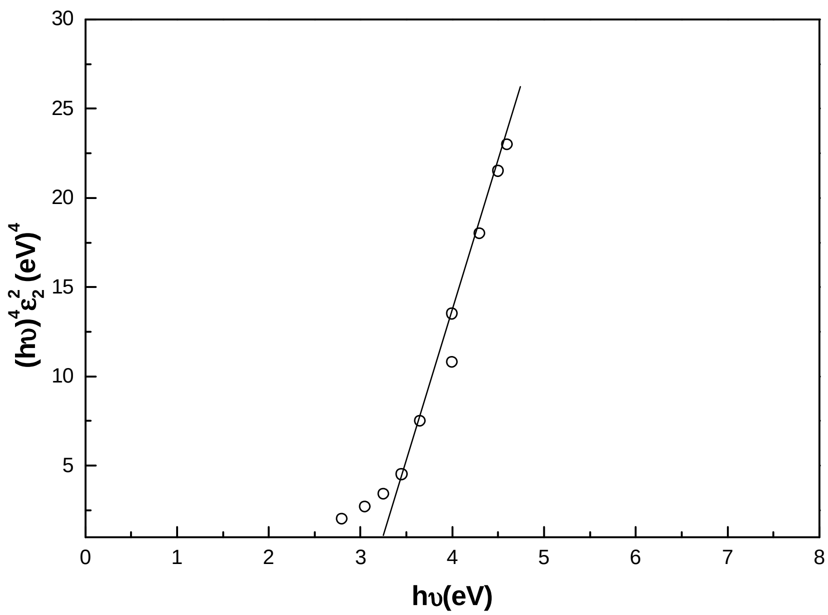

Figure (5) shows the plote of $(hv)^4\ \varepsilon_2^2$ versus photon energy.

Acknowledgement

The Auther would like to thank Dr.W.A.S.Abdul Ghafor for valuable discussions and would also thank the staff of physics department college of Education for their interest in the subject

References

[1]-K.L Chopra and S.Major . Thin solid film . 102, 32 (1983).
[2]- O.P. Roth D.F williams.J.Appl . phys. 59,11. (1981).
[3]- S.Major A.Baneerjee thin solid film, 122,31(1984).
[4]- S.Ray B.Banejee A.K.Barua Jpn Appl 19,1889(1980).
[5]-M.Takeuchi y Sakagawa .H. Nagasaka. Thin solid films ,33 ,89(1976).
[6]- H.Kwak and W.E.Siu, Thin solid films. 61,249(1979).
[7]- S.Major. A.Banerjee K.I Chopra. Thin solid films22,31(1984).
[8]- S.Major A.Banerjee K.IChopra. Thin solid films 108,333(1983).
[9]- J.F. Hall and W.E. Ferguson .J.opt soc Amer .45,14(1955).
[10]- T.Minami .H.Nanto .S.Takata. Thin solid films .124,43(1985).
[11]- T.Minami .H.Nanto .S.Takata. jpn j.appl phys1,280(1984).
[12]- L.Bond .J.Appl .phys .36,1674(1965).
[13]- W.A.S Abdul Ghafor . International renewable energy conference . Jordon793 (1992).
[14]- F.Abeles .Optical properties of solids (North Holland publ. co) , Amsterdam (1972).
[15]- T.Minami ,H.Nanto and S.Takata. Jap. Appl. phys. 24,605(1985).

المستخلص:

حضرت اغشية ZnO المطعمة بالالمنيوم Al بتقنية الرش الحراري . تم دراسة الخصائص البصرية لهذه الاغشية والمتضمنة فجوة الطاقة, معامل الامتصاص, معامل الانكسار.وكذلك معامل التشتت. فسر الانكماش في فجوة الطاقه على اساس التفاعل بين الذرات المانحة والبلورة المضيفة.