

**STRUCTURAL, OPTICAL, AND ELECTRICAL PROPERTIES OF ZnO:
Al PREPARED BY CVD****A.D. Pogrebnyak¹, N.Y. Jamil², A.K.M. Muhammed¹**¹*Sumy State University, Ukraine*²*University of Mosul, Iraq*

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In this paper we will prepared thin films from transparent conductive oxide(TCO) ZnO pure, and doped for various concentration of aluminum (4,8%) using technique chemical vapor deposition (CVD) at different substrates temperatures (400, 450, 500 °C) 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 that we obtained $E_g = 3.6$ in case of 8% doping Al, and then we noticed the transmittance increases with increasing the substrate temperature and doping percentage with aluminum and the highest value was observed at 500 °C 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 and 500 °C).

Keywords: thin film, chemical vaporous deposition, ZnO, doping, energy gap.

В работе тонкие пленки получены из прозрачного проводящего оксида (ППО), чистого ZnO, легированного алюминием Al (4,8%) различной концентрации. Пленки формировались методом химического осаждения из газовой фазы (CVD) на стеклянные подложки при различных температурах (400 °C, 450 °C, 500 °C). Пленки чистого ZnO и (ZnO: Al) исследовались с помощью метода рентгеновской дифракции с использованием УФ спектрометра. Исследования показали гексагональную поликристаллическую структуру типа вюрцита. Диагностика показала преимущественные пики роста кристаллических зерен в направлениях (002). Оптическими измерениями показано, что пик поглощения смещается в сторону коротких волн, что указывает на увеличение энергетического зазора с повышением концентрации алюминия в ZnO. Отметим также, что коэффициент пропускания увеличивался с повышением температуры подложки и процентного соотношения легированного алюминия. Максимальное значение наблюдалось при 500 °C и процентном соотношении легированного алюминия (8%). Электропроводность пленок ZnO, легированных алюминием, возрастала с увеличением процентного соотношения легируемого материала до (4%), а затем начинала уменьшаться, не смотря на увеличение процентного соотношения легированного материала при температуре подложки (400 °C и 500 °C). **Ключевые слова:** тонкие пленки, химическое парообразное осаждение, ZnO, импульсное лазерное напыления.

У роботі тонкі плівки виготовлені з прозорого провідникового оксиду (ППО) чистого ZnO, легованого алюмінієм (4,8 %) різної концентрації. Нанесення здійснювалося методом хімічного осадження з газової фази (CVD) на скляні підкладки при різних температурах (400 °C, 450 °C, 500 °C). Плівки чистого ZnO і (ZnO: Al) досліджувалися за допомогою методу рентгенівської дифракції з використанням УФ спектрометра. Дослідженнями встановлено гексагональну полікристалічну структуру типу вюрциту. Диагностика показала переважні піки росту кристалічних зерен у напрямках (002). Оптичними вимірюваннями встановлено, що пик поглинання зміщується у бік коротких хвиль, яка вказує на збільшення енергетичного зазору із підвищенням концентрації алюмінію в ZnO. Зазначимо також, що коефіцієнт пропускання підвищувався зі зростанням температури підкладки і процентного співвідношення легованого алюмінію. Максимальне значення спостерігалось при 500 °C та відсотковому співвідношенні легованого алюмінію (8%). Электропроводність плівок ZnO, легованих алюмінієм, зростала зі збільшенням процентного співвідношення легованого матеріалу до (4%), а потім спостерігається-

ся зменшення, не зважаючи на зростання процентного співвідношення легованого матеріалу при температурі підкладки (450 °C і 500 °C).

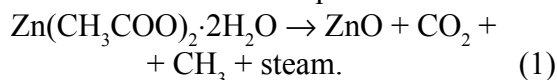
Ключові слова: тонкі плівки, хімічне пароподібне осадження, ZnO, імпульсне лазерне напilenня.

INTRODUCTION

In the recent years, ZnO have received considerable attention due to its application in electrical, optical, mechanical and scientific research's as well as industry. 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 its 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 optoelectronic 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 450 °C. 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 as the optical, and electrical properties of the films.

EXPERIMENTAL PROCEDURE

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 $Zn(CH_3COO)_2 \cdot 2H_2O$ with 98% purity. After preparing the substrates, they were placed and adjusted in the deposition unit while the temperature degrees were varied between (400 – 500 °C) 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 visual and microscopic inspection. Various temperature degrees were tested when heating the deposition material and it was found that the temperature of (340 °C – 350 °C) is the appropriate temperature degree range. Deposition time was kept constant at (20 min.) 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



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

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

where a , C is lattice constant, h , k , L is Miller indices.

The crystalline structure was analyzed by X-ray diffractometer (DROT-20 v Cu- k_{α}) in the range 2θ of 30 – 80, the surface morphology of the films was analyzed using scanning electron microscope model (REM-106) before and after annealing. The optical transmittance was measured using a ENGLAND (1000 SERIES a" CECIL 1021) spectrophotometer in the wavelength range from 300 to 1000 nm.

RESULTS AND DISCUSSION

STRUCTURAL PROPERTIES

X-ray diffraction studies of the structure of the material were carried out on an automated DRON-4-07 ("Bourestnik", www.bourestnik.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.

Fig. 1, table 1 displays the XRD spectrum of ZnO films. Three lines (100) at $2\theta = 31.76^\circ$, (002) at $2\theta = 34.47^\circ$, (101) at $2\theta = 36.24^\circ$ 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

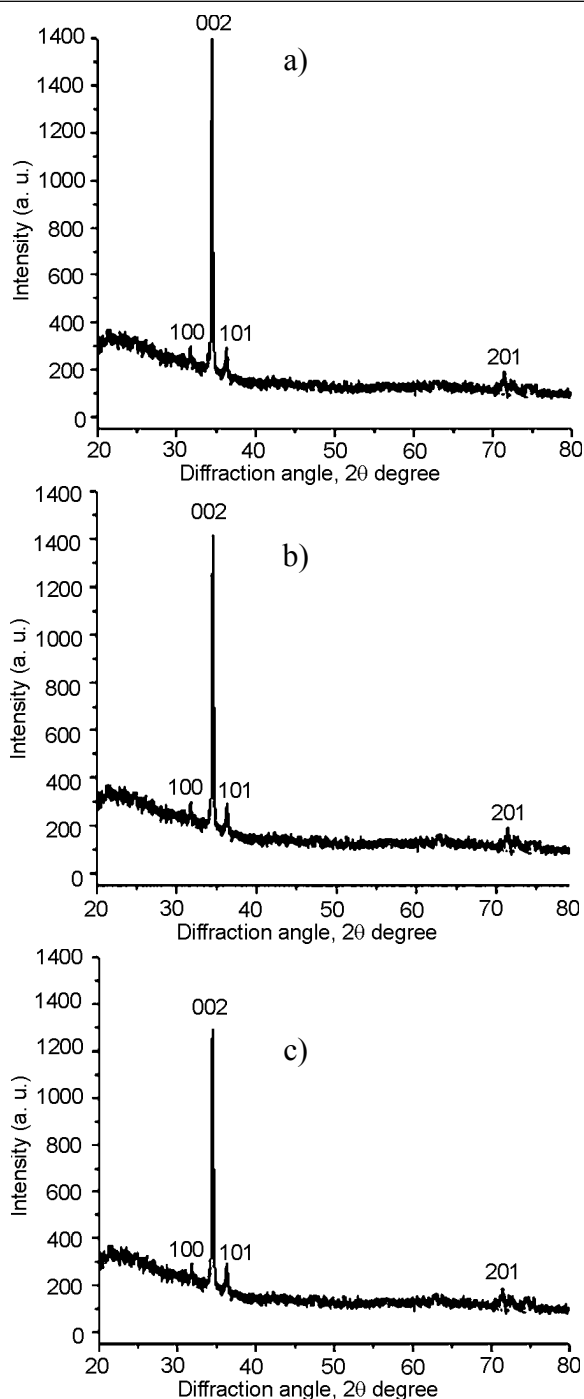


Fig. 1. X-ray diffraction of ZnO, a) – pure, b) – 4% doping, c) – 8% doping.

increase in the bond. These result were confirmed with those obtained from the Joint committee of powder diffraction standards JCPDS for the ZnO.

Table 1

Lattice parameter of ZnO

No	2θ, Degree	h k L	d_{hkl} , Å	a, Å	c, Å	Result standard	
						d_{hkl} , Å	(a, c), Å
ZnO	31.72	1 0 0	2.816	3.24	5.17	2.814	a = 3.249 c = 5.206
	34.76	0 0 2	2.56			2.603	
	36.6	1 0 1	2.456			2.475	

SURFACE MORPHOLOGY

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% as shown in fig. 2.

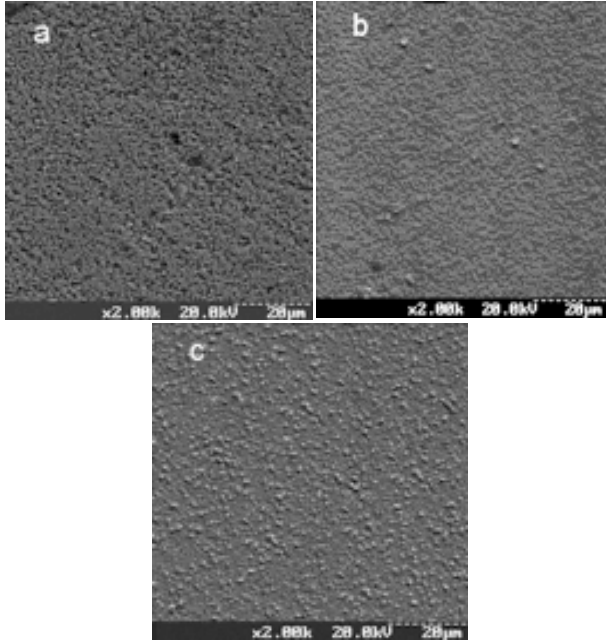


Fig. 2. Scem image of thin film ZnO, a) – pure, b) – 4 % doping Al, c) – 8 % doping.

OPTICAL PROPERTIES

Fig. 3 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 figures, 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 ($E_g > 3$ eV) which equals to ($\lambda < 400$ nm) as du-

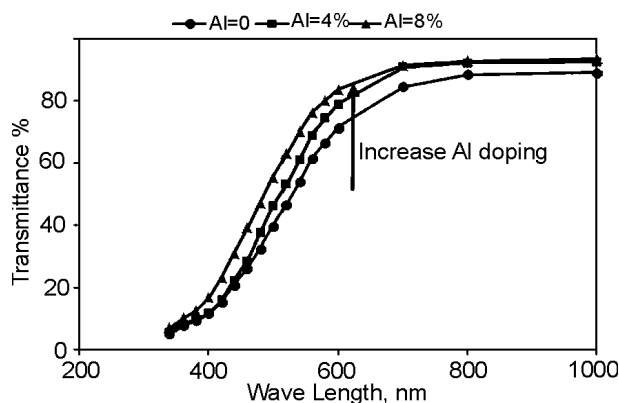


Fig. 3. Transmittance spectra as a function of wave length for ZnO samples deposited at various temperatures (400, 450, 500 °C).

ring 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 fig. 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. 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 within 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:

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

and can be rewritten as follows

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

and when $(\alpha h\nu)^2 = 0$, then $E_{opt} = h\nu$.

The relationship between $(\alpha h\nu)^2$ and $(h\nu)$ can be plotted as a curve and the extended part of the curve intersects with the photon energy axis at $(h\nu)^2 = 0$ and from it we determine the energy gap of direct allowed traveling as shown in fig. 4, 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 proposition that the ZnO: Al films are semiconductors in which the Fermi level lies in the conductive 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. For these films, E_{opt} is determined from the inter-

section of the straight lines of the curve with the energy axis at $(h\nu)$, and E_{opt} was found to be (3.25, 3.4, 3.6) eV.

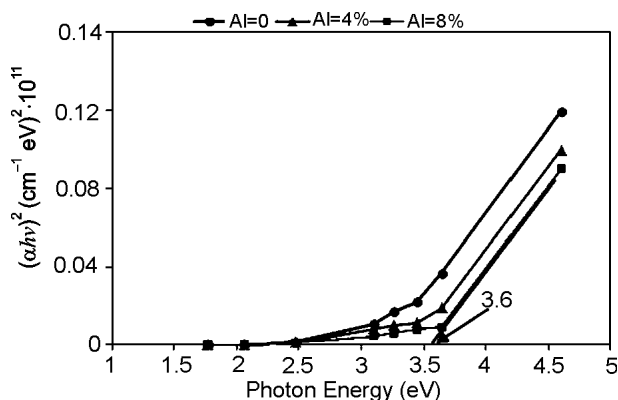


Fig. 4. Measurement of energy band gap for ZnO deposited at various temperatures (400, 450, 500 °C).

ELECTRICAL PROPERTIES

Fig. 5 shows the change in the electric conductivity of ZnO un doped and doping with aluminum at (4,8%). The effect of doping on the electric conductivity was determined at various doping percentages and it was shown in figure that doping had a significant effect of the electric conductivity of ZnO doped with aluminum.

Fig. 5 shows the change in the electric conductivity of pure ZnO films doped with aluminum at (4,8%) at substrate temperatures of (400, 450, and 500 °C). 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 500 °C. 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

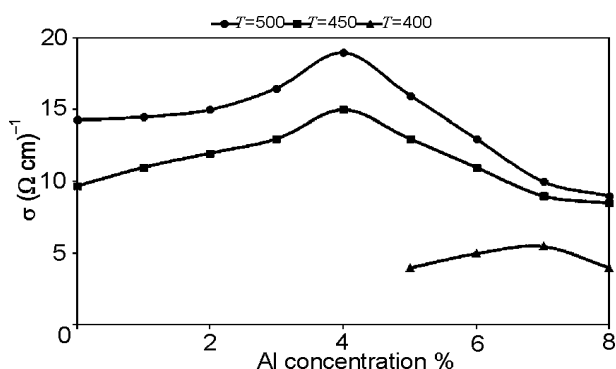
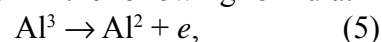


Fig. 5. Electric conductivity of ZnO un doped, and doping with (4,8%) for various substrate temperature (400, 450, 500 °C).

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. 5 that doping had a significant effect of the electric conductivity of ZnO doped with aluminum. At ($T = 400$ °C) the electric conductivity is low in general when compared with the substrate temperatures of (450, and 500 °C). At (450 and 500 °C) 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^{2+} occupies the locations in the ZnO lattice and (e) the free electrons that participate in electric conductivity.

CONCLUSION

The most important conclusions reached by the study are as follows: 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 seam 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 3.25 eV (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. The ZnO films show good electric conductivity at (450 and 500 °C) and was found to be $9.740741 (\Omega \text{ cm})^{-1}$ and $14.34615 (\Omega \text{ cm})^{-1}$, and then the electric conductivity of The ZnO films doped with aluminum increases with the increase in temperature and doping, the highest was $19.34615 (\Omega \text{ cm})^{-1}$ at 500 °C and 4% doping, then starts to decrease with the increase in doping percentages at the temperatures (450 °C and 500 °C).

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