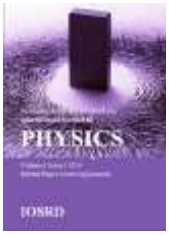
Available online at www.iosrd.org

International Journal of Physics
Volume 1, Issue 1, June 2015, Pages 20-25

Journal home page: http://iosrd.org/journals



ZnO Nanostructure-Based Amperometric Biosensors

Ali Jasim Mohammed[1*], Wafaa Mehdi Salih[1], Gerhard Wilde[2], Marwa Abdul-Muhsein Hassan[1]
[1]*Department of Physics, College of Science, Al-Mustansiriyah University, Baghdad, IRAQ*
[2] *Institute of Material Physics, Muenster University, Westfalisch Wilhelm-University, Wilhelm-Klemm-Str.10,*
**Corresponding Author E-mail Address: spiritjabir63@yahoo.com*

Article history: Received 07 April 2015, Accepted 01 August 2015, Available online 02 August 2015

Abstract: *ZnO pure thin films were prepared using the thermal chemical spray pyrolysis technique on glass substrates preheated at (450 ^{o}C) with a spray rate of 2–3 mL /min, for obtaining thicknesses of (150 nm). The investigation by XRD indicates that the (ZnO) films are a polycrystalline type with Wurtzite structure. The surface morphology of the prepared films were studied by SEM, showing that the surface of the ZnO thin films are smoother and the average grain size is less than 50 nm. The sensitivity behaviours of ZnO based on the amperometric biosensor to CaSO4.2H_2O salt were investigated at 250 ^{o}C with different salts concentrations, the resistance of the film increased with increasing of concentration.*

Keywords: *ZnO thin films, Nano sensors, Amperometric biosensors, Salts detection.*

1. Introduction

Biosensor is an analytical device, which converts the modification of the physical or chemical properties of a bio-matrix (e.g., enzyme, antibodies, receptors, organelles, microorganisms) into electric or other kinds of signal whose amplitude depends on the concentration of defined analyts in the solution [1]. They are becoming essential in the field of healthcare, chemical and biological analysis, environmental monitoring, and food processing industries. According to the receptor type, biosensors can be classified as enzymatic biosensors, geno-sensors, immune-sensors, etc. Biosensors can also be divided into several categories based on the transduction process, such as electrochemical, optical, piezoelectric [2], and thermal or calorimetric biosensors. Among these various kinds of biosensors, electrochemical biosensors are a class of the most widespread, numerous and successfully commercialized bimolecular electronic devices [1]. Particularly, enzyme-based electrochemical biosensors are attracting ever-increasing attention due to their potential applications in many areas [3], [4]. Among nanomaterial's, ZnO has attracted much attention due to its wide potential range of applications. As a wide band gap (3.37 eV) semiconductor, ZnO plays an important role in optics, optoelectronics, sensors, and actuators due to its semiconducting, piezoelectric, and pyroelectric properties [5], [6]. The physical and sensing properties of ZnO thin films studied [7]. Nanostructured ZnO not only possesses a high surface area, good biocompatibility and chemical stability and is non-toxicity, but it also shows biomimetic and high electron communication features [8]-[10], making it a preferred material for potential applications in biosensors. More importantly, as a biocompatible material, it has an isoelectric point (IEP) as high as about 9.5. The low (IEP) makes nanostructured ZnO as a good absorber of proteins, because the protein immobilization is primarily driven by electrostatic interaction.

2. Materials and Methods

2.1. Thin Film Preparation

Chemical techniques for the preparation of thin films have been studied extensively because such processes facilitate the designing of materials on a molecular level. Spray pyrolysis, one of the chemical techniques applied to form a variety of thin films, results in good productivity from a simple apparatus. In the current research, zinc oxide thin films are deposited on glass substrates employing a custom-designed spray pyrolysis deposition chamber whose main components set up is illustrated in the schematic diagram of Figure (1). It is essentially made up of a precursor solution, carrier gas assembly connected to a spray nozzle, and a temperature – controlled hot plate heater. The atomizer, illustrated in Figure 2-B, has an adjustable copper capillary tube nozzle of 0-0.8 mm inner diameter clamped to a holder and supported by a metal tripod. The nozzle is driven by a compressed atmospheric air. The prepared precursor solution is pumped through the metal nozzle with a solution flow rate ranging from 1 to 2 mL/min. Due to the air pressure of the carrier gas; a vacuum is created at

the tip of the nozzle to suck the solution from the tube after which the spray starts [11]. To regulate spraying time, a 16 – Bar Tork solenoid valve controlled by an adjustable timer has been incorporated. The atomizer and the 1500 Watts hot plate heater are enclosed in a $1m3$ ventilation hood, Figure 2-A. A 220 V a.c. power was applied to the heater and temperature was measured using a type K (nickel-chromium) thermocouple and precision digital temperature controller (GEMO DT109 Figure 2-C).

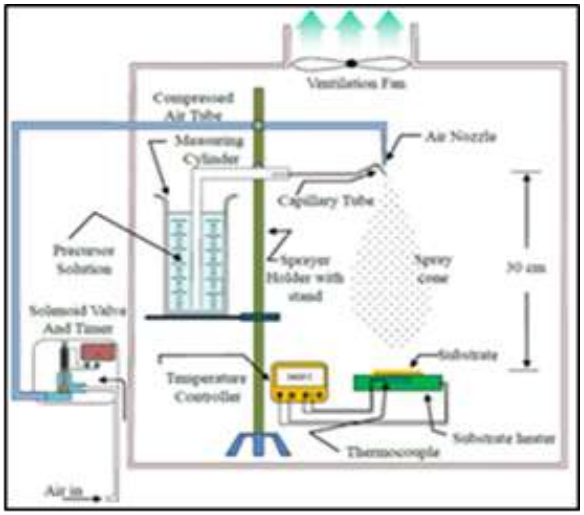


Fig. 1: Spray pyrolysis experimental setup.

A 0.1 M concentration precursor solution of zinc chloride ($ZnCl_2$) (molecular weight 136.29 g/mole) has been prepared by dissolving a solute quantity of 1.36 g of ($ZnCl_2$) (as weighed by a10^{-4} g -precision balance) in 100 mL dissolved in ethanol alcohol C_2H_5OH and distilled water has been employed in getting ZnO thin films. A magnetic stirrer is incorporated for this purpose for about 10 –15 minutes to facilitate the complete dissolution of the solute in the solvent. Organic solvents are preferable over distilled water because the former enables the attainment of homogeneous, highly – transparent, thin films of small grain size. Prior to depositing the films, the substrates, which are commercial glass slides of 76×25×1 mm^3 dimensions, are firstly cleaned by dipping in distilled water to remove the dust and then are ultrasonically cleaned in methanol for about 10 min. Finally they are soaked in distilled water, dried, and polished with lens paper.

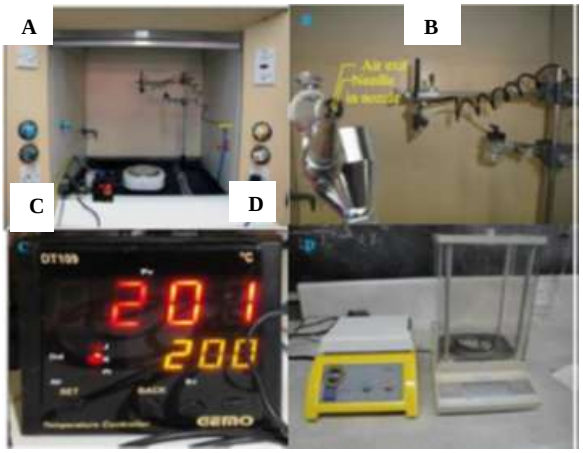


Fig. 2 A: experimental set up of the spray pyrolysis deposition SPD. B: Air atomizer. C: Gemo DT109 temperature controller, and D: Digital balance with the magnetic stirrer.

The pre-treatment of the substrates is carried out to facilitate nucleation on the substrate surface. Presence of contamination on the substrate surface is one of the reasons of the appearance of pinholes and film inhomogeneity [12]. The spray rate is

usually in the range 2–3 mL min^{-1}. The optimum carrier gas pressure for this rate of solution flow is around 5 kg cm^{-2}. At lower pressures, the size of the solution droplets becomes large, which results in the presence of recognized spots on the films and then reduction of transparency. This situation increases the scattering of light from the surface and then reduces the transmittance of the films. The spray pyrolytic substrate temperature is maintained at 450 ± 5 °C during the deposition. Film thickness is controlled by both the precursor concentration and the number of sprays, or alternatively, spraying time. Thus, a 5 –second spray time is maintained during the experiment. The normalized distance between the spray nozzle and substrate was fixed at 30 cm. All the undoped ZnO thin films of four different doping concentrations were prepared separately in different depositions under the same parametric conditions, given in Table 1. Film thickness was determined by the weight- difference method using an electronic high-precision balance Model: AE 166 Meter.

Table 1Spray Parameters for Film Deposition

Parameter	Value
Concentration of precursor	0.1 M
V0lume of sprayed precursor	100 mL
Solvent	Ethanol and water
Substrate temperature	450 ^oC
Spray rate	2.3 mL
Carrier gas pressure	1 bar
Nozzle-substrate distance	30 m

2.2. ZnO Based-Biosensing

$CaSO_4.2H_2O$/ZnO biosensor at different salt concentrations, as one of the most popular biosensors, has been intensively investigated. The application of the ZnO nanostructure in the $CaSO_4.2H_2O$ biosensors just appeared in the last several years. The experimental setup is shown in Figure (3).

Fig. 3 Biosensor experimental set up.

3. Results and Discussion

The structure and lattice parameters of ZnO films are analyzed by an X-ray Diffractometer (SHIMADZU 6000) with Cu Kα radiation (wavelength 1.54059 Å, voltage 30 kV, current 15 mA, scanning speed = 4 °/min) as illustrated in Figure (4). Diffraction pattern spectra are obtained with 2θ starting from 20 ° to 90 ° at 10 ° glancing angle. X – Ray diffraction spectra possess one sharp and four small peaks of ZnO thin films. It means that the film is polycrystalline with crystal planes (100), (002), (101), (102) and (103). The film is crystallized in the hexagonal wurtzite phase and presents a preferential orientation along the c – axis indicated by the plane (002). The result is in a good agreement with data mentioned in the literature (JCPDF card no 36-1451) [13]. The strongest peak, observed at 2θ = 34.3562 ° (d = 0.260 nm), can be attributed to the (002) plane of the hexagonal ZnO. Another major orientation present is (100) observed at 2θ = 31.7566 ° and (101) at 2θ = 36.1526

°. The other orientations like (102) and (103) at 2θ = 47.5342 ° and 62.8463 °, respectively are also seen with comparatively lower intensities. Therefore, the crystallites are highly oriented with their c–axes perpendicular to the plane of the substrate.

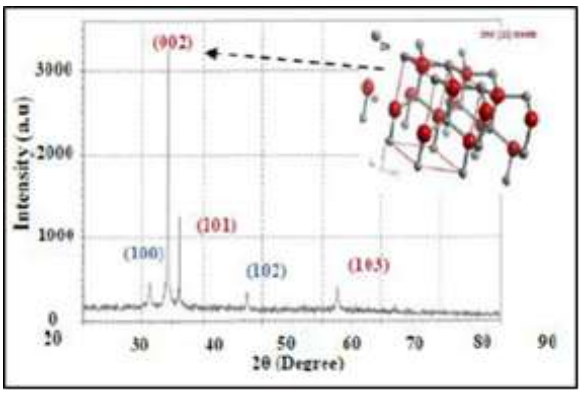


Fig. 4 X-ray diffraction of ZnO film prepared at 450 ^{o}C.

Surface morphologies obtained through Scanning Electron Microscopy (SEM) studies carried out (Hitachi FE-SEM model S-4160, Japan) at 15 kV of ZnO films prepared at a substrate temperature of 450 ^{o}C. The SEM micrograph shows that the surface of ZnO thin film is smooth as shown in Figure 5. Films consist of small particles distributed on the surface that shows a nano scale microstructure. The structure is polycrystalline with a small surface roughness that gives rise to regions of different scattering cross section. We can observe a dense granular structure. The grains have different shapes and sizes. The grain size found using SEM is smaller than that derived from X-ray diffraction. From SEM observations given by Fig. 5, we note that the average grain size is comparable to the film thickness which is less than 50 nm.

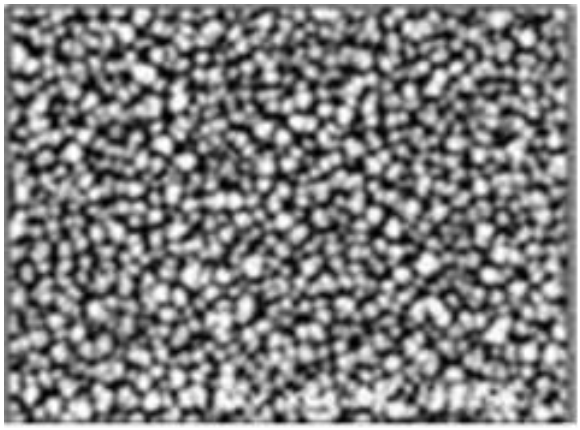


Fig. 5 Scanning electron microscope of ZnO film prepared at 450 ^{o}C.

The chemical interaction between the drop of $CaSO_4.2H_2O$ solution and the zinc oxide thin film caused some variations in the output signal recorded as increase of the resistance of the film for all salt concentrations at the substrate temperature of 250 ^{o}C, as shown in Figure (6). At the beginning of the interaction the adsorption occurs on the surface caused an increase of the resistance followed by chemisorption that caused a decrease of the resistance by means of the generation of oxygen vacancies. Also the figure shows that film saturated (no interaction appears) after about 200 seconds of interaction. The effect of salt concentrations on the sensing resistance is shown in Figure (7). It is clearly shown that the increase of concentration will cause an increase of the sensing resistance especially at concentration higher than 4 mg/L.

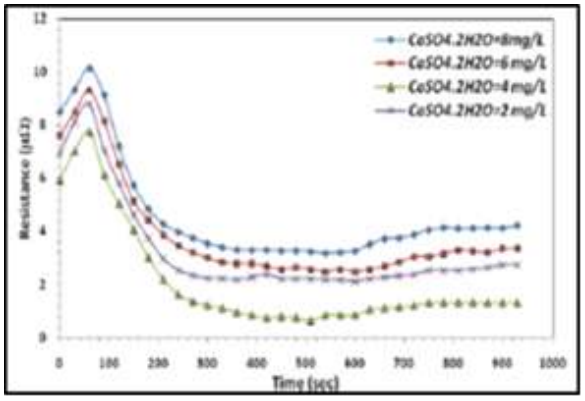


Fig. 6 Relation between resistance and time of ZnO film prepared at 450 ^{o}C.

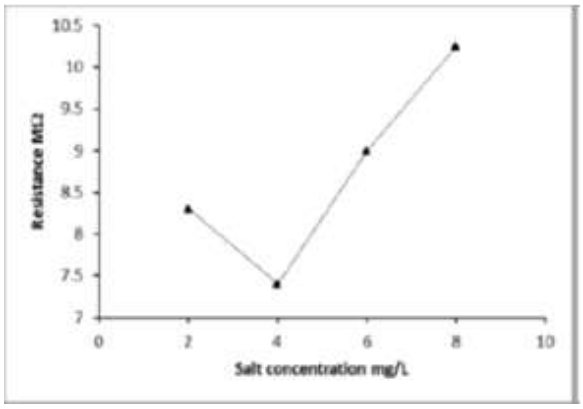


Fig. 7 Sensing resistance vis salt concentration.

4. Conclusion

A nanostructured ZnO thin film was fabricated to produce an amperometric biosensor for salt detection. Good rise time was obtained (about 50 sec). Based on the $CaSO_4.2H_2O$-ZnO interaction, the oxygen vacancies interact and bond with the salt structure which caused a growing barrier between grains, then the resistance was increased.

5. Abbreviation

(JCPDS): Joint Committee on Powder Diffraction Standards , International Center for Diffraction Data, Swarthmore, card no. 36 –1451,PA,1980.

References

[1] Dzyadevych, S.V.; Arkhypova, V.N.; Soldatkin, A.P.; El'ska ya, A.V.; Martelet, C.; Jaffrezic- Renault, N. "Amperometric enzyme biosensors: Past, present and future", IRBM 2008, 29, 171-180.W.-K. Chen, Linear Networks and Systems (Book style). Belmont, CA: Wadsworth, 1993, pp. 123–135.
[2] A. J. Mohammed and M. A. Hassan, "Effect of Glucose (C6H12O6) Addition on Piezoelectrical Properties for Sensor Applicationsǁ", American Journal of Biomedical Engineering (SAP), Vol.2, Issue 6, December 2012.
[3] Wang, J. Electroanalysis and biosensors. Anal. Chem. 1995, 67, 487-492..

[4] Burmeister, J.J.; Gerhardt, G.A. "Self referencing ceramic based multisite microelectrodes for the detection and elimination of interferences from the measurement of L-glutamate and other analytes", Anal. Chem. 2001, 73, 1037-1042.
[5] J. Wang, "Fundamentals of erbium-doped fiber amplifiers arrays (Periodical style—Submitted for publication)," IEEE J. Quantum Electron., submitted for publication.
[6] Norton, D.P.; Heo, Y.W.; Ivill, M.P.; Pearton, S.J.; Chisholm, M.F.; Steiner, T. "ZnO: growth, doping & processing. Mater. Today", 2004, 7, 34-40.
[7] Sun, X.W.; Kwok, H.S. "Optical properties of epitaxially grown zinc oxide films on sapphire by pulsed laser deposition", J. Appl. Phys. 1999, 86, 408-411.
[8] A. J. Mohammed, A. M. Mousa, and K. H. Hussain, "Physical and Sensing Properties of Zinc Oxide Thin Film", Lambert Academic Publishing, ISBN 978-3-659-18898-5, 2012.
[9] Tian, Z.R.R.; Voigt, J.A.; Liu, J.; Mckenzie, B.; Mcdermott, M.J. "Biommetic arrays of oriented helical ZnO nanorods and columns", J. Am. Chem. Soc. 2002, 124, 12954-12955.
[10] Sberveglieri, G.; Groppelli, S.; Nelli, P.; Tintinelli, A.; Giunta, G. "A novel method for the proparation of NH3 sensors based on ZnO-In thin films", Sens. Actuat. 1995, 24-25, 588-590.
[11] Rodriguez, J.A.; Jirsak, T.; Dvorak, J.; Sambasivan, S.; Fischer, D. "Reaction of NO2 with Zn and ZnO: Photoemission, XANES, and density functional studies on the formation of NO3", J. Phys. Chem. 2000, 104, 319-328.
[12] D. Perednis & L. J. Gauckler, "Thin film deposition using spray pyrolysis", Journal of Electroceramics, 14, pp. 103 – 111, (2005).
[13] E. Arca, K. Fleischer, and I. V. Shvets, "Influence of the precursors and chemical composition of the solution on the properties of ZnO thin films grown by spray pyrolysis", J. Phys. Chem. C 113, 21074–21081 (2009).

