

Synthesis, Characterization and Dielectric Properties of ZnO Nano Structure

Mohamed Khazal Hussien
Middle Technical University, Baghdad, Iraq

Abstract: ZnO nanostructures were synthesized in low cost efficient method, chemical reaction was obtained by dissolving (0.05 M) of zinc nitrate and Hexamethylenetetramine (HMT) in distilled water. The reaction product were examined by X-Ray Diffraction (XRD) and the Scanning Electron Microscope (SEM) and UV-visible spectrophotometer. Thick films were deposited by drop casting on different substrates. The electrical and thermo power were studied. C-V measurement and dielectric parameter as a function of frequency of the films were obtained with LCR meter.

Key words: Nano structure, electrical properties of semiconductors, ZnO films, function, frequency, films

INTRODUCTION

Metal-oxide semiconductors are widely used as promising technological materials for the development of recent electronic and photonic devices (Yakuphanoglu *et al.*, 2010) ZnO is one of the metal oxide semiconductors which has great attention in this field because of ZnO unique properties, the unsymmetrical in wurtzite combined with large electromechanical coupling, results in strong piezoelectric and pyro electric properties and the resultant use of ZnO in mechanical piezoelectric sensors (Kumar and Kim, 2012). In addition, ZnO is a wide band-gap (3.37 eV) compound semiconductor that is suitable for short wavelength optoelectronic applications. The high exciton binding energy (60 meV) in ZnO crystal can ensure efficient excitonic emission at room temperature (Shashidhara *et al.*, 2016; Klimov, 2003).

ZnO is transparent to visible light and can be made highly conductive by doping. And the aperture of growth of its nanostructures on many types of substrates. For these properties ZnO become an important potential used as a functional material applied in different applications (Han *et al.*, 2008; Abbas *et al.*, 2016).

Also, ZnO nano materials of different morphologies such as nanowires, nanotubes, nanorods and nanoparticles, appear potential as enabling materials in wide domain of applications such as field effect transistors optically pumped lasers, photo detectors, optical switches and sensors due to their unique and exciting electronic, optical and piezoelectric properties (Dhaware and Lokhande, 2011; Sun *et al.*, 2012).

In addition, ZnO nanostructures have also got more interest due to the chemical detection applications because of the high sensitivity of its surface conductivity to the presence of adsorbed gases (Gurav *et al.*, 2012). However, many technological applications of ZnO depends on the development of growth and processing techniques to control the surface morphology, concentration and distribution of the bulk and surface

defects that effect on the physical properties. In other hand the developing of synthesis methods to control the surface morphology of ZnO nanostructures because it is well known that the surface-to-volume ratio also has a significant effect on the material's physical properties (Gurav *et al.*, 2012).

MATERIALS AND METHODS

ZnO nanostructure powder was prepared chemically, All reaction materials used in this research, NaOH and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with high purity ($\geq 99\%$) from Sigma Aldrich. A solution of 1 M-NaOH was prepared by dissolving 4 g of NaOH in 100 mL of deionized water. A solution of equal molarity 0.05 M) of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and (HMT) were dissolved in 200 mL of double distilled water under continues stirring with heating at 70°C . The NaOH was added wisely to the solution till the PH reach (10) and the prepared pressures was continues stirred under heated at 70°C for 3 h. White powder settled down at the end of the process, the product was collected and washed with ethanol and deionized water 4 times using a centrifuge. The ZnO product was dried at 120°C in furnace for 1 h. The crystalline structure and morphology of ZnO powder was examined by x-ray diffractometer with ($\text{Cu K}\alpha$, 1.5406 \AA) as X-ray source.

Structural properties: X-ray characterizations the X-ray diffraction test is very important to identify the product and studying its structural properties. The crystallite size is calculated using Scherer's equation (Chaari *et al.*, 2011):

$$D = \frac{0.9\lambda}{(\beta \cos \theta)} \quad (1)$$

Where:

D = The crystallite size

λ = 1.5406 \AA

β = The FWHM

θ = The diffraction angle

Due to preparation condition and growth process, thick film undergoes a micro strain and dislocations in its structure (Kumar *et al.*, 2013). The dislocation density are calculated from equation:

$$\delta = \frac{1}{D^2} \quad (2)$$

While micro strain of the film was obtained using the equation:

$$\varepsilon = \beta \cos \frac{\theta}{4} \quad (3)$$

Optical transition measurement: The optical properties are examined using UV-Vis-NIR (Split-beam optics, dual detectors) spectrophotometer equipped with a xenon lamp. The wavelength range (300-900 nm). ZnO film was deposited on glass substrate. the transmission of the film is defined as I/I_0 and depends on many parameters such as thickness. The absorption coefficient and optical Energy band gap (E_g) for direct transition obey the equation (Wang *et al.*, 2004):

$$\alpha h\nu = (h\nu - E_g) \frac{1}{2} \quad (4)$$

The electrical and dielectric measurements: Many films were prepared for different electrical measurements purpose aluminum electrodes were deposited on the ZnO thick films using vacuum thermal evaporation technique to study the electrical resistivity and thermoelectric power which is represent the ratio of generated voltage to temperature difference. These two measurements obtained using homemade system in the range 300-500 K while the dielectric measurement were obtained using LCR meter, first conductive layer of Al evaporated on galas substrate then ZnO thick film was deposited on conductive substrate and in the upper face of ZnO thick film (1 cm² Al electrode). The dielectric properties as a function of frequency can be represented by the relation (Rahman *et al.*, 2013):

$$\varepsilon(\omega) = \varepsilon_i(\omega) - \varepsilon_r(\omega) \quad (5)$$

where, the imaginary part ε_i represent the energy loss and the real part ε_r represent the storage energy for one period of the electric field. The Capacitance (C) were measured using LCR meter in order to calculate the real part according to the relation (Latif *et al.*, 2012):

$$\varepsilon_r = \frac{C d}{\varepsilon_0 A} \quad (6)$$

Where:

D = The thickness of the film

A = Represent area of the electrode

ε_0 = The permittivity of space = $8.85 \times 10^{-12} \text{ (Nm}^2\text{)}^{-1}$

While the energy lose (ε_i) calculated from the obtained measurements of Dissipation factor (D):

$$D = \frac{\varepsilon_i}{\varepsilon_r} \quad (7)$$

$$\varepsilon_i = D \varepsilon_r \quad (8)$$

RESULTS AND DISCUSSION

Structural and morphology characterizations: Figure 1 refers to the diffraction spectra of the prepared thick film it have polycrystalline structure with major peaks in the direction (100, 002 and 101) comparing with (JCPDS) cards. The peaks are sharp with high intensity indicating a good crystallinities. From the diffraction pattern it's clear that the growth is dominated in the direction of 100 indicate preferential c-axis orientation because of synthesis condition and heat treatment process, the thick film experience a micro strain and dislocations in its structure. The grain size, dislocation density and the micro strain of the film were estimated from XRD and the obtained data from it using Eq. 1-3 and illustrated in Table 1.

Figure 2 shows the morphology of the prepared ZnO film the (FESEM) pictures appear homogeneous and confirm the nanostructure of the film.

Optical properties: Figure 2 shows the transmittance of ZnO thick films it's obvious that the absorption edge in UV-Visible range (around 360 nm) with high transmittance ratio ($\geq 60\%$) depends on film thickness. The absorption coefficient calculated using lambert equation and the energy gap (E_g) was estimated from Fig. 3 and 4, it was found (3.41 eV) indicating a blue shift (Kolodziejczak-Radzimska and Jesionowski, 2014).

Electrical and Die electric characterizations: The electrical resistivity (ρ) of the prepared film was tested and measured in range of 300-550 K using a

Table 1: Structural parameters of ZnO thick films prepared by chemical method

Plane No.	Crystallite size D (nm)	Dislocation Density δ (line ² /m ²) $\times 10^{15}$	Micro strain $\varepsilon \times 10^3$
100	16.38	1.46	1.41
002	18.50	1.69	1.34
101	21.10	1.89	1.42

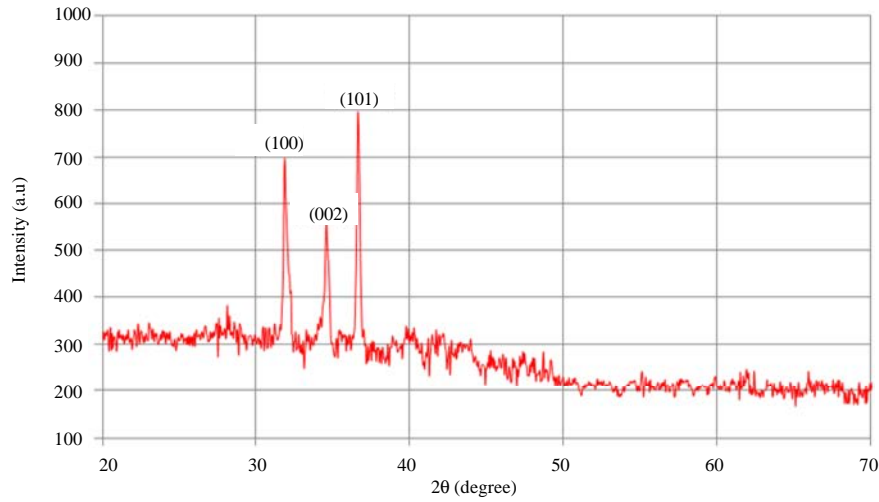


Fig. 1: XRD pattern for ZnO thick films prepared by chemical method

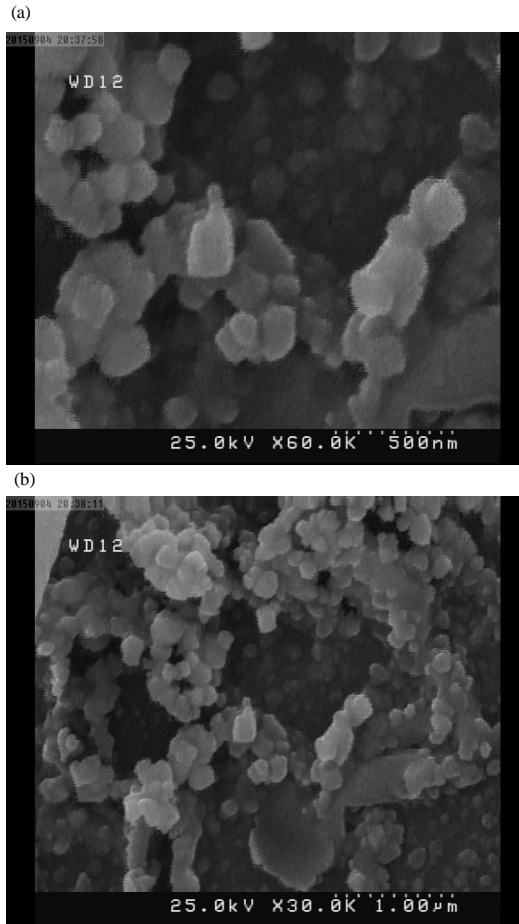


Fig. 2: FESEM pictures for ZnO thick

homemade setup. The room temperature electrical resistivity for film was found of the order of $10^{-4} \Omega \text{ cm}$.

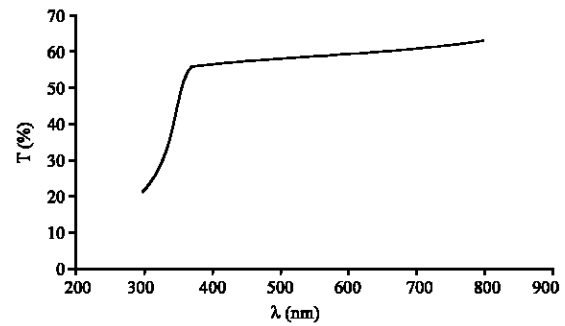


Fig. 3: Transmittance for ZnO thick film via. wave length

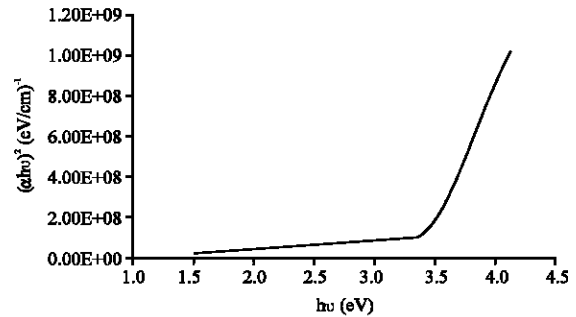


Fig. 4: $\alpha h\nu^2$ via. photon energy for ZnO thick film

The electrical resistivity decreases with increase in temperature confirming the semiconducting behavior of the film. Figure 5 shows temperature dependence of resistivity (ρ) for ZnO film.

Figure 6 represent the change of thermo-electro motiveforce (ΔE) with temperature difference (ΔT). this curves gives a good information about charge carriers in the tested film. The polarity of thermo-electro motive force at the hot end generated voltage at hot end confirm

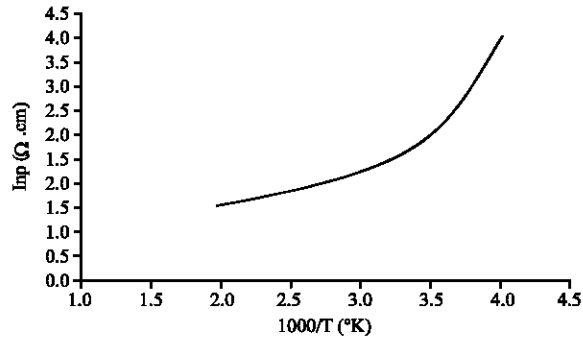


Fig. 5: $\ln p$ via. $1000/T$ for ZnO film

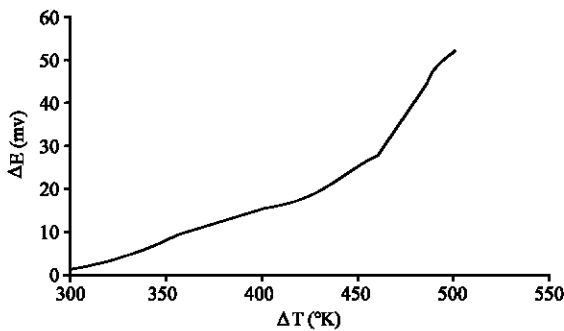


Fig. 6: ΔE as function for ΔT

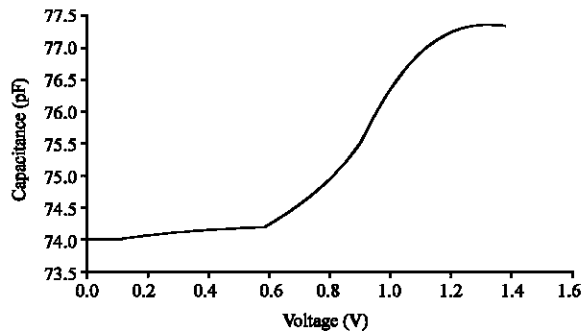


Fig. 7: Capacitance via. voltage at frequency 200 kHz

that the films exhibit an n type electrical conductivity. The variation of thermo-emf with temperature difference (ΔT) increases with increasing of temperature difference.

Die electric characterizations: From the estimated of C-V data as shown in Fig. 7 under a fixed field of 200 kHz, it can be conclude that the capacitance of the Al/ZnO/Al device increased exponentially with voltage which is the characteristics of a Schottky junction (Dhale *et al.*, 2015).

The storage energy ϵ_r and energy loss ϵ_i electric field were study as a function of frequency in the range 1200 kHz. The storage energy significant decrease at

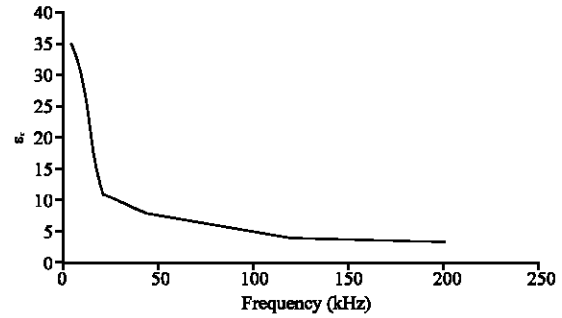


Fig. 8: ϵ_r as a function of frequency

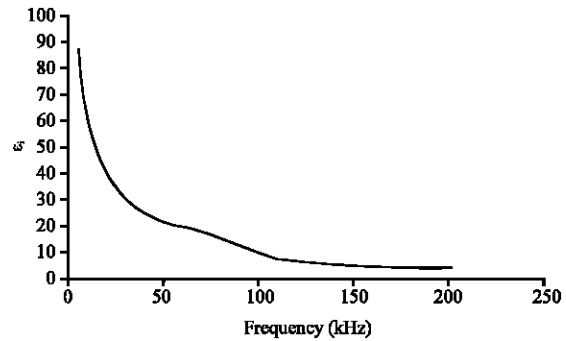


Fig. 9: ϵ_i as a function of frequency

low frequency region (1-20 kHz) then the decreasing become slower in the region 20-100 kHz then ϵ_r become steady at high frequencies = 100 kHz as shown in Fig. 8.

The energy loss decrease with increasing frequency in the region (1-50 kHz) then relatively slower decrease until 110 kHz and no change observed at (≥ 120 kHz) as shown in Fig. 9. This behavior of ϵ_r and ϵ_i indicate that ZnO thick film able to store potential and study as a capacitance.

CONCLUSION

ZnO polycrystalline nanostructure (n) type thick films were successfully synthesized with simple efficient chemical method. The thick film can absorb and stored electrical potential. The relative permittivity of the film decreases with increasing of frequency because of the polarization, the relaxation time of the film increase when decreasing of frequency so it can be store more energy due to the decrease of dielectric loss.

REFERENCES

- Abbas, K.N., N. Bidin and R.S. Sabry, 2016. Controllable ZnO nanostructures evolution via synergistic pulsed laser ablation and hydrothermal methods. *Ceram. Intl.*, 42: 13535-13546.

- Chaari, M., A. Matoussi and Z. Fakhfakh, 2011. Structural and dielectric properties of sintering zinc oxide bulk ceramic. *Mater. Sci. Appl.*, 2: 764-769.
- Dhale, B.B., S.H. Mujawar and P.S. Patil, 2015. The preparation of zinc oxide thin films and the study of their electrical and optical properties. *Intl. J. Emerging Res. Manage. Technol.*, 4: 207-212.
- Dhawale, D.S. and C.D. Lokhande, 2011. Chemical route to synthesis of mesoporous ZnO thin films and their liquefied petroleum gas sensor performance. *J. Alloys Compd.*, 509: 10092-10097.
- Gurav, K.V., U.M. Patil, S.W. Shin, S.M. Pawar and J.H. Kim *et al.*, 2012. Morphology evolution of ZnO thin films from aqueous solutions and their application to Liquefied Petroleum Gas (LPG) sensor. *J. Alloys Compd.*, 525: 1-7.
- Han, J., W. Chen, J. Zhang, M. He and A.K. Azad *et al.*, 2008. Terahertz response of bulk and nanostructured ZnO. *Piers Online*, 4: 391-395.
- Klimov, V.I., 2003. Semiconductor and Metal Nanocrystals: Synthesis and Electronic and Optical Properties. CRC Press, New York, USA., ISBN:9780824747169, Pages: 500.
- Kolodziejczak-Radzimska, A. and T. Jesionowski, 2014. Zinc oxide-from synthesis to application: A review. *Materials*, 7: 2833-2881.
- Kumar, B. and S.W. Kim, 2012. Energy harvesting based on semiconducting piezoelectric ZnO nanostructures. *Nano Energy*, 1: 342-355.
- Kumar, V., D.K. Dwivedi and P. Agrawal, 2013. Optical, structural and electrical properties of nanosized zinc oxide sintered films for photovoltaic applications. *Sci. Sintering*, 45: 13-19.
- Latif, I., E.E. AL-Abodi, D.H. Badri and J. Al Khafagi, 2012. Preparation, characterization and electrical study of (Carboxymethylated Polyvinyl Alcohol/ZnO) nanocomposites. *Am. J. Polym. Sci.*, 2: 135-140.
- Rahman, M.A.A., S. Mahmud, A.K. Alias and A.F.M. Nor, 2013. Effect of nanorod zinc oxide on electrical and optical properties of starch-based polymer nanocomposites. *J. Phys. Sci.*, 24: 17-28.
- Shashidhara, B., B.V. Shrisha and K.N. Gopalakrishna, 2016. Temperature dependent electrical properties of n-ZnO/p-Si hetero junction prepared by spray pyrolysis growth of ZnO thin film on p-Si. *IOSR J. Appl. Phys.*, 8: 126-130.
- Sun, Y.F., S.B. Liu, F.L. Meng, J.Y. Liu, Z. Jin, L.T. Kong and J.H. Liu, 2012. Metal oxide nanostructures and their gas sensing properties: A review. *Sensors*, 12: 2610-2631.
- Wang, Z.L., 2004. Zinc oxide nanostructures: Growth, properties and applications. *J. Phys.: Condens. Matter*, 16: R829-R858.
- Yakuphanoglu, F., Y. Caglar, M. Caglar and S. Ilican, 2010. ZnO/p-Si heterojunction photodiode by sol-gel deposition of nanostructure n-ZnO film on p-Si substrate. *Mater. Sci. Semiconductor Process.*, 13: 137-140.