History of Medicine, 2023, 9(1): 1075–1082
DOI: 10.17720/2409-5834.v9.1.2023.127

Study of the Effect of Annealing Temperature on the Structural and Electrical Properties of Zinc Oxide Nanofilms Deposited by Pulsed Laser Technology for the Manufacture of Freon Gas Sensor R410a (CHF2 CH3/F2 CH2)

Othman Mizban Talib[1*], Kasim H. Mahmoud[2]

[1] Department of Physics, College of Education, University of Tikrit/Iraq
EM: Mzbanthman314@gmail.com
[2] Specialty: Laser and Molecular Spectrum/Iraq
EM: qasimhmady@gmail.com

*Corresponding author: Othman Mizban Talib (Mzbanthman314@gmail.com)

Received: 20 January 2023 **Accepted:** 15 April 2023

Citation: Talib OM, Mahmoud KH (2023) Study of the Effect of Annealing Temperature on the Structural and Electrical Properties of Zinc Oxide Nanofilms Deposited by Pulsed Laser Technology for the Manufacture of Freon Gas Sensor R410a (CHF2 CH3/F2 CH2). History of Medicine 9(1): 1075–1082. https://doi.org/10.17720/2409-5834.v9.1.2023.127

Abstract

Zinc oxide (ZnO) nanomembranes were prepared by pulsed laser deposition technique (PLD), the membrane deposition occurred through the interaction between the falling laser rays with the atoms of the target material, then the plasma state inside the sedimentation chamber is formed upwards towards the sedimentation bases installed higher than the disk (target) at a distance of 20 mm, and the vacuum pressure (10-3) mbar The membranes are deposited and grow on the surface of the quartz base so that the distance between the target material and the laser rays is (150 mm), with a annealing temperature of different values (550, 750, 950) ˚C and a time of two hours on quartz slices, the effect of annealing temperature change on structural properties, surface topography and electrical was studied using XRD, AFM, SIM, Hall effect testers, gas sensor devices, this is for the purpose of knowing the nature of the surface of the prepared membrane and observing the change in granular size with increasing annealing temperatures after sedimentation, it was found that the average grain size (42.16) nm, the scanning electron microscopy examination showed that the grain size increases with increasing annealing temperature, that the structures are all nano, and that the elements that make up the membrane are zinc and oxygen, which were illustrated by the X-ray energy dispersion spectroscopy (EDX). Tests of the Hall effect phenomenon of the samples showed that they are n-type and that conductivity, Hall modulus and electrical mobility increase with increasing annealing temperature, the continuous conductivity test (D.C) showed that the electrical conductivity increases with the temperature of annealing and that the activation energy increases in order with the temperature change within the range (90-180) ˚C more than within the range (30-90) ˚C, the results of the examination of the gas sensor with different operating temperature showed that the best value of sensing in plasticized samples with a temperature of 750 ˚C, which is typical samples, as a sensor layer was formed that appears to be active, where the conductivity changes when exposed to gas.

Keywords
Zinc Oxide Nanofilms; pulsed LASER; sensors; higher technology

The term thin film is a description of one or several layers of atoms of one or several substances whose thickness may not exceed one micron, as the study of the thin film began using the chemical reaction technique[1], zinc oxide is an inorganic compound with the chemical formula ZnO, which is in the form of a white powder that is almost insoluble in water, and it is one of the most commonly used semiconductors in various fields such as flat screen displays, audio devices and photocatalysis, it is also used as an additive to many products including plastics, ceramics, glass, rubber, paints and ointments, and electric batteries.

It is a good material with multiple properties and is suitable for high technology such as light-emitting diodes, optical detectors, and sensors, interest in zinc oxide nanotechnology has increased because of its properties that enable it to enter many fields and applications, as it is characterized by high strength, and light weight, as well as excellent chemical reaction, very small size[2] and in biological applications[3], there are several different methods of preparation of zinc oxide nano-ZnO NPs including physical and chemical methods such as thermal evaporation, chemical vapor deposition, physical vapor tripping, spray thermal decomposition, sol-gel deposition, electrochemical deposition, and pulsed laser ablation method [4]. Due to the thinness of the thin film layer, it is deposited on bases of glass, quartz, silicon and other sedimentation bases according to the scientific need or application required for research or study [5], the physical properties of the thin film differ from the properties of the basic materials from which it was formed and are in the volumetric state [6].

There are many techniques for membrane deposition, but in this research we will use pulsed laser deposition (PLD) technology because of its many advantages [7, 8] including that the laser source is outside the chamber and thus the developing membrane is less polluted, and the laser energy can be controlled, the number of pulses, the angle of incidence and the pressure of the chamber, the prepared membranes are of high quality and the largest number of them can be prepared in record time and they are relatively cheap techniques and target preparations and sedimentation bases are easy and uncomplicated.

The membranes prepared with pulsed laser deposition technique have made these membranes prepared for the manufacture of a gas sensor to detect toxic gases and smoke and to detect Freon gas leakage with a relatively low response time than other techniques for zinc oxide with multiple crystallines as an indication of annealing temperatures.

Practical Side

Prepared tablets of powder zinc oxide nanopurity (99.9) and manufactured by the American company SKY SPRING NANOMATERIAL was used delicate balance sensitive company Metller A.K-160 as sensitivity (10^{-5} gr) weight g (3) and pressed with a hydraulic press strongly 8 KN in special molds the inner diameter of the mold 1.2 cm, and these tablets were annealing with a thermal oven degree (400) C°, the thin films of zinc oxide (ZnO) are prepared with pulsed laser deposition (PLD) technology with a laser energy of 700 mj, pulse number of pulse 650, frequency 7 Hz and discharge pressure (10^{-3}) mbar and quartz slices were cleaned by hand with alcohol and then distilled water for 15 minutes and dried and the pulsed laser deposition process began.

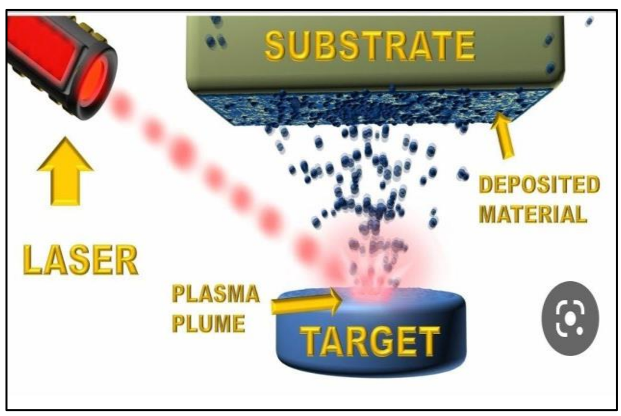


Figure 1 : Diagram showing the pulsed laser deposition (PLD) system.

The sedimentation process of the membrane occurs through the interaction between the laser beams from the shooter with the atoms of zinc oxide, so the plasma state inside the chamber is formed upwards towards the sedimentation bases installed above the disk (target) at a distance of (20) mm, (10^{-3}) mbar The membranes are deposited and grow on the surface of the quartz base so that the distance between the target material and the laser rays (150) mm, then the membrane is annealed with a thermal oven and for two hours with an atmosphere of oxygen, at different temperatures of values (550, 750, 950) ˚C and the benefits of annealing [9] work to reduce crystal defects and rearrange the crystal structure of the material and annealing can remove some local levels within the energy gap, the thickness of the membranes was measured by optical interference method according to the relationship ΔX/X ˣ λ/2.t= and Figure (1) shows an illustrative diagram of the pulsed laser deposition system.

Devices Used

The examination was carried out with an X-ray diffraction device (XRD) with specifications voltage 40 kv, Current 30 mA,1.5 A˚ and the surface nature of the deposited samples was studied according to the results of the atomic force microscope (AFM) type AA 3000 (made by Angstrom Advanced Company), and the scanning electron microscopy (SEM) images were analyzed to identify the crystal structure of the prepared thin films. The results of examining the effect of the Hall phenomenon were studied to know the type of semiconductor and to know the type of carriers and their concentration in addition to mobility and electrical conductivity. In addition, the electrical properties were studied by the continuou

Results and Discussion

Structural Properties: X-Ray Diffraction

The results of X-ray examination (XRD) of thin films prepared from ZnO nanoprecipitated on quartz bases by pulsed laser deposition technique (PLD) for a number of different samples at annealing temperatures ranging from (550, 750, 950) ˚C showed a multicrystalline structure where we have seven peaks in order (100),(002),(101)(102),(110),(103),(201), which correspond to the angles (31.85), (34.65) , (36.36) , (47.82) , (56.75) , (63.01) , (69.30) = ϴ2 respectively, it was compared with the global standard file for zinc oxide and the results were consistent with the card (0206-079-01). It contains a hexagonal geometric structure (α=90˚), (β=90˚), (ɤ=120˚), (Hexagonal) and Figure (2) shows the effect of increasing annealing temperature on the structural properties of thin films. The figure shows the increase in intensity of the peaks (100), (002), (101) when the temperature of annealing increases became more acute than it was at the lower annealing point due to the improvement of the crystallization of the thin ZnO film with this increase in annealing temperature, we also note that the width of the curve of the mid-intensity (FWHM) decreases with increasing annealing temperature as in Table (1) and the explanation of this according to the equation of D-pi Scherrer(G.S=k λ/B cos ϴ), the decrease in B curve width of the middle of the peak of the peak will increase the grain size and the intensity of peak diffraction will increase accordingly due to the improvement in crystallization of the thin films prepared from ZnO and these are similar to the results of the research [10].

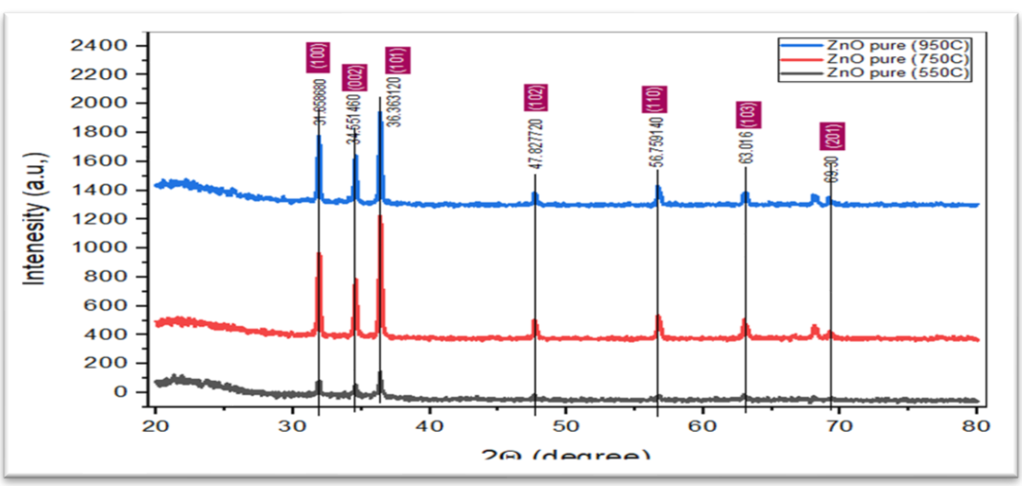


Figure 2 : Shows the X-ray diffraction (XRD) of ZnO samples at annealing temperatures (550, 750, 950) °C.

Table (1) : Shows the results of (XRD) tests for samples of ZnO with annealing temperature (550, 550, 950 °C).

Sample	Formula	2 θ (deg) Exp..	2 θ - Stander	d(A°)	Intensity	FWHM	(hkl)	System	D (nm) G.S
Zno Annealing 550 C°	ZnO nano.	31.85	31.765	2.80	84.23	0.196	100	Hexagonal	38.80
		34.55	34.42	2.59	86.53	0.157	002	Hexagonal	48.16
		36.35	36.25	2.47	179.61	0.157	101	Hexagonal	47.92
		47.63	47.53	1.90	38.93	0.118	102	Hexagonal	61.52
		56.74	56.59	1.62	24.30	0.314	110	Hexagonal	22.15
		62.97	62.85	1.47	31.36	0.263	103	Hexagonal	28.67
ZnO Annealing 750 C°	ZnO nano.	31.88	31.67	2.80	266.5	0.157	100	Hexagonal	48.49
		34.55	34.42	2.59	488.9	0.157	002	Hexagonal	48.16
		36.37	36.25	2.46	844.9	0.196	101	Hexagonal	38.33
		47.64	47.53	1.90	128.8	1.90	102	Hexagonal	36.91
		56.70	56.59	1.62	149.0	0.157	110	Hexagonal	44.38
		62.95	62.85	1.47	117.2	0.157	103	Hexagonal	43.01
ZnO Annealing 950 C°	ZnO nano.	31.88	31.76	2.80	453.0	0.157	100	Hexagonal	48.49
		34.53	34.42	2.59	303.3	0.157	002	Hexagonal	48.16
		36.36	36.25	2.47	627.4	0.196	101	Hexagonal	38.38
		47.16	47.53	1.90	76.3	0.263	102	Hexagonal	30.76
		56.67	56.59	1.62	132.5	0.157	110	Hexagonal	44.39
		62.79	62.85	1.47	76.62	0.144	103	Hexagonal	47.02

Structural Properties: Atomic force Microscope

Atomic force microscopy (AFM) was used to study the surface nature of ZnO membranes prepared on quartz bases with different annealing temperatures, from Figure (3), an increase in the granular size as evidenced by the data in Table (2) shows an increase in the square root of the average height (Rq) and an increase in the surface roughness rate (Ra) with increasing annealing temperature, this indicates that the greater the rate of square root, the greater the surface roughness of the membrane and explains the surface roughness, which confirms the large size of the grains due to annealing and its largeness, which explains that the surface has a dense arrangement, these results coincide with the researcher's findings[11] and the number of nanoparticles per unit size was added in the research, which explains the crystal development and the improvement of membrane specifications by increasing the annealing temperature.

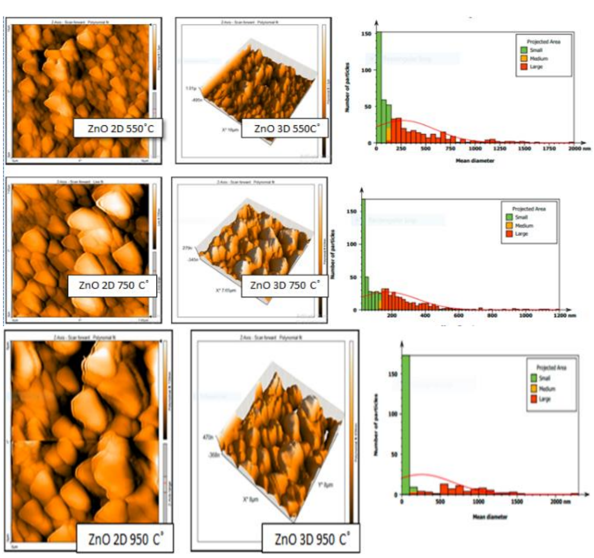


Figure (3): Atomic force microscopy (AFM) images of ZnO samples with annealing temperature C°C (550,750,950).

Table (2): Showing the results of the atomic force microscope (AFM)

Quartz slice	Particle size rate	Square root of mean height	Surface roughness
Annealing 550 C˚ ZnO	36.4nm	261.2nm	203.4nm
Annealing 750 C ˚ZnO	72.2nm	252.1nm	188.3nm
Annealing 950 C˚ZnO	111.9nm	174.8nm	147.9nm

Scanning electron microscopy examination: The samples deposited with ZnO were examined using pulsed laser deposition technique (PLD) using scanning electron microscopy (SEM) technology in order to identify the nature of membrane surfaces and study the change of granular size (G.S) with the change in annealing temperature, through which it was found that the increase in annealing temperature had a significant impact on the formation of the final form of the surface structure of the thin film, it was found that all thin films possess uniformly distributed granules and with increasing annealing temperatures showing an increase in granular size [12] we note from SEM images the disappearance of cracks and defects as a result of the preparatory conditions of the membrane and annealing at high temperature, figure (6, 7, 8) shows images of scanning electron microscopy and EDX Energy Dispersive X-ray Spectroscopy, X-ray energy dispersion spectroscopy, an analytical technique used to analyze elements to know the type of chemical elements and their properties for samples, which shows the elements that make up the membrane and the granular distribution diagram and shows that the average granular size ranges between (34-250) nm. These results from the scanning microscope examination were almost identical to what we obtained from the X-ray diffraction test using the D-pi equation, the distribution of the granular diameter begins to increase with increasing annealing temperature and seems identical to what we obtained from the images of the atomic force microscope, which also showed that all the membranes were very high adhesion to the surface of the quartz substrate floor and without cracks or defects, the results of scanning electron microscopy (SEM) tests of quartz strips on which ZnO was deposited using pulsed laser deposition technique (PLD) and with different annealing temperatures (550,750,950) °C showed that the general composition of the samples and all the peaks shown in the three-dimensional images are for zinc and oxygen only, microimages with magnification capabilities and standardized nanoscales of 200nm were selected.

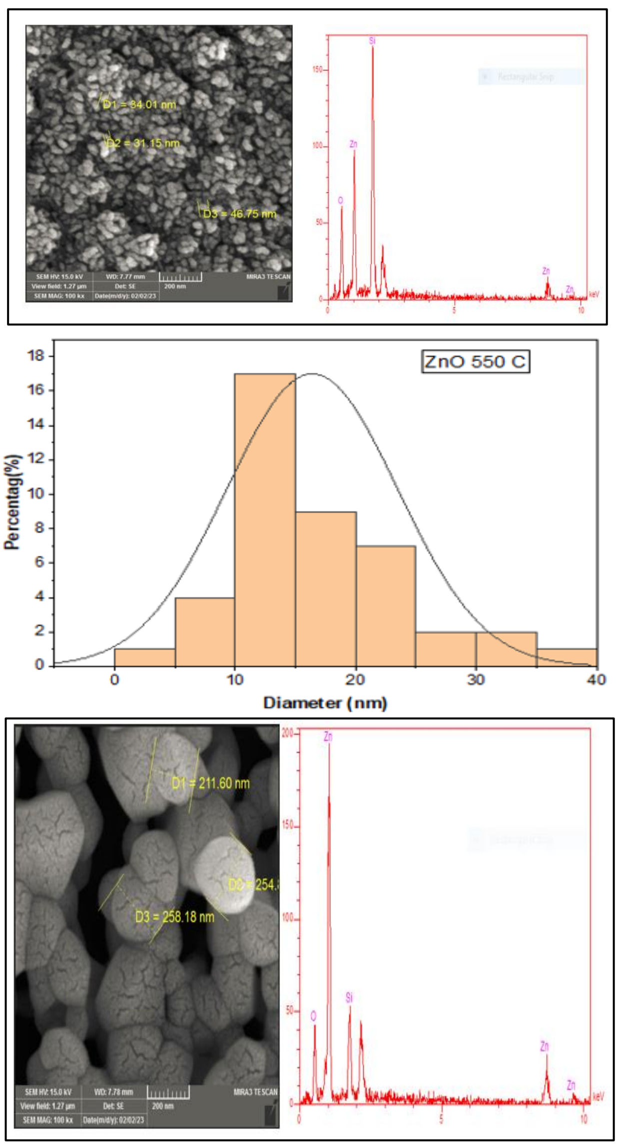


Figure (4) SEM images, EDX examination and nanoscale size distribution of ZnO membrane with annealing temperature 550 C°.

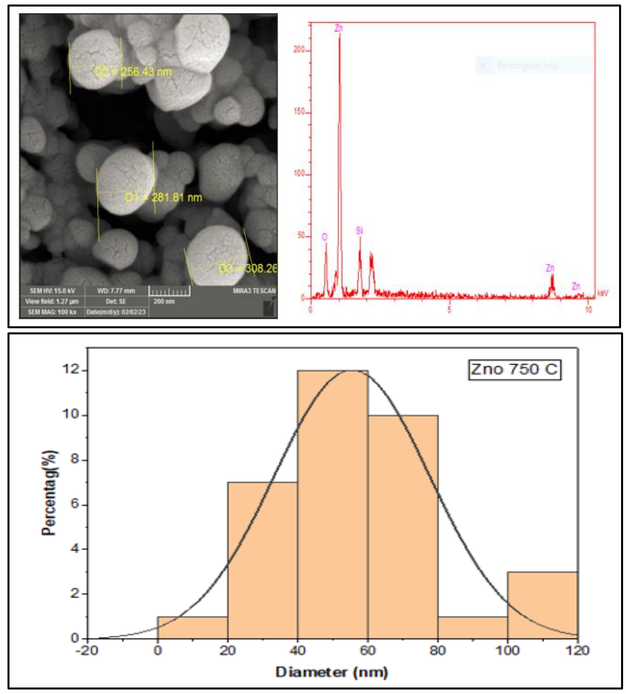


Figure (5) SEM images, EDX examination and nanoscale physical distribution of ZnO membrane with annealing temperature 750 °C.

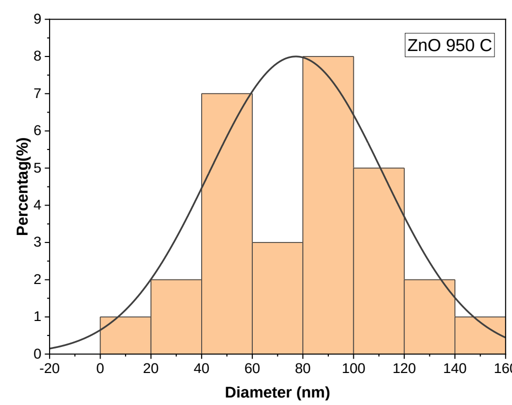


Figure (6) Images of SEM and EDX scanning electron microscope of ZnO membrane with annealing temperature 950°C with nanoscale size distribution.

Electrical Characteristics: Hall Effect Test

The results of the electrical tests conducted on the samples prepared on quartz from ZnO with PLD technology were analyzed and studied by knowing the electrical characteristics of the semiconductor, its suitability for the manufacture of electronic devices such as electrical conductivity, the concentration of charge carriers and the type of those carriers, there are many factors on which the electrical properties of polycrystalline semiconductors depend such as heat, light, density of impurity atoms, magnetic field and the effect of annealing temperature on them, the phenomenon of

Hall effect to know the type of semiconductor and the amount of conductivity, resistance and mobility of each heat annealing zinc oxide, the results of Hall effect of quartz strips on which ZnO was deposited were calculated by pulsed laser deposition technique PLD and annealing temperatures (25,550,750,950) °C to examine Hall coefficient, electrical conductivity, electrical mobility, number and type of charge carriers, where the tests of the prepared models showed that the Hall coefficient decreases with increasing annealing temperature and that zinc oxide membranes are good in electrical conductivity and this conductivity is produced due to the presence of Zn atoms in the compensatory sites within the crystal lattice or because of O_2 spaces, which indicates that the zinc atoms are donors, and this is shown by the slope of the negative Hall coefficient and indicates that the semiconductor is of the negative type (n-type) and that the carriers are electrons, these results are consistent with the research [13] , the signal of Hall coefficient did not change with the change in annealing temperatures, and using the Hall coefficient and electrical conductivity, the mobility (H_M) and charge carriers (nH) were calculated, it was also found that the conductivity and (H_M) gradually increase with the increase of annealing, and Table (3) shows the results of the electrical properties tests, where we note the proportionality of the amount of conductivity with the increase in the annealing temperature.

Table (3) : Shows Hall coefficient, conductivity, mobility, number and type of free carriers for zinc oxide membranes with increasing annealing temperature.

Sample	$R_H(cm^3/c)$	$\sigma(\Omega.cm)^{-1}$	$M(Cm^2/v.se)$	$n(cm)^{-3}$	Type
ZnO 950C°	-1.659E+6	4.851E-6	4.851E+0	-3.763E+12	n
ZnO 750C°	-5.113E+5	1.816E-5	2.461E+1	-5.991E+12	n
ZnO 550C°	-7.250E+6	1.702E-6	2.209E+1	-7.106E+12	n

Continuous conductivity (D.C) test

ZnO membranes have activation energy resulting from the movement of electrons between levels in the energy gap present at this position, the movement of the electron is restricted from one beam to another, especially at low temperatures, there is another activation energy that often occurs at high temperatures and the conduction process is carried out depending on the movement of electrons between the levels extending between the valence beam and the conduction beam, because of the heat the catalysis process, the change of the value of (Lnσ) with respect to the magnitude (1000/T) represented by Figure (7), where the slope of the curves shows the first and second activation energies and that the electrical conductivity increases with the temperature of annealing, the heat treatment led to the regularity of the atoms and their long-term arrangement and growth in the crystal structure and increase their size, it has led to the emergence of inter-levels that reduce the energy gap, which leads to a decrease in the energy that the carriers will need to move from the valence beam to the conduction beam, which is the cause of increased conductivity, and Table (4) shows the activation energy values of Zno membranes prepared on quartz with different annealing temperatures [14].

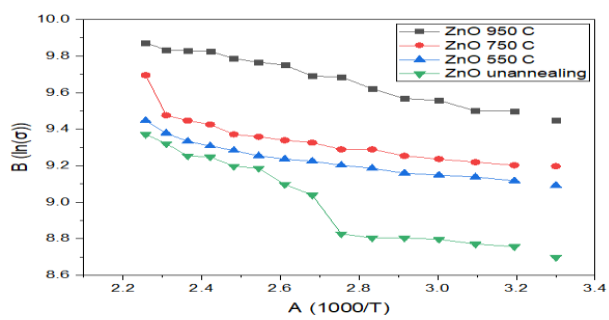


Figure (7) : Shows the continuous electrical conductivity of ZnO membranes with different annealing temperatures.

Table (4) : Shows the values of activation energy and continuous conductivity of zinc oxide membranes with different annealing temperatures.

sample	Ea1(ev) at Range (303-363)K	Ea2(ev) at Range (363-453)K	σ_{DC} at R.T$(\Omega.Cm)^{-1}$
ZnO un annealing	0.029	0.056	0.013
ZnO 550 C°	0.027	0.022	0.019
ZnO 750 C°	0.008	0.024	0.022
ZnO 950 C°	0.024	0.044	0.028

From the observation of the table, it is clear that the activation energy increases in order with the change of temperature within the range (90-180) C° more than within the range (30-90) C° and this explains that the additional temperature has provided the electrons with energy that enabled them to move and move from one level to another within the energy gap, where we notice an increase in conductivity with increasing annealing temperature.

Gas Sensor

It is clear from the figures that the resistance changes over time for the gas sensor segments R410a Freon gas has the chemical formula (CHF_2 CH_3 / F_2 CH_2) prepared by pulsed laser deposition method (PLD) of the ZnO nanocomposite at different annealing temperatures (550, 750, 950) ˚C respectively, the red arrow indicates the opening of the gas and the green arrow indicates the closure of Freon gas at various test temperatures, the figures show us that all the slices behave similar to semiconductors of the type (n-type), as Freon gas is a reducing gas and when adsorbed on the surface of the material, it draws oxygen to the surface and thus releases more electrons inside the membrane and thus increases the current or decreases the resistance inside the material, which leads to the formation of additional electrons in the conduction beam, which in turn will contribute to the electrical conduction process, we can see that the magnitude of the change in the resistance value and the time required to reach a stable state in the case of opening Freon gas, which is called the response time, In the case of closing the gas valve, called recovery time, it varies from sample to sample according to annealing temperatures and test temperature in the vacuum chamber, the sensitivity (S%) of the No compound at different operating temperature (150, 200, 250, 300) ˚C is calculated using the relationship Ra / Rg * 100% = S and this relationship is specific to the reduction case [15]. In addition, the increase in operating temperature adversely affects the response time, as the response time decreases with increasing operating temperature, as the temperature leads to an increase in conductivity in the semiconductor because the electrons obtain sufficient energy to move to the conduction beam.

Table (5) : Shows the results of the calculations of response time, retrieval time and sensitivity of zinc oxide nanomembranes with different annealing temperatures.

Samples	T(°C)	Response time (sec)	Recovery time (sec)	Sensitivity%
ZnO pure Annealed 750C°|	150	37.06667	37.2	5.874026893
	200	10.46671	8.2819	10.4
	250	17.01667	12.86667	10.2526003
	300	10.20321	9.24526	16.66666667
ZnO pure Un annealed	200	11.995	6.50226	12.05821206
	250	8.85894	5.81489	22.14719784
	300	-------	--------	1.386481802

The results showed that the best value of sensing in plasticized samples with a temperature of 750 ˚C, which is the typical samples, as a sensor layer was formed that seems active, where the conductivity changes when exposed to the gas, so the fusion of rarefactive gas molecules in the surface of the thin film leads to a reduction reaction, so it pulls oxygen to the surface and thus releases more electrons from the membrane, so the resistance decreases accordingly, figure (8) a, b, c, d shows the response time, recovery time and gas sensitivity [16] with an operating temperature of (150, 200, 250, 300) respectively

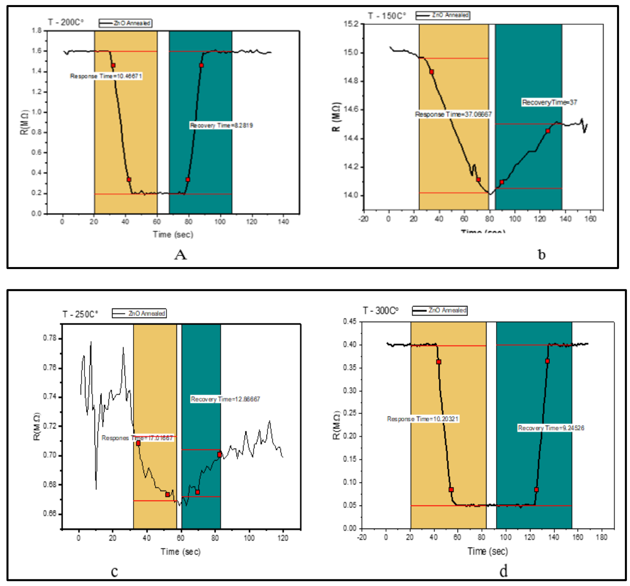
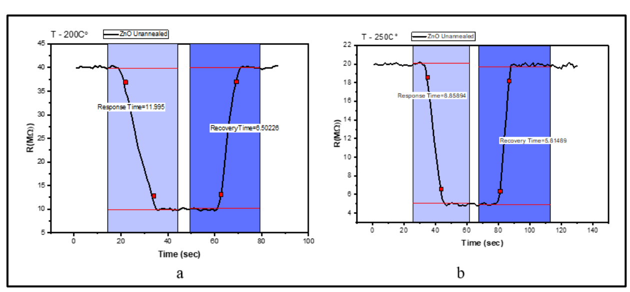


Figure (8) : Response time, retrieval time and gas sensitivity of annealed ZnO membranes at 750 °C.

Figure (9) a, b and c respectively shows the results of the gas sensor examination of non-plasticized samples response time and retrieval time at operating temperature (200, 250, 300) C° it was found that it showed sensitivity at lower operating temperatures than annealed samples, but the response time was greater, due to the randomness in the crystal structure that contributed to the free movement of electrons by moving to the conduction beam, as the operating temperature provided the electrons with the energy necessary for movement in the inter-planes.



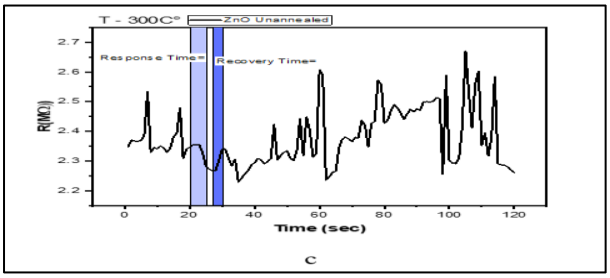


Figure (9) Response time, retrieval time and gas sensitivity of unplasticized ZnO samples at operating temperature (200,250,300) °C.

Figure (10) shows the sensitivity change for samples deposited of zinc oxide on quartz slices at operating temperature (150, 200, 250, 300) °C and for samples that were annealed at 750°C.

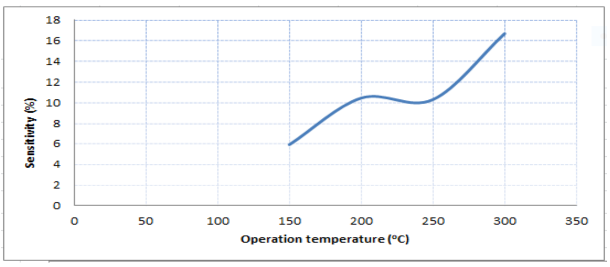


Figure (10) Change of sensitivity to zinc oxide with operating temperature.

Thanks to everyone who provided us with support in completing this research:

1. Faculty of Science - University of Tikrit.
2. University of Technology – Baghdad.
3. University of Baghdad.
4. University of Tabriz – Republic of Iran.
5. Faculty of Engineering – University of Tikrit.

References

A.Tribble, (2002) "Electrical Engineering Materials and Devices" University of Lowa .

Hamida E. S., Hanaa A. A.,& Mayes -1 A.K.(2019). Adsorption Study Of the Interaction Between Zinc Oxide Nanoparticles with Albumin And Creatinine. College of Education for pure Science, University of Karbala.

Noor, H. A., Mohamed, H., & Nehad, A. A. (2017). Preparation and Surface Modification of Zinc Oxide Nanoparticles. Journal of Babylon University, 25, 497503.

Chen, W. J., Liu, W.L., Hsieh, S. H., & Tsai, T. K. (2007). Preparation of nanosized ZnO using α brass. Applied Surface Science, 253(16), 6749-6753.

H.Salah Saaba , (2005) "study of the electrical and optical properties for GaSe4, GeSe4Te thin films" M .ScThesis university of Al-Mustansiriyah,

Te. Al.Aswad , (2010) "study the effect of Doping by cobalt on the some physics). Properties of (cds) thin films" M.Sc .Thesis university of Tikrit,.

R.Eason , (2007). "pulsed laser Deposition of thin films Application-led growth of function materials ",Johnwiley & sons,

C. Phipps(2007)." laser Ablation and its Application " ,New Maxico Springer

R.Lynn Johnson, (2012). "characterization of piezoelectric ZnO thin films an the Fabrication of piezoelectric micro-cantilevers", M.Se, thesis, Iowa state university of Tikret,

A. H.Omran Alkhayattl , I.A.Dishar Al-hessians ,O.A. chichan Alrikaby (2014). "Annealing Effect on the Structural and Optical Properties of sol-gel Deposited Nanocrystalline CdO Thin Films" Vol.34,

P.Sagar , M.Kumar ,R.M. Mehra (2005) "Electrical and optical properties of sol-Gel derived ZnO-Al thin films "Materials science –poland , 23.3. 685-696.12

Ali ‹H. M. ‹& Hakeem ‹A. M. A. (2015). Characterization of n and p-type(SnO2) x (ZnO) 1-x nanoparticles thin films. The European Physical Journal Applied Physics ‹72(1) ‹ 10301.

Z. Bi-Ju, LIAN Jian-She, Zhao Lei, Jiang Qing (2008) "Optical and Electrical Properties of ZnO/CdO Composite Thin Films Prepared by Pulse Laser Deposition" Chin. Phys. Lett., 1, 016801.

Joishy ,Sumanth , et al. (2019) "Influence of solution molarity on structure, surface morphology , non-liner optical and electric properties of CdO thin films prepared by spray pyrolysis technique." Materials Research Express 6.10: 106447.

A. J. Aljabiry , (2007). "studying the effect of molarity on the physical and sensing properties if ZnO thin films prepared by spray pyrolysis technique, " M. Sc . Thesis, University of Technology.

Sun ‹Y. F. ‹Liu ‹S. B. ‹Meng ‹F. L. ‹Liu ‹J. Y. ‹Jin ‹Z. ‹Kong ‹L. T. ‹& Liu ‹J. H. (2012). Metal oxide nanostructures and their gas sensing properties: a review. Sensors ‹12(3) ‹2610-2631.