ELECTRICAL AND OPTICAL PROPERTIES OF ZnO:AL FILMS PREPARED BY CHEMICAL VAPOUR DEPOSITION (CVD)

Alexander D.Pogrebnjak[1*], Nawfal.Y.Jamil[2] , Abidalkarem.M.Muhammed[1]

1 Sumy State University, St Rimsky-Korsakov 2, 40002 Sumy, Ukraine,
2 University of Mosul, Mosul, St Culture, Iraq,

ABSTRACT

In this paper we will prepared thin films from transparent conductive oxide(TCO) ZnO pure, and doped for Various concentration of aluminum Al(4,8%) using technique chemical vapor deposition (CVD) at different substrates temperatures (400,450,500C°). on glass substrates. The films were characterized by X- ray diffraction and UV spectrometer , pure ZnO films and (ZnO: Al) shows , a polycrystalline structure of the hexagonal Wurtzite Type, the diagnostics show preferred peaks for the growth of the crystal grains in the directions (002). The optical measurements have shown that the absorption edge is shifted towards the shortwave lengths which mean that the energy gap increases with the increase of Aluminum concentration in ZnO, and then we noticed the transmittance increases with increasing the substrate temperature and doping percentage with aluminum and the highest value was observed at $500C^0$ and (8%)doping .The electric conductivity of ZnO films doped with aluminum increases with the percentage of doping until the doping percentage of (4%) , then starts to decrease with the increase in doping percentages at substrate temperatures (450 C^0 and $500C^0$) ,also an increase in the concentration of charge carriers and Hall Effect mobility was observed at doping (4%) ,while it decreased at (8%) doping, as well as we can see from the seem image, the smoothly surface was obtained in case of 4% doping Al.

Key words: thin film, chemical vaporous deposition, ZnO, ZnO: Al, doping, energy gap

INTRODUCTION

Zinc Oxide is an II–VI wide band gap semiconductor with a large band gap of about 3.3 eV is one of the most potential materials for being used as a TCO because of it's good electrical and optical properties, abundance in nature, absence of toxicity [1,2] and the ability to deposit these films at relatively low temperatures [3]. The oxygen vacancies and/or zinc interstitials correspond to the n-type conductivity of the ZnO films. The resistivity of these films can be further lowered by doping them with group III elements like B, Al, Ga or In. Among all these elements, Al is considered to be a good dopant for opto-

* e-mail: alexp@i.ua tel:(+38)0686529647 tel: (+38)0542783986

electronic applications like solar cells due to the high transmittance that Al-doped ZnO films exhibit. ZnO: Al is fabricated by RF magnetron sputtering [4, 5], sol–gel process [3], pulsed laser deposition [5], spray pyrolysis [6] and chemical vapor deposition [7], etc. Among them, chemical vapor deposition that used in this paper, The process of deposition and producing homogeneous films is not a simple process but requires a number of tests including the selection of the precursor material, the temperature of substrates, the evaporation temperature and the flow rate of the carrier gasses in addition to the location of the sample in the deposition chamber. All these factors have a direct effect on the type of the required prepared film that and on its physical properties. In this study we observed a number of observations concerning the films. In some instance the films did not grow over the substrates or they only partly covered them. In other instances we observed that the films were formed as stripes. These cases took place at temperatures less than $450C^0$. While at this temperature and above, we found that the films status was enhanced significantly concerning the rate of growth and homogeneity while the optimal temperature degree in this study was found to be $500\ C^0$ as the optical, and electrical properties of the films

METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

In order to prepare pure ZnO films using chemical vapors deposition (CVD) techniques on glass and substrates the deposition material used was pure zinc acetate hydrous $Zn(Ch_3COO)_2.\ 2H_2O$) with 98% purity. After preparing the substrates, they were placed and adjusted in the deposition unit while the temperature degrees were varied between ($400\text{-}500C^O$) in order to ensure optimum film properties. The pressurized air flow was also adjusted to the best flow rate which was found to be 2 L/min to produce the best samples as .The rate of airflow is related to the uniformity of the deposited film and it must be adjusted to prevent the formation of colored strips on the glass substrates that can interfere with visional and microscopic inspection. Various temperature degrees were tested when heating the deposition material and it was found that the temperature of ($340\ C^O$ -$350C^O$) is the appropriate temperature degree range. Deposition time was kept constant at (20 minutes) for the both the pure and doped samples in order to determine the combination of optimal duration with temperature degree that produces the best results of zinc oxide deposition and the samples were left afterwards to cool. The first choice of doping material was to use chloride aluminum hydrous as a doping material but it was not possible to produce a doped film in any of the varied deposition conditions. The reasons were attributed to the weak or lack reaction ability between the Zn and hydrous aluminum. This led us to seek a different material which was aluminum nitrate hydrous with a purity of (98.5%). After using this compound, aluminum doped ZnO films were successfully produced with good homogeneity.

The various weight percentages of this used material were between (4,8%) that were added to the weight percentages of zinc acetate. The following equations show how ZnO is produced.

$$Zn(Ch_3COO)_2.2H_2O \rightarrow ZnO + CO_2 + CH_3 + steam \quad (1)$$

The following equation used to get the lattice constant [3],

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \times \frac{h^2 + hk + k^2}{a^2} + \frac{L^2}{C^2} \; ; \quad (2)$$

where a, c = lattice constant , hkL =miller indices.

The crystalline structure was analyzed by X-ray diffractometer (DROT-20 v Cu-$k_ц$) in the range 2 ц of 30 – 80, the surface morphology of the films was analyzed using aScanning electron microscope model (REM - 106) before and after annealing. The optical transmittance was measured using a ENGLAND (1000SERIESцCECIL 1021) spectrophotometer in the wavelength range from 300 to 1000 nm.

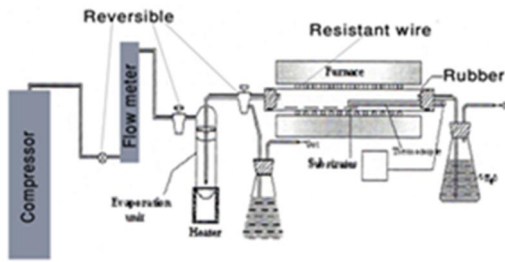

Fig . 1 – Components diagram of (CVD)

RESULTS AND DISCUSSION

X-ray diffraction studies of the structure of the material were carried out on an automated DRON-4-07 (Bourevestnik », www.bourevestnik.spb.ru). Automation system using a DRON-4-07 is based on a microprocessor controller that provides control of the goniometer GUR-9 and data transmission in digital form on a PC.

Table 1– *Lattice parameter of ZnO*

No	2ц Degree	h k L	d_{hkl}, E	a ,ц	c ,ц	Result standard	
						d_{hkl}, E	(a , c),ц
ZnO	31.72	1 0 0	2.816	3.24	5.17	2.814	a=3.249
	34.76	0 0 2	2.56			2.603	c=5.206

	36.6	1 0 1	2.456			2.475	

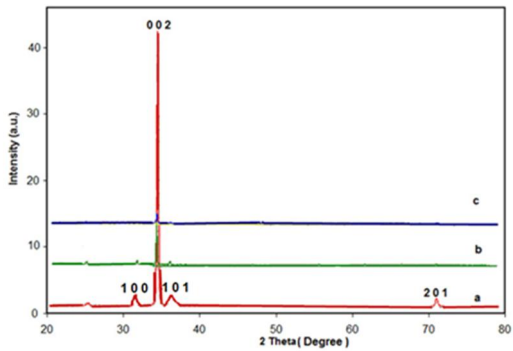

Fig. 2– X-ray diffraction patterns of ZnO

Fig. 2, Table 1 displays the XRD spectrum of ZnO films. Three lines (100) at 2θ = 31.76°, (002) at 2θ = 34.47°, (101) at 2θ = 36.24° are pointed, they will be considered for structural characterization of ZnO. We measured the XRD spectra for ZnO:Al with different Al ratio (weight) from 4% to 8 % and found the following results**,** The films exhibit a dominant peak corresponding to the (002) plane of ZnO, and other peaks corresponding to (100), (101) , and indicating the polycrystalline nature of the films. It is seen from the figure that the relative intensity of the (002) peak decrease with increasing Al dopant concentration. The decrease in peak intensity indicates an improvement in the crystalline of the films . Besides, a slight shift was observed in the peaks in the direction of the lesser angles which may be attributed to the small increase in the bond. These result were confirmed with those obtained from the Joint committee of powder diffraction standards JCPDS for the ZnO .

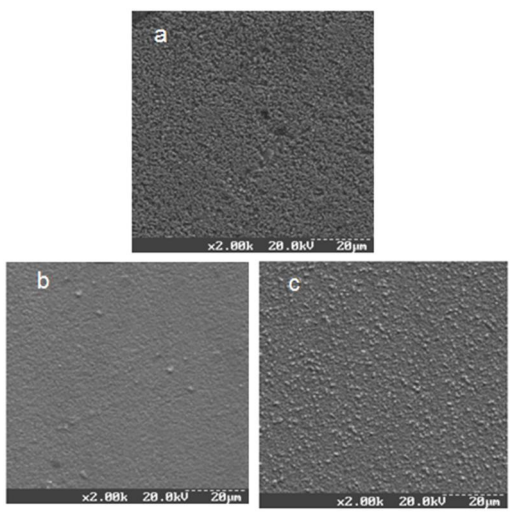

Fig. 3– Seem image of thin film ZnO, *a*– pure, b – 4% doping Al, c – 8% doping

Microscope test process has been done after finishing from depositing ZnO thin film on glass substrate by (CVD).

It can be easily seen that the grains are tightly packed. And we can see that the smoothly surface was obtained in case of Al doping in 4%. *Fig. 4* show the absorption spectra as a function of the wavelength of the pure ZnO films and the ZnO films doped with (4, 8%) aluminum. From these fig-

ures, we can see the transmission decreased with decrease wavelength, also we can see two regions are obvious: The first was the region wave length energy larger than the energy gap (Eg>3eV) which equals to ($\lambda < 400$ nm) as during this region, the absorption increase sharply therefore shows that the ZnO: Al can be used as UV protection films The second region lies within the wavelengths range of ($400 < \lambda < 1000$nm) in which the energy of the incident photon is low and the (ZnO:Al) film is transparent to this range and the absorption is lowest. We can see from the figure (4) that the increase in the percentage of aluminum added to the ZnO leads to the shift in the absorption towards the short wavelengths, a shift that is termed (Burstein-Moss) shift.

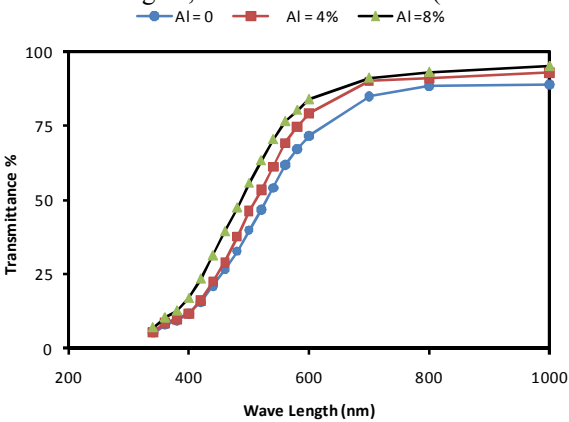

Fig. 4 – Transmittance spectra as a function of wave length for Zno samples deposited at various temperatures(400,450,500 C^0)

This type of shift leads to an increase in the optical energy gap, also we can see the decrease of wave length, as its value very high at the wave length which is located with in optical spectrum and infra – red radiation, which indicates that these films have large energy gap to allow most of the visible light to pass as shown in figure, also the results show that the transmittance is higher than 80 % in all thin films. The optical energy gap (E_{opt}) is defined as the lowest energy required for the electron to travel from the peak of the coordinate band to the peak of conductivity band and can be calculated directly using the electron traveling formula as follows:

$$\alpha(h\upsilon) = A(h\upsilon - E_{opt})^{1/2} \quad (3)$$

And can be rewritten as follows

$$(\alpha h\upsilon)^2 = A^2(h\upsilon - E_{opt}) \quad (4)$$

And when $(\alpha h\upsilon)^2 = 0$, then $E_{op}t = h\upsilon$

The relationship between $(\alpha h\upsilon)^2$ and $(h\upsilon)$ can be plotted as a curve and the extended part of the curve intersects with the photon energy axis at $(\alpha h\upsilon)^2 = 0$ and from it we determine the energy gap of direct allowed traveling as shown in *fig. 5* ,as shows the energy gaps for pure ZnO and doped with a(

4,8%) aluminum .An obvious increase is observed for the values of the energy gap with the increase in the concentration of aluminum and is in accord with previous studies (4,5) within various preparation techniques ,this increase is explained by the preposition that the ZnO:Al films are semiconductors in which the Fermi level lies in the conducive band which means that the levels at the bottom of the conductivity band are occupied by electrons and the shielding of electronic traveling to these levels is termed the Burstein-Moss effect

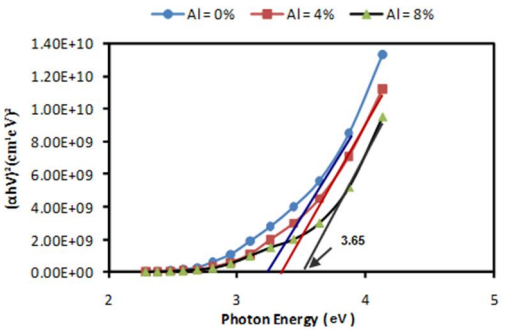

Fig. 5 – Measurement of energy band gap for ZnO deposited at various temperatures (400,450,500500 C^0)

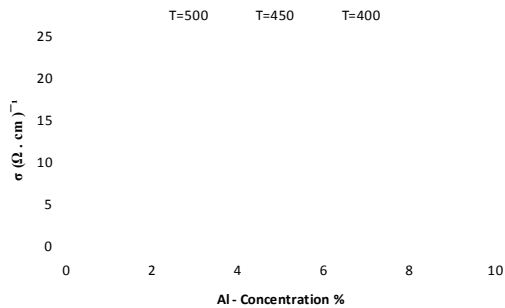

Fig . 6 – Electric conductivity of ZnO un doped ,and doping with (4,8%) for various substrate temperature (400,450,500 C^0)

For these films, E_{opt} is determined from the intersection of the straight lines of the curve with the energy axis at (hv), and Eopt was found to be (3.25, 3.4, 3.65) eV. *Fig. 6* shows the change in the electric conductivity of pure ZnO films doped with aluminum at (4,8%) at substrate temperatures of (400, 450, and 500C^0). It is shown that the electric conductivity increases with the increase in the temperature of the substrate and reaches it highest level at a substrate temperature of 500C^0. The reason attributed to this increase in conductivity with the increase in the substrate temperature is the improvement of crystal structure and then increase in the crystal grains which leads to a decrease in the scattering of the charge carriers at the edges of the grains and in turn increases the mobility of the carriers and conductivity. And then the effect of doping on the electric conductivity was determined at various doping percentages and it was shown in fig (6) that doping had a significant effect of the electric conductivity of ZnO doped with aluminum. At(T= 400 C^0) the electric conductivity is low in general when compared with the substrate temperatures of (450, and 500C^0).

At (450 and 500 C^0) the electric conductivity increased when the doping with aluminum increased until 5% were after that percentage of doping the electric conductivity decreased. The increase in electric conductivity of films doped with an average percentage of aluminum is due to the atoms of triple metals like aluminum that interacts with him film in various was and the aluminum atoms compensate the Zn locations in the Al_{zn} lattice acting as donors as shown in the following formula:

$$Al^{3+} \rightarrow Al^{2+} + e; \quad (5)$$

Al^{2+} occupies the locations in the ZnO lattice and (e) the free electrons that participate in electric conductivity

CONCLUSIONS

From the X-ray diffraction we found, the effects of different aluminum concentrations on the structural properties, electrical resistivity and optical transparency of the films were studied. **,** the films exhibit a dominant peak corresponding to the (002) plane of ZnO, and other peaks corresponding to (100), (101) , and indicating the polycrystalline nature of the films. It is seen from the figure that the relative intensity of the (002) peak decrease with increasing Al dopant concentration. The decrease in peak intensity indicates an improvement in the crystalline of the films.The seem morphology shows the grains are tightly packed., and we can see that the smoothly surface was obtained in case of Al doping in 4%,,from the optical properties we can see the transmission increases with the increase in concentration of doping aluminum, the highest transmission is observed at (8%) doping, also the results show that the transmittance is higher than 80 % in all thin films. The value of the band gap is enhanced from 3.25eV(un doped ZnO thin film) to 3.65 in case of doping with 8% .The increase in the band gap can be explained by the Burstein – Moss effect . ZnO films show good electric conductivity at (450and $500C^0$) and was found to be $(9.740741\ (\Omega\ cm)^{-1}$ and $(14.34615(\Omega\ cm)^{-1}$,and then the electric conductivity of The ZnO films doped with aluminum increases with the increase in temperature and the highest was and $(14.34615(\Omega\ cm)^{-1}$ at $500C^{0.}$

REFERENCES

[1] Joseph B., Manoj P.K., Vajdyan V.K. Bull.Mater. Sci. – 2005. – V. 28, №5. – P.487-493.

[2] Yusta F.J., Hitsman M.L., Shamlian S.H. J. Mat. Chem. – 1997. – V.7, № 8. – P.1421-1427.

[3] De Merchant J., Cocivera M. Chem. of Mater. - 1995. – V.7, №9. – P.1742-1749.

[4] Sushea M., Christoulakis S., Moschovisk K.,) Rev. Adv. Materials Science. – 2005. – V.10. – P.335-340.

[5] Рентгенографический и электронноoптический анализ,(Горелик С.С., Расторгуев Л.Н., Скаков Ю.А.). Приложение. – М.: Металлургия, 1970. – 109 с.