Aleksander D. POGREBNJAK[1], Abid A. MUHAMMED[1], Emad T. KARASH[2], Nawfal Y. JAMIL[3], Janusz PARTYKA[4]

Sumy State University, Sumy, Ukraine (1), Technical of Education, Institute of Mosul, Mosul, Iraq (2), University of Mosul, Mosul, Iraq (3), Lublin University of Technology, Lublin, Poland (4),

Effects of Al dopant on structural and optical properties of ZnO thin films prepared by sol-gel

Abstract. *Transparent and conductive Al doped ZnO thin films were synthesized at room temperature by sol gel technique both pure ZnO and Al-doped(1,3,and5%) thin films were deposited on a glass substrate. The sols were prepared using zinc acetate dehydrate and aluminum chloride provides Al ions, played an important role in improvement of the c – axis, the structural characteristics have been studied by X-ray diffraction, and UV–Vis-NIR spectroscopy. The films are transparent from the near ultraviolet to the near infrared, SEM image also showed that the average grain size is decreased with increasing of Al concentration, band gap values of prepared thin films varied in the range of (3.18 – 3.42 eV).*

Streszczenie. *Przejrzyste i przewodzące cienkie warstwy Al domieszkowane ZnO zostały zsyntetyzowane w temperaturze pokojowej techniką zol-żel. Na podłożu szklanym naniesiono cienkie warstwy Al niedomieszkowanego oraz domieszkowanego ZnO w stosunku 1, 3, i 5%. Zole zostały przygotowane wykorzystując dwuwodny octan cynku i chlorek aluminium. Jony Al odegrały ważną rolę w ulepszaniu osi c. Charakterystyki stukturalne przebadano metodą dyfrakcji rentgenowskiej i spektroskopii UV-Vis-NIR. Warstwy są przejrzyste od bliskiego ultrafioletu do bliskiej podczerwieni. Obrazy SEM wykazały również, że średni rozmiar ziarna zmniejsza się wraz ze wzrostem poziomu domieszkowania Al. Wartości przerw między pasmami w przygotowanych cienkich warstwach zmieniały się w zakresie (3.18 – 3.42 eV). (**Wpływ domieszki Al na właściwości strukturalne i optyczne cienkich warstw ZnO wytworzonych metodą zol-żel**).*

Key words: thin films, sol-gel, ZnO:Al, doping, optical properties, pulsed laser deposition.
Słowa kluczowe: cienkie warstwy, zol-żel, ZnO:Al, domieszkowanie, właściwości optyczne, impulsowe osadzanie laserowe.

1. Introduction

Zinc Oxide (ZnO) film 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, [1, 2] and the ability to deposit these films at relatively low substrate temperatures [3]. The oxygen vacancies and/or zinc interstitials correspond to the n-type conductivity of the ZnO films. ZnO has a hexagonal wurtzite structure with the divalent cation (Zinc) in tetrahedral coordination with oxygen, and each oxygen in tetrahedral coordination with four divalent cations (zinc) [4]**.** Thin films of un doped and doped ZnO are utilized for a wide variety of electronic and opto-electronic applications, such as surface acoustic wave devices [4], transparent conducting electrodes [2], heat mirrors [3]. Nano scale porous structures of ZnO with a high surface area find their application in chemical sensors [5] and dye-sensitized solar cells [6].Various techniques have been used to deposit of un doped and doped ZnO films on different substrates, including spray pyrolysis [7], organ metallic chemical vapor deposition [8], pulsed laser deposition [9], sputtering [10], and sol-gel process [6]. Among these, the sol-gel technique is credited with several advantages, such as deposition of high purity, homogeneous, cheaper, large-area films at relatively low temperatures. There are scarcely any reports on the transport parameters of ZnO:Al films prepared by the sol-gel technique. In this paper, we concentrate on the structural, electrical conductivity and optical properties of sol-gel derived ZnO and ZnO:Al films deposited by spin coating.

2. Experimental Procedure

ZnO thin films were prepared by the sol–gel method. As a starting material, zinc acetate dehydrate was used. In order to deposit Al doped ZnO thin film, solutions were prepared by dissolving zinc acetate, Zn (CH3COO)2·2H2O (purity 99.95%), in anhydrous methanol in increasing Al doping concentrations (98.5% purity AlCl3) ranging from 1 to 5%ppv was added to solution and this solution were continuously stirred for 24 h at room temperature, , then the sol filtered which then it was ready to be used to prepare the film by spin coating method as before using as sols in the dip – coating process, the AZO and ZnO films were deposited on glass substrate, which cleaned ultrasonically, first in acetone, and subsequently in methanol for 10 minutes each. They were further cleaned with ion exchanged distilled water for 20 minutes and kept in an oven at 75ºC for 20 minutes. Thin films were then dried at 70ºC for 20 min., this process repeated 6 times after each film cooled down to room temperature, then these films were annealed at 500ºC for one hour for decomposition and oxidation of the precursors. The crystalline structure was analyzed by X-ray diffract meter (DRON-2.0 in Cu-kα) in the range (30-70)of 2θ.

The optical transmittance was measured using a scanning ENGLAND (1000SERIES≡CECIL 1021) spectrophotometer in .the wavelength range from 300 to 1000 nm. The electrical resistance was measured by a four-point probe method.

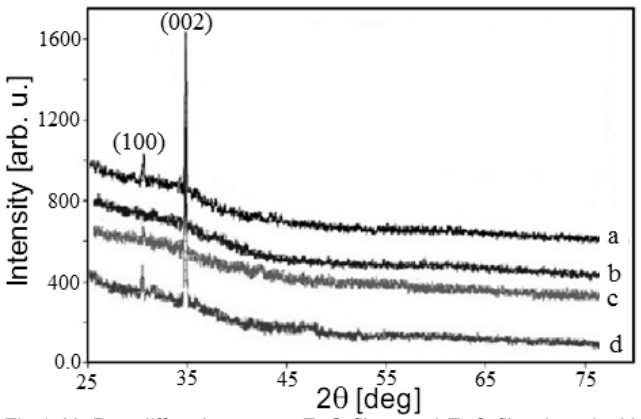

Fig.1. X- Ray diffraction , pure ZnO films and ZnO film doped with Al, (1, 3, and 5 %) (a,b,c,d)

3. Results and Discussion

3.1 Structural properties

Figure 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 1% to 5 % 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), indicating the polycrystalline nature of the films. It is seen from the figure that the relative intensity of the (002) peak decrease with increasing of Al dopant concentration. The decrease in peak intensity indicates an improvement in the crystallinity of the films. Besides, a slight shift was observed with the peaks in the direction of the lesser angles which may be attributed to the small increase in the bond.

3.2 Surface morphology

The film microstructure was studied using Scanning Electron Microscopy. Scanning electron micrographs showed a close packed morphology for both pure ZnO and Al-doped films and a decrease in grain size with doping was clearly seen in the micrographs (figures 2(*a*), (b), (c), and (*d*)). This figure depicts the surface morphological study of pure ZnO,and AZO (1 – 5 % doping AL),had been observed that the AZO thin film exhibited a predominant rod shape (hexagonal ZnO particles in figure 2),as a result of the high degree of c – axis orientation .The SEM image showed that the average grain size is decreased with increasing of Al doping.

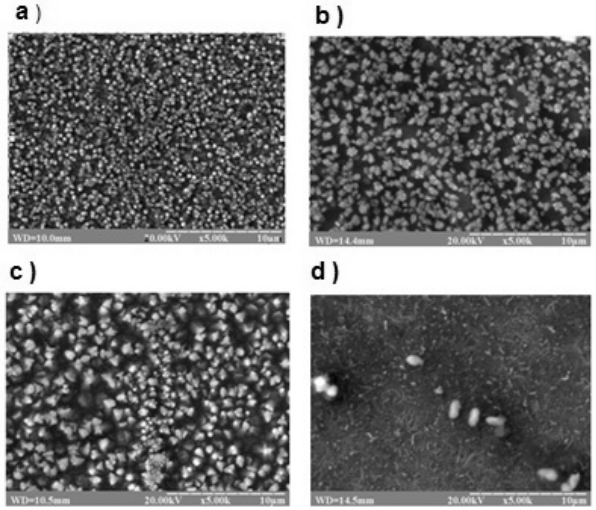

Fig.2. SEM images of (a) pure ZnO ZnO,(b) 1% AZO ,(c) 3% AZO (d)5% AZO

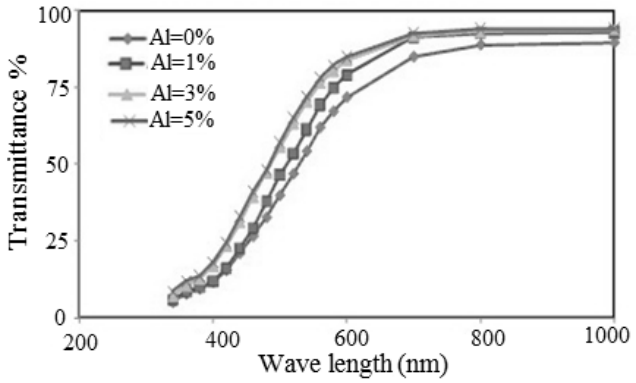

Fig.3. transmittance spectra as a function of the wavelength for pure ZnO, and doping alumiium,1%, 3%, 5%

3.3 Optical properties

From these figures, we can see ,the absorption spectra as a function of the wavelength of the pure ZnO films and the ZnO films doped with (1, 3, 5%) aluminum. The highest transmission is observed at (5%) doped aluminum, this can be explained , the increase in concentration of doping aluminum causes to improve the crystal structure. X-rays diffraction displays, two regions are obvious: The first was , energy gap (Eg>3eV) which equals to λ < 400 nm.

The second region lies within the wavelengths range of (400 < λ < 1000nm) 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 (2) 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, the decrease of wave length, optical spectrum and infra – red radiation, which indicates that these films have large energy gap to allow most of the visible light to pass .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:

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

And can be rewritten as follows

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

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 $(\alpha h\nu)^2 = 0$ and from it we determine the energy gap of direct allowed traveling as shown in figures (3).

Figure (3) shows the energy gaps for pure ZnO and doped with a (1,3,5%) aluminum. An obvious increase is observed for the values of the energy gap with the increase in the concentration of aluminum. 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. Figure (4) shows the change in the electric conductivity of pure ZnO and doping with aluminum at (1, 3, 5%). The effect of doping on the electric conductivity was determined at various doping percentages and it was shown in figure (4) that doping had a significant effect of the electric conductivity of ZnO doped with aluminum.

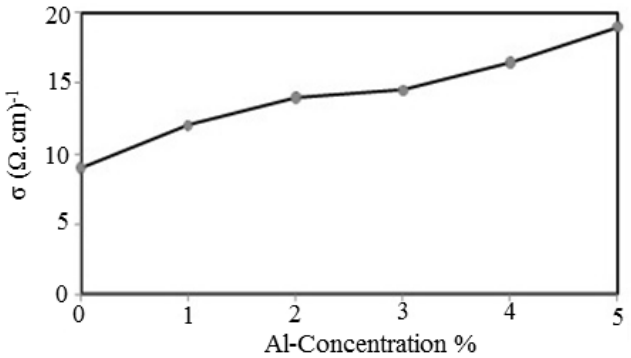

Fig.4. Electric conductivity of ZnO un doped, 1%AZO, 3%AZO, 5%AZO

The increase in electric conductivity of films doped with an average percentage of aluminum is due to the aluminum atoms compensate the Zn locations in the Al_{zn} lattice acting as donors as shown in the following formula:

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

Al^{2+} occupies the locations in the ZnO lattice and (e) the free electrons that participate in electric conductivity. When doping with aluminum at percentages of (1%) and (5%) there was an increase in the electrons with the increase in the values of mobility. The results indicate that the increase in the percentages of doping to (5%) has led to the increase in the donor levels and which in turn led to an increase in the number of atoms that donate electrons and become ions, the value of electric conductivity of thin films is changed from 8.7 $(\Omega \cdot cm)^{-1}$ for ZnO un doped to 18.7 $(\Omega \cdot cm)^{-1}$ in case of ZnO doped with 5 %.

4. Conclusion

Transparent and high conductive Al-doped ZnO thin films on glass substrates were prepared by sol–gel method using spin-coating technique for film deposition. 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) indicating the polycrystalline nature of the films, the SEM image also showed that the average grain size is decreased with increasing of Al. The optical properties we can see the transmission increases with the increase in concentration of doping aluminum, the highest transmission is observed at (5%) doping. The results show that the transmittance is higher than 80 % in all thin films. The value of the band gap is enhanced from 3.18eV(un doped ZnO thin film) to 3.42 in case of doping with 5% .The increase in the band gap can be explained by the Burstein – Moss effect. The increase in electric conductivity of films was determined at various doping percentages and it was shown that doping had a significant effect the electric conductivity of ZnO doped, the conductivity of thin films is changed from 8.7 $(\Omega\ cm)^{-1}$ for pure ZnO to 18.7 $(\Omega\ cm)^{-1}$ in case of ZnO doped with 5 %.

REFERENCES

[1] Shan F.K., Yu Y.S., Band gap energy of pure and Al-doped ZnO thin films, *Journal of the European Ceramic Society*, 24 (2005), 1869-1872

[2] Kim Y.S., Tai W.P., Shu S.J., Effect of preheating temperature on Structural and optical properties of ZnO thin films by sol–gel process, *Thin Solid Films*, 491 (2005), 54-60

[3] Pogrebnjak A.D., Jamil N.Y., Muhammed A.K.M. Structural and optical properties of ZnO prepared by CVD before and after annealing, *Metallofiz. Noveishie Tekhnol,* 33 (2011), 235-241

[4] Rozati S.M. Influence of substrate temperature on the structure of ZnO:Al thin films / S.M. Rozati, S.H. Akese, *Cryst. Res. Technol*, 43(2007), n.1-3, 273-275.

[5] Wienke J. ZnO:In deposition by spray pyrolysis -influence of the growth condition of the electrical and optical properties , *Thin Solid Films*, (2007) ,n. 4, 5-11.

[6] Tang P., Zu Z.K., Wong G.K.L., Kawasaki M., Ohtomo A., Koinuma H., Segawa Y., Ultraviolet spontaneous and stimulated emissions from ZnO microcrystallite thin Film at room temperature, *Solid State*, 103 (1997), 459-463

[7] Aqili A.,K.S. Ali A.M., Characterization of zinc telluride thin films deposited by two-source technique and post-annealed in nitrogen ambient , *J. Crystal Growth*,317(2011),47-51.

[8] Bandyopadhyay S., Paul G.K, Sen S.K., Study of optical properties of some sol–gel derived films of ZnO, *Solar Energy Materials and Solar Cells,* 71 (2002), 103-113

[9] Pogrebnjak A.D.Jamil N.Y.,Muhamed A.M, Electrical and optical properties of ZnO:Al films prepared by chemical vapour deposition (CVD) / Proceedings of 1st International conference "Nanomaterials: Applications & properties" (NAP-2011). – Ukraine, Crimea, Alushta, Sptember 27-30, (2011). 226-232.

[10] Pogrebnjak A.D.,Muhamed A.K.M., Simulation Study of Effect on Thin Film GIGS Solar Cell Perfomence, *J. Nano-Electron. Phys,* 3(2011),52-59

Authors:

Prof. Aleksander D. Pogrebnjak, Abid Alkarem Muhammed, Sumy State University, St-Rimsky ,Korsakov 2, 40002 Sumy, Ukraine, E-mail: apogrebnjak@simp.sumy.ua;

Emad Toma Karash, Technical of Education, Institute of Mosul, Mosul, Iraq, E-mail: emadbne2007@yahoo.com;

Dr Nawfal Y. Jamil, University of Mosul, Mosul, Set Culture, Iraq, E-mail: nawfaljamil@yahoo.com;

Prof. Janusz Partyka, Department of Electrical Devices and High Voltage Technology, Lublin University of Technology, 38a Nadbystrzycka Str., 20-618, Lublin, Poland.