Fabrication of Glucose biosensor electrode based on the CuO /ZnO nanostructures

Wafaa K. Khalef¹, Ali A. Aljubour¹, Abdulqader D. Faisal¹

¹² Applied Science Department / University of Technology/Baghdad/Iraq

Abstract: Zinc oxide nanowires (ZnO NWs) were successfully synthesized by Zn- metal evaporation and deposition of a thin metal film about 20 µm on quartz substrates. Followed by the subsequent oxidation process in the air at 550 oC for 4h. Copper oxide nanoparticles (CuO NPs) were then deposited on ZnO NWs, using the drop-casting technique. The crystal structure and morphology of ZnO nanowires were investigated by X-ray diffraction (XRD) and scanning electron microscope (SEM). The results of XRD confirmed that the ZnO has the Wurtizite polycrystalline structure along [101] direction. The SEM images revealed that the highest density of ZnO nanowires was distributed over a large area of the substrate with many wrinkles. The current response to glucose of the CuO/ZnO/Qz electrode gives a linear dependence range from 50 µM to 500 µM of glucose. The typical sample of CuO/ZnO NWs was used for a glucose biosensor electrode. It was found that CuO NPs layer on ZnO NWs has well improved the performance of the electrode and increased the electrocatalytic ability towards glucose oxidation.

Keywords: ZnO nanofilm, Optical properties of ZnO, ZnO nanowires.

1. Introduction
One of the most transparent conductive oxides (TCO) is Zinc oxide (ZnO), which possess a wide band gap of 3.37 eV, and large exciton binding energy (60 meV)) with high electron mobility up to 2 cm2 /V·s). It has many applications, mainly in photovoltaic and optoelectronics [1-5]. ZnO nanostructures have been studied as a photovoltaic solar cell [6,7] chemical sensors [8, 9], a transparent electrode[10, 11],blue and ultraviolet (UV) light-emitting diodes [12, 13], and a storages [14, 15]. Pulsed laser deposition (PLD) technique [16, 17], is one of many techniques that used to synthesize ZnO nanowires, Sol-gel [18, 19], chemical vapor deposition [20, 21], vacuum evaporation [22, 23]. Also, ZnO nanowires prepared via dry oxidation of Zinc thin films. YG Wang et al., studied and prepared of ZnO nanofilms by conventional oxidation of Zinc films [24, 25]. Mohammad et al., investigated the formation of ZnO NWs via physical evaporation of metallic zinc powder in a vapor of water at different temperatures [26, 27]. A very simple and non-catalytic growth technique was used in this work, for the synthesis of ZnO NWs. The ZnO NWs, were grown on the substrates of quartz of zinc thin films oxides in air at a temperature of 550°C. The synthesis of ZnONWs by thermal oxidation of zinc films is reported here. But there are no reports on the synthesis of ZnO NWs via thermal oxidation of Zn metal films, which will be useful for the fabrication of optical devices such as solar cells, etc. The manufactured sensor has the advantage of being easily manufactured from inexpensive materials. Tetsuro Soejima et al., reported the production of CuO/ZnO composite which showed high electrocatalytic activity toward glucose oxidation.[28-32 ]. Shin SoYoon et al., synthesis the CuO/ZnO NRs for non-enzymatic glucose sensor applications [33, 34].

2. Experimental

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

Published under licence by IOP Publishing Ltd
The quartz slides substrates were used for supporting a copper film. The preparation process of the film can be summarized as follows: Firstly, slides were cleaned with acetone and deionized water. Secondly, it cleaned in acetone, alcohol in an ultrasonic bath for about 15 minutes for each step of cleaning process, then wash with D.W, and dried with nitrogen gas. Then Pure zinc was thermally evaporated via physical vapor deposition (PVD) technique on the substrates of quartz. After that, an oxidation process for the deposited film was carried out by furnace. The oxidation experiments were continued for (4h) in the Atmospheric condition at a temperature of 550 °C and a heating rate is ≈ 25 °C/min. The furnace was switched off at the final of the oxidation experiments and left to normally cool down. The deposited film thickness was measured using an interference method via laser light and it found to be 20 µm. The samples were investigated and characterized by XRD, SEM, and glucose biosensor measurement.

Characterization part
X-ray diffraction (Shimadzu XRD-6000, X-ray diffractometer) technique with Cu kα radiation (λ = 0.15406 nm) in the range of 2θ (30°–80°) were used in the characterization of structural properties. The morphologies of the oxidized Zinc metallic films were investigated using a scanning electron microscope (SEM-Tescan Vega II- Cheek).

3. Device assembling
Quartz slides were cleaned using soap, distilled water, acetone, and ethanol each for 15 min in an ultrasonic bath. First, Zn films thickness of 20 µm were deposited on these slides using a thermal evaporator (Balzer) under a high vacuum 10⁻⁵ mbar. The deposited films were then oxidized at 550 °C for 4 hours in the air. After that, a very thin film of CuO was deposited on the oxidated films by drop-casting technique. Finally, the thermal evaporation technique was used to deposit the surface plate of aluminum (Al). The resulting device structure (CuO/ ZnO/ Qz) is shown in Fig. 1.

![Figure 1. Schematic representation of the glucose biosensor device.](image)

4. Results and Discussion
4.1. XRD analysis
The crystal structure of ZnO NWs was tested using X-RD technique as in figure 2. The peaks at 2Θ ≈32°, 34.68°, 36.52°, 47.79°, 56°, 63.68°, 68.14°, and 77.23° (which is a hexagonal wurtzite polycrystalline structure) are corresponding to the planes (100), (002), (101), (102), (110), (103), (112), and (202) reflection planes respectively. The accurate values of 2Θ are listed in the table (1). The dominated peak in figure 2 at 2Θ=36.52° is related to the ZnO (101). The weak peaks of (002) plane could be due to the low Zn and O ions moving to the proper sites producing low crystal quality. The peaks of diffraction for the pattern is in a good agreement with the standard data of JCPDS card number 36-1451 [35].

| Reflection plane | 2Θ° at 550°C |
|------------------|---------------|
| (100)            | 32.0          |
| (002)            | 34.68         |
The crystallite size (D) was calculated using equation of Debye–Scherrer’s [36-38].

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]  

(1)

Where \( \lambda \) is the used wavelength of radiation (\( \lambda = 1.5406 \, \text{Å} \)), \( \theta \) is the Bragg angle and the full width at half maximum (FWHM) represent \( \beta \). The crystallite size value is shown in table (2).

**Table 2:** Characteristics of ZnO oxidized at the 550 °C according to the Debye–Scherrer’s equation.

| Sample No. | Oxidation temperature (°C) | 2θ° | FWHM | D (nm) |
|------------|----------------------------|-----|------|-------|
| S1         | 550                        | 36.52 | 0.5738 | 15.2  |

**Figure 2** XRD of ZnO film at oxidation temperature of 550 °C.

4.2. **SEM analysis**

The SEM images at different magnifications of ZnO on the quartz substrate prepared at an oxidation temperature of 550 °C for 4h in the air are shown in Figure 3. The highest density of ZnO nanowires was distributed over a large area of the substrate with many wrinkles as are shown in figures 3a and b. The length and diameters of the wires could not be measured. There are no preferred wire orientations that can be seen in images even at a high SEM magnification shape of the wrinkles of figure 3c. Furthermore, the nanowires direct via these wrinkles, which was caused by the creation of the film strain due to the thermal oxidation process [39].
Figure 3. SEM images at different magnifications of ZnO film deposited on a quartz substrate and oxidized at 550 °C in the air.

4.3. Glucose biosensor of CuO/ZnO/Qz junction

The sensing behavior of the modified electrode CuO/ZnO/Qz at a bias voltage (0.5 Volt), and with the addition of glucose concentrations (ranging from 50 μM to 500 μM in 100 mL of DW) was shown in figure 4a. The first addition of glucose was made after 10 s with 50 μL (0.9 mg) added to the DW. Then, 100 μL (1.8 mg) was added at 20 s. After that, 200 μL was added once every 10 s. A near-linear current increasing behavior was observed. This indicates that CuO NPs over ZnO NWs improved the performance of the CuO/ZnO/Qz electrode and increased its electrocatalytic ability towards glucose oxidation, which may be attributed to their large surface area, high surface energy, and enhanced electron transfer ability [40, 41]. As can be seen from figure 4b a linear dependence of the current response to glucose for the CuO/ZnO/Qz electrode. The strong electron transfer rate from the electrode of glucose and the large surface area of manufactured CuO/ZnO/Qz electrode, are two important responsible for the excellent sensing properties. The manufactured CuO/ZnO/Qz electrode, showed more accessible reaction sites provided by the high-density CuO nanoparticle building units may generate more Cu species in the adsorption and reaction of glucose molecules, while abundant spacing among the maze-like building units may improve the diffusion of glucose molecules [42].
5. Conclusion

CuO/ZnO/Qz electrode as a glucose biosensor was fabricated utilizing a simple thermal evaporation technique. The structural and morphological properties of ZnO nanostructure have been studied; the crystallite size of ZnO NPs was 15.2 nm. The XRD data confirm the formation of the ZnO polycrystalline with a wurtzite structure, and the [101] direction is the preferred orientation. The SEM investigation revealed that the deposited nanowires with different dimensions. The typical yield of CuO/ZnO NWs could be used for a glucose biosensor electrode application.

References

[1] Faisal A. D., Işmail R. A., Khalef W.K., and Salim E.T. 2020 Synthesis of ZnO nanorods on a silicon substrate via hydrothermal route for optoelectronic applications Optical and Quantum Electronics 52 1-12.

[2] Fakhri M.A ., & Hassan M.M. 2020 Morphological and structural properties of Cu2O/2-D photonic silicon nano structure for gas sensors, AIP Conference Proceedings 2213 (1) 020244
[3] Elmer K., Klein A., & Rech B. (Eds) 2007 *Transparent Conductive Zinc Oxide – Basics and Application in Thin Films Solar Cells (Berlin)* vol 104 (Springer Science & Business Media).

[4] Mohammed Q.Q., Badr. B.A., Banoosh A.M., Fakhri M.A., Abdulwahab A.W. 2020 Oxygen pressure effects on optical properties of ZnO prepared by reactive pulsed laser deposition, *AIP Conference Proceedings* **2213** 020237

[5] Umit O., Hofstetter D., and Morkoc H. 2010 ZnO Devices and Applications: a Review of Current Status and Future Prospects, *Proc.IEEE* **98** 1255–1268.

[6] Taha J.M., Azeez H.N., Basheer R.A., Fakhri M.A., Abdulwahab A.W. 2020 Effects of oxygen pressure on the structural and morphological properties of ZnO prepared by RPLD, *AIP Conference Proceedings* **1268** (1) 020238

[7] Vittal R., and Ho. K.C. 2017 Zinc oxide based dye-sensitized solar cells, A review, Renewable and Sustainable Energy Reviews **70** 920-935.

[8] Hassan M.M., Fakhri M.A., Adnan S.A. 2020 Structural and Morphological Properties of Nano Photonic Silicon Structure for Photonics Applications, *Defect and Diffusion Forum* **398** 29-33.

[9] Xu S. & Wang. Z. L. , 2011 One-dimensional ZnO nanostructures” Solution growth and functional properties, *Nano Research* **4** 1013–1098.

[10] Hassan M.M., Fakhri M.A., Adnan S.A. 2019 2-D of Nano Photonic Silicon Fabrication for Sensing Application, *Digest Journal of Nanomaterials and Biostructures* **14** 873-878.

[11] Minami T., Nanto H., Shooji S., & Takata S.. 1984 The stability of zinc oxide transparent electrodes fabricated by R.F. magnetron sputtering, *Thin Solid Films* **111** 167-174.

[12] Badr B. A., Numan N. H., Khalid F. G., Fakhri M. A., Abdulwahhab A. W., 2019 All optical investigations of copper oxide for detection devices, *Journal of Ovonic Research* **15** (1) 53-59.

[13] Cao X. A., LeBoeuf S. F., D’evelyn M. P., Arthur S. D., Kretchmer J., Yan C. H., & Yang Z. H.. 2004 Blue and near-ultraviolet light-emitting diodes on free-standing GaN substrates, *Applied Physics Letters* **84** 4313-4315. https://doi: 10.1063/1.1756683

[14] Asady H., Salim E.T., Ismail R.A.. 2020 Some critical issues on the structural properties of Nb2O5 nanostructure film deposited by hydrothermal technique, *AIP Conference Proceedings* **2213** (1) 020183

[15] Wan Q., Lin C. L., Yu X. B., & Wang T. H. 2004 Room-temperature hydrogen storage characteristics of ZnO nanowires *Appl. Phys. Lett.* **84** 124-126. https://doi.org/10.1063/1.1637939.

[16] Aawayiz M.T., Salim E.T. 2020 Silver oxide nanoparticle, effect of chemical interaction temperatures on structural properties and surface roughness, *AIP Conference Proceedings* **2213** (1) () 020247

[17] Zhao J. L., Li,J X. M., Bian M., Yu W. D., & Gao X. D. 2005 Structural, optical and electrical properties of ZnO films grown by pulsed laser deposition (PLD), *Journal of Crystal Growth* **276** 507-512.

[18] Mahdi R. O., Fakhri M. A, Salim E. T. 2020 Physical Investigations of Niobium Oxide Nanorod Imploring Laser Radiation, *Materials Science Forum* **1002** 211-220.

[19] Rani S., Suri P., Shishodia P. K., and Mehr R. M. 2008 Synthesis of nanocrystalline ZnO powder via sol–gel route for dye-sensitized solar cells, *Solar Energy Materials and Solar Cells* **92** 1639-1645.

[20] Aawayiz M. T., Salim E. T.., 2020 Photo Voltaic Properties of Ag-O/Si Heterojunction Device: Effect of Substrate Conductivity, *Materials Science Forum* **100** () 211-220

[21] Purica M., , Budianu E., Rusu E., Danila M., & Gavrilu R. 2002 Optical and structural investigation of ZnO thin films prepared by chemical vapor deposition (CVD), *Thin Solid Films* **403-404** 485-488.
[22] Salim E.T., Awayiz M.T., Mahdi R.O. 2019 Tea Concentration Effect on the Optical, Structural, and Surface Roughness of Ag2O Thin films, *Digest Journal of Nanomaterials and Bionanomaterials* 14 1151-1159.

[23] Zheng J. H., Jiang Q., & Lian J. S. 2011 Synthesis and optical properties of flower-like ZnO nanorods by thermal evaporation method, *Applied Surface Science* 257 5083-5087.

[24] Salim E. T., Ismail R. A., Fakhri M. A., Rasheed B. G., Salim Z.T. 2019 Synthesis of Cadmium Oxide/Si Heterostructure for Two-Band Sensor Application, *Iranian Journal of Science and Technology, Transactions A: Science* 43 1337–1343.

[25] Wang Y. G., Lau S. P., Lee H. W., Yu S. F., , Tay B. K., Zhang X. H., & Hng H. H. 2003 Photoluminescence study of ZnO films prepared by thermal oxidation of Zn metallic films in air *Journal of Applied Physics* 94 354-358.

[26] Al Wazny M. S., Salim E. T., Bader B. A. and Fakhry M. A. 2018 Synthesis of Bi2O3 films, studying their optical, structural, and surface roughness properties, *IOP Conference Series: Materials Science and Engineering* 454(1) 012160. DOI: 10.1088/1757-899X/454/1/012160.

[27] Khanlary M. R., Vahedi V., & Reyhani A., 2012 Synthesis and Characterization of ZnO Nanowires by Thermal Oxidation of Zn Thin Films at Various Temperatures, Molecules 17 5021–5029.

[28] Fakhri M. A., Rashid B. G., Numan N. H., Bader B. A., Khalid F. G., Zaker T. A., and Salim., E. T. 2018 Synthesis of nano porous silicon heterostructures for optoelectronic applications, AIP Conference Proceedings 2045 020016; https://doi.org/10.1063/1.5080829.

[29] Tetsuro S., Kohei T., Seishiro I. 2013 Alkaline vapor oxidation synthesis and electrocatalytic activity toward glucose oxidation of CuO/ZnO composite nanoarrays, *Applied Surface Science* 277 192–200.

[30] Hassen H.H., Salim E.T., Taha J.M., Mahdi R.O., Numan N.H., Khalid F.G., Fakhri M.A., 2018 Fourier transform infrared spectroscopy and photo luminesance results for Zno NPs prepared at different preparation condition using LP-PLA technique, *International Journal of Nanoelectronics and Materials*, 11(Special Issue BOND21) 65-72.

[31] Hassan M.A.M., Al-Kadhemy M.F.H., Salem E.T. 2014 Effect irradiation time of Gamma ray on MSISM (Au/SnO2/SiO2/Si/Al) devices using theoretical modeling *International Journal of Nanoelectronics and Materials* 8 69-82.

[32] Badr B.A., Mohammed Q.Q., Numan N.H., Fakhri M.A., Abdul Wahhab A.W. 2019 Substrate temperature effects on optical properties and constants of ZnO *International Journal of Nanoelectronics and Materials* 12(3) 283-290

[33] Fakhri M. A., Abdulwahhab A. W., Kadhim S. M., Alwazni M. S., Adnan S. A. 2018 Thermal oxidation effects on physical properties of CuO2 thin films for optoelectronic application, *Materials Research Express*, 6(2) 026429. DOI: 10.1088/2053-1591/aaf217

[34] Shin S.Y., Ananthakumar R.,Balasubramaniam S., Sang J. K. 2014 Novel Cu/CuO/ZnO hybrid hierarchical nanostructures for non-enzymatic glucose sensor application *Journal of Electroanalytical Chemistry* 717 90–95.

[35] Bouzour M. B., Naciri A. En., Moadhen A., Rinnert H., Guendouz M., Battie Y., Chaillou A., Zaibi M. A., Oueslati M. 2016 Effects of silicon porosity on physical properties of ZnO films *Materials Chemistry and Physics* 175 233-240.

[36] Khalef W.K., Aljubouri A.A., & Faisal A.D. 2020 Photo detector fabrication based ZnO nanostructure on silicon substrate, *Optical and Quantum Electronics* 52 1-14.

[37] Fakhri M. A.., Salim E. T., Abdulwahhab A. W., Hashim U., Minshid M. A., Salim Z. T. 2019 The Effect of Annealing Temperature on Optical and Photolumence Properties of LiNbO3, *Surface Review and Letters* 26 1950068. https://doi.org/10.1142/S0218625X19500689

[38] Salim E. T., Wahib M.H.A., Abdulwahhab A. W., Salim Z. T., Hashim U. 2019 Heat treatment assisted-spin coating for LiNbO3 films preparation: Their physical properties, *Journal of Physics and Chemistry of Solids* 131 180-188. https://doi.org/10.1016/j.jpcs.2019.03.033
[39] Suttinart N., Supakorn P., Worasak S., Bualoy K., Prayoon S., Ki. S.A. 2013 Zinc Oxide Nanostructures Synthesized by Thermal Oxidation of Zinc Powder on Si Substrate, *Applied Mechanics and Materials* **328** 710-714.

[40] Reitz E., Jia W., Gentile M., Wang Y., & Lei Y. 2008 CuO nanospheres based nonenzymatic glucose sensor, *Electroanalysis* **20** 2482–2486.

[41] Aljubouri A.A., Faisal A.D., Khalef W.K. 2018 Fabrication of temperature sensor based on copper oxide nanowires grown on titanium coated glass substrate, *Materials Science-Poland*, **36** 460-468.

[42] Xue W., Chenguo H., Hong L., Guojun D., Xiaoshan H., Yi X. 2010 Synthesis of CuO nanostructures and their application for nonenzymatic glucose sensing" *Sensors and Actuators B* **144** 220–225

[43] Faisal A.D., Khalef W. K., 2017 Morphology and structure of CuO nanostructures grown via thermal oxidation on glass, silicon, and quartz at different oxidation temperatures, *Mater Sci: Mater Electron* **28** 18903–18912