

Study of the Effect of Annealing on the Optical and Structural Properties of ZnO Films Doped with Magnesium and Prepared Using Chemical Bath Deposition (CBD) Technique

Manea Mohammed Khlaif

Nineveh Education Directorate, Iraq. E-mail: maneh.mh.88@gmail.com

Abstract - The present study included a study of the effect of grafting on the optical and structural properties of (ZnO) membranes grafted with magnesium, which were prepared using the chemical bath deposition method. (SEM, High, reaching (85-98%). The energy gap was also studied, and it was found that it increases when doping with magnesium oxide increases and decreases with its decrease. Also, the effect of annealing at a temperature ($T=350^{\circ}\text{C}$) on these properties was studied, and it was found practically that these membranes It gets rearranged in the crystal structure with increasing temperature as a result of the formation of new patterns of structures.

Keywords: zinc oxide, XRD annealing, SEM, MgO.

Introduction

Zinc oxide is a semiconductor material that possesses distinctive and unique properties. It is used in industrial applications. It is one of the transparent conductive oxides that is classified among the compounds of the second and sixth groups of the periodic table [1] because it has a direct energy gap of 3.37 eV and a high binding energy of 60 mV [2]. It is used in optoelectronic devices, which include light-emitting diodes and laser diodes, as well as optical detectors [3, 4]. In addition to its use in the manufacture of transistors as a result of its high optical transmittance in the visible region [5-7], zinc oxide is also considered an important material in Acoustic wave devices, gas sensors, solar cells, and transparent electrodes due to its superior photoelectric properties and stability against photocorrosion [8, 9]. To prepare zinc oxide films, there are many methods, including the chemical vapor deposition method [5], the pulsed laser deposition method [10], the thermal evaporation method [11], and the sol-gel method [12], in addition to the chemical bath deposition method, which we will focus on in this research [13].

Practical aspect:

The chemical bath deposition method consists of several devices and tools available and simple locally. Figure (1)

below shows the deposition system used in preparing these membranes. The system consists of the following devices and tools: [13]

- 1) Magnetic stirrer with heat source (magnetic stirrer hot plate).
- 2) Holder with mask.
- 3) A thermometer is used to measure the temperature of the solution.
- 4) Beakers.

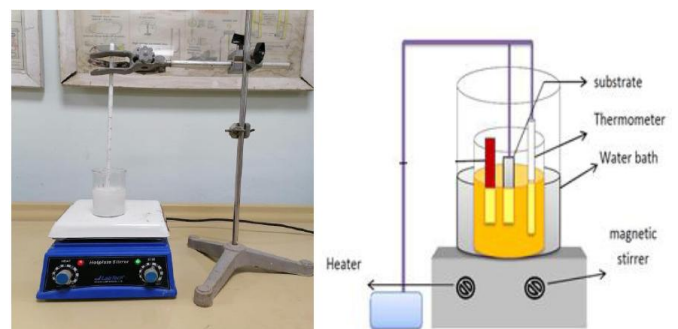


Figure (1): chemical bath deposition (CBD)

Solution preparation

To prepare thin films of oxide (ZnO) doped with proportions of oxide (mgo) by chemical bath deposition (CBD) method, glass bases with dimensions (7.5 * 2.5 cm) were used after cleaning, where (1gm) of MgO (ZnO) was weighed according to Table (1-3) and dissolve it in 50 ml of distilled water at a temperature of 85 °C for three hours, gradually dissolving it and using a magnetic stirrer. Place it in a 100 ml glass beaker, then heat it to 85 °C. When the solution reaches this temperature, the glass bases are immersed. in the solution at an angle of 10o for 10 minutes, after which the glass bases are withdrawn and the solution is left for 15 minutes to separate the precipitate from the filtrate. The aim of changing the weight percentages of impregnation is to know the extent to which the energy gap of those bases is affected. After completing the deposition process for these membranes, they are placed in an electric oven to conduct the annealing

process is in order to rearrange the atomic structure of these membranes (nanostructures) and obtain crystalline regularity. All oxides were weighed using a sensitive balance with an accuracy of up to four orders of magnitude after sorting.

Optical properties

Optical properties are of great importance in studying the behavior of optical materials for thin films, through which the practical application of these films is known. Therefore, the optical behavior is closely related to the crystalline structure of the material and the structure of the energy levels [15].

Permeability

The transmittance spectrum was measured using a spectrometer for a range of wavelengths (320-800nm), and all curves were plotted with respect to the wavelength. Figure (2)

shows the change in transmittance values for grafted and annealed membranes at $T=350^{\circ}\text{C}$ for $\text{MgO}_{(40\%)}$ and $\text{ZnO}_{(60\%)}$. It is noted from the figure that the transmittance values begin to gradually increase with increasing wavelength, and this indicates a decrease in their granular sizes as a result of grafting, after which they stabilize at the wavelength (320-480) nm [14].

As for the grafted and annealed membranes $T=350^{\circ}\text{C}$ for $\text{MgO}_{(60\%)}$ and $\text{ZnO}_{(40\%)}$, it was found that the permeability differed with the annealing temperature, which indicates that thermal annealing has reduced its value because annealing has increased the cohesion of the grains and thus increased their size. As shown in Figure (3). [14]

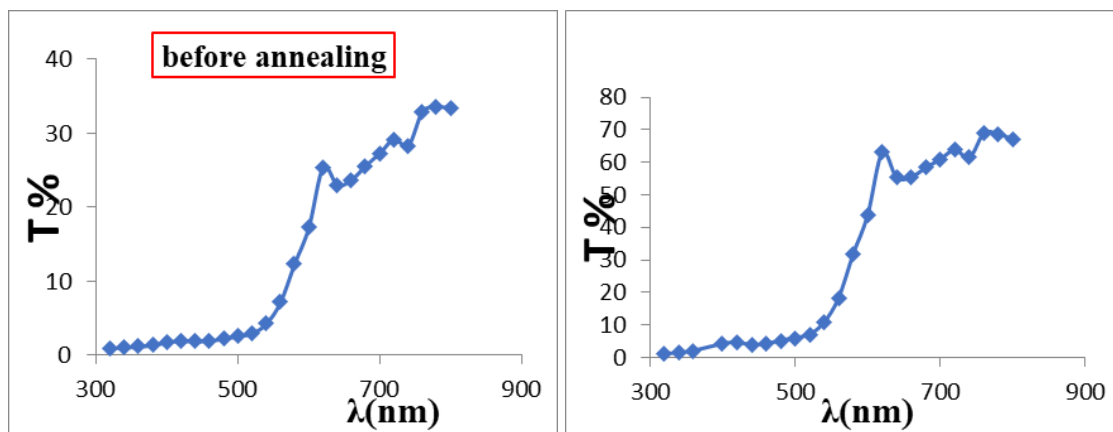


Figure (2): Change in permeability values for grafted and annealed membranes $\text{MgO}_{(40\%)}$ $\text{ZnO}_{(60\%)}$

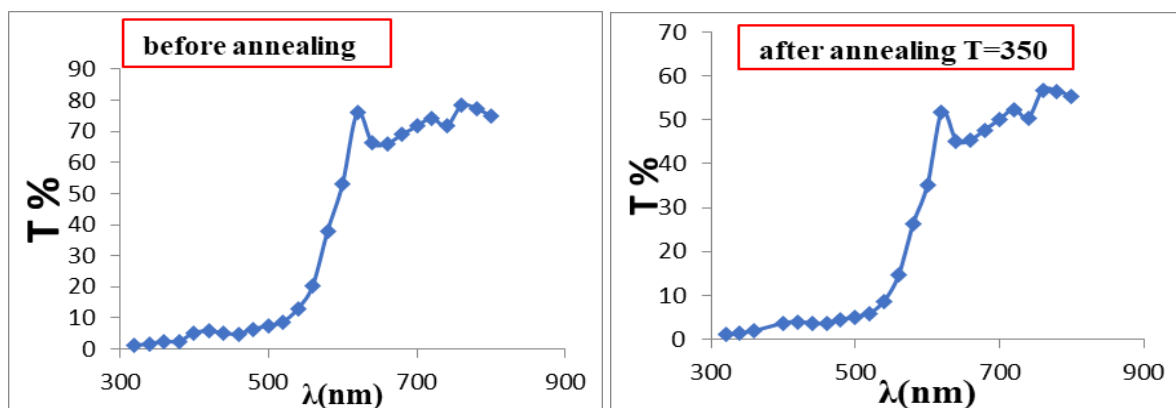


Figure (3): Change in permeability values for grafted and annealed membranes $\text{MgO}_{(40\%)}$, $\text{ZnO}_{(60\%)}$

Absorbency

Figure (4) shows the decrease in the absorbance values of the grafted and annealed films at $T=350^{\circ}\text{C}$ for $\text{MgO}_{(40\%)}$ and $\text{ZnO}_{(60\%)}$. The decrease is sharp in the visible spectrum region within the wave range (350-620)nm and then begins to stabilize after this range of the spectrum. [16]

As for Figure (5), it shows the decrease in absorbance values for the grafted and annealed films at $T=350^{\circ}\text{C}$ for $\text{MgO}_{(60\%)}$ and $\text{ZnO}_{(40\%)}$. It is noted from the two figures that the absorbance values differ with the annealing temperature, and the reason for this is the emergence of new phases as a result of annealing. [16]

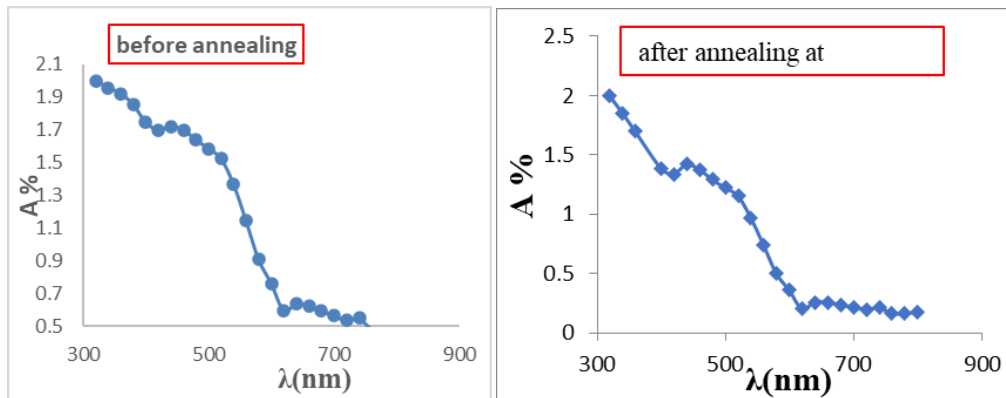


Figure (4): The absorbance values of the grafted and annealed

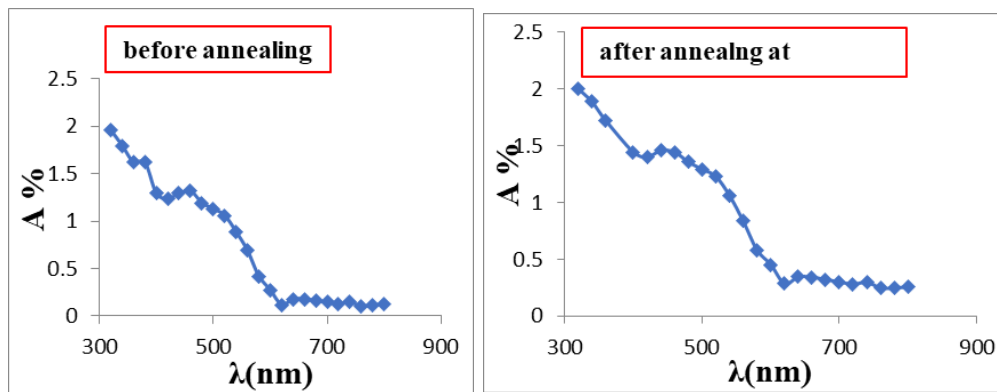


Figure 5: The absorbance values of the grafted and annealed films $\text{MgO}_{(60\%)}$ $\text{ZnO}_{(40\%)}$

Reflexivity

As for the reflectivity spectrum of the grafted and annealed films at $T=350^{\circ}\text{C}$ for $\text{MgO}_{(40\%)}$ and $\text{ZnO}_{(60\%)}$, it showed no change at high photon energies, and therefore its increase indicates a phase change in the crystalline structure of those structures. The reflectivity increased with the annealing temperature. 'As in Figure (6). [16]

As for the prepared films grafted and annealed at $T=350^{\circ}\text{C}$ for $\text{MgO}_{(60\%)}$ and $\text{ZnO}_{(40\%)}$, it is noted that the reflectivity spectrum is not affected by the annealing temperature within the range (320-550)nm, and after this range we notice a sharp decrease in its value with increasing wavelength. The effect of annealing appears on the structures, which leads to a change in the phases of the structures, as in Figure (7).[15]

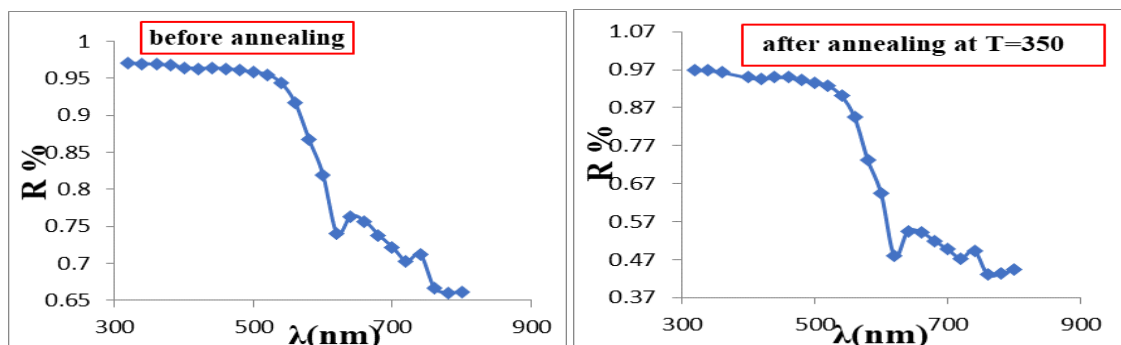


Figure 6: The reflectivity spectrum of the grafted and annealed films

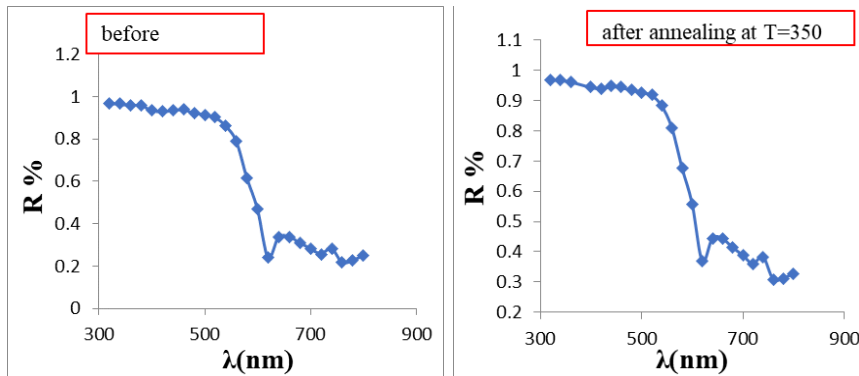


Figure 7: The reflectivity spectrum of the grafted and annealed films MgO_(60%) ZnO_(40%)

Refractive index

The refractive index curve was drawn as a function of wavelength. It can be seen from Figure (8) that the refractive index differs for the grafted and annealed films at T=350°C for MgO_(40%) and ZnO_(60%), then the refractive index stabilizes in the range (320-550)nm, and begins to decrease sharply in the spectral range (550-620)nm. The refractive index fluctuates with the annealing temperature. [16]

Figure (9) shows the difference in the refractive index of the grafted and annealed films at T=350°C for MgO_(40%) and ZnO_(60%), which behaves similar to the reflectivity curve due to its association with them. [16]

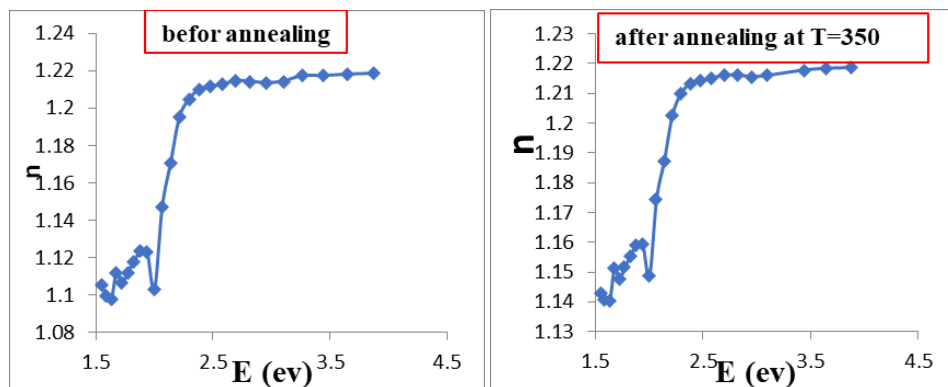


Figure 8: The difference in the refractive index of the grafted and annealed films MgO_(40%) ZnO_(60%)

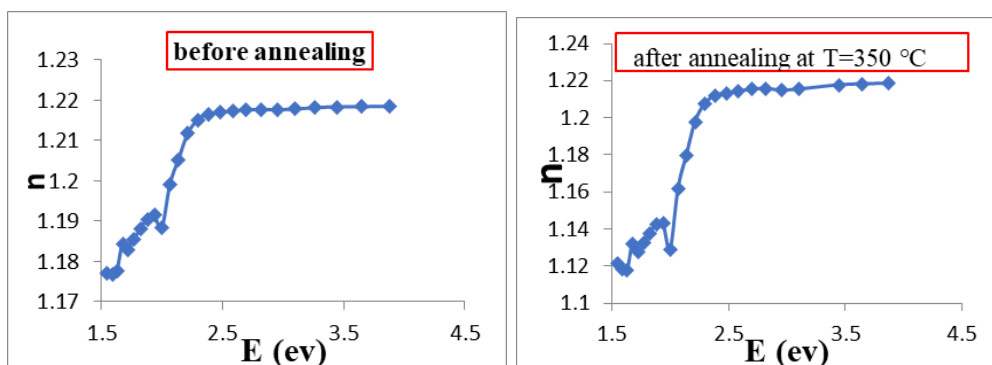


Figure 9: The difference in the refractive index of the grafted and MgO_(60%) ZnO_(40%)

Energy gap

The recrystallization of the prepared films depends on the energy gap, which is affected by the annealing temperature, or the corresponding increase or decrease in the energy gap. The optical energy gap of the grafted and annealed films at T=350°C and in the ratio of ((MgO_(40%) and ZnO_(60%) %)) It was found by drawing the relationship between $(\alpha h\nu)^2$ and $(h\nu)$ and from the

intersection of the straight part of the curve $(\alpha h\nu)^2=0$. The value of the energy gap appears from the point of intersection as in Figure (10), as it was found that the energy gap increases at The annealing process is performed and its value ranges, respectively, before and after annealing (3.1eV) and (3eV), due to the local levels between the valence and conduction bands, as well as the crystal structure of the membrane, and this is consistent with published research [17-19].

The optical energy gap of the grafted and annealed films at $T=350^\circ\text{C}$ (MgO_(60%) and ZnO_(40%)) ranged (2.55 ev-3 ev) as in Figure (11). The reason for this is due to the change in compositions. The interior of the membrane, as scanning electron microscope images show clusters of granules in different shapes and at annealing temperature [15].

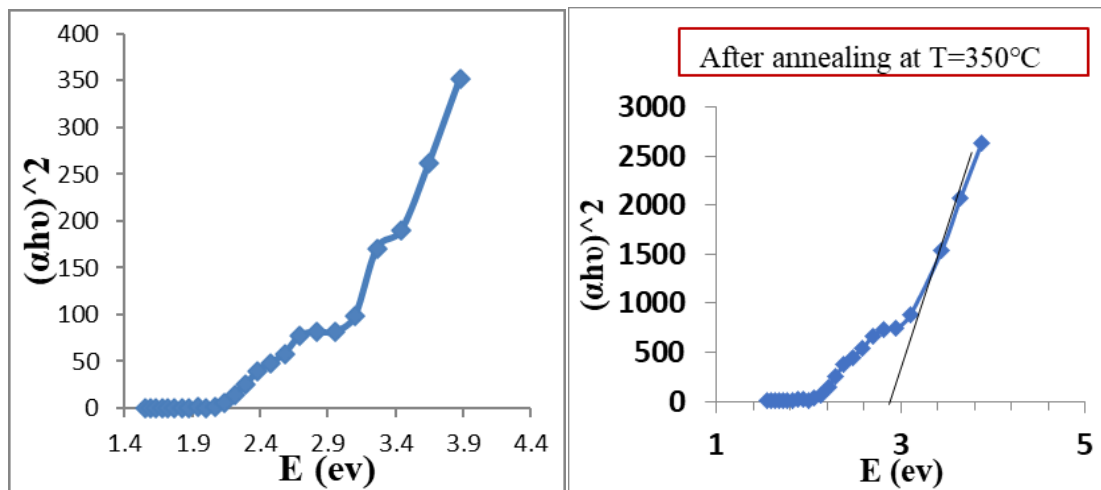


Figure 10: Energy gap increases at the annealing process MgO_(40%) ZnO_(60%)

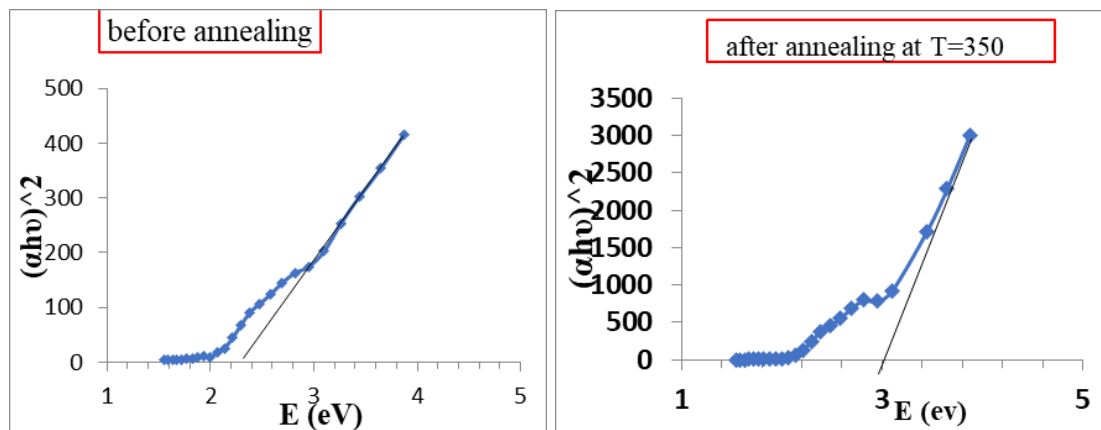


Figure 11: The optical energy gap of the grafted and annealed films MgO_(60%) ZnO_(40%)

Scanning electron microscope (SEM) results

The scanning electron microscope (SEM) images of the grafted and annealed structures showed a ratio of (MgO_(40%) and ZnO_(60%)). We notice that there is homogeneity in the crystalline structure. After performing the thermal annealing process at temperatures ($T=350^\circ\text{C}$), it was found that its effect was It is clearly visible on the structures, but in a negative way, which leads to the merging and cohesion of the granules, increasing their granular size. We notice a change in the structural structure of those prepared membranes, such that these nanoclusters transform into unknown shapes [20-21], as in Figure (21).

Scanning electron microscope (SEM) images of the grafted and annealed structures (MgO_(60%) and ZnO_(40%)) showed structural homogeneity of the grains before performing the annealing process at temperatures ($T=350^\circ\text{C}$). After annealing these films, the aggregation of these grains and their cohesion with The temperature increases, and thus its granular size increases, and this is accompanied by the appearance of some unknown geometric shapes with some surface defects, as in Figure (31).[14].

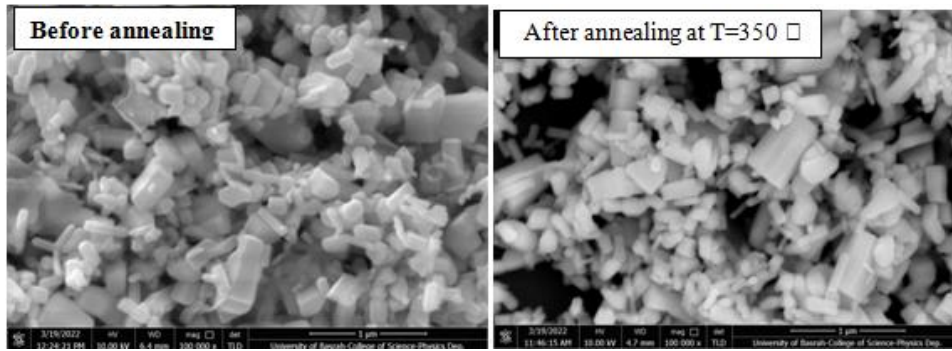


Figure 12: Scanning electron microscope (SEM) images of the grafted

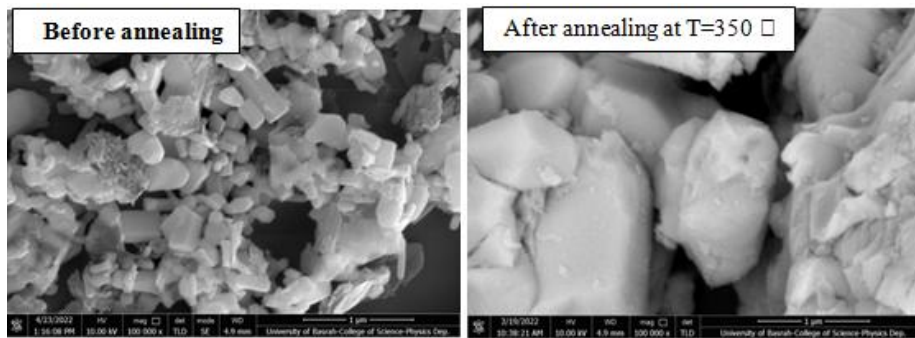


Figure 13: Scanning electron microscope (SEM) images of the grafted

XRD spectra

Through the results of X-ray examinations (XRD) of the grafted and annealed films at a temperature of 300(1^o)C and in the proportions of (MgO_(40%), ZnO_(60%), (MgO_(60%), and ZnO_(40%) (We notice a decrease in the intensity of the spectrum with temperature, which in turn led to a deterioration in the crystalline structure of the grafted films [20-21]. Which were matched with the international cards bearing the numbers (ICDD 00-041-1292) and (ICDD 01-079-0208),) and (ICDD 00-001-1141), as shown in Figures (14), (15), (16), and (17).

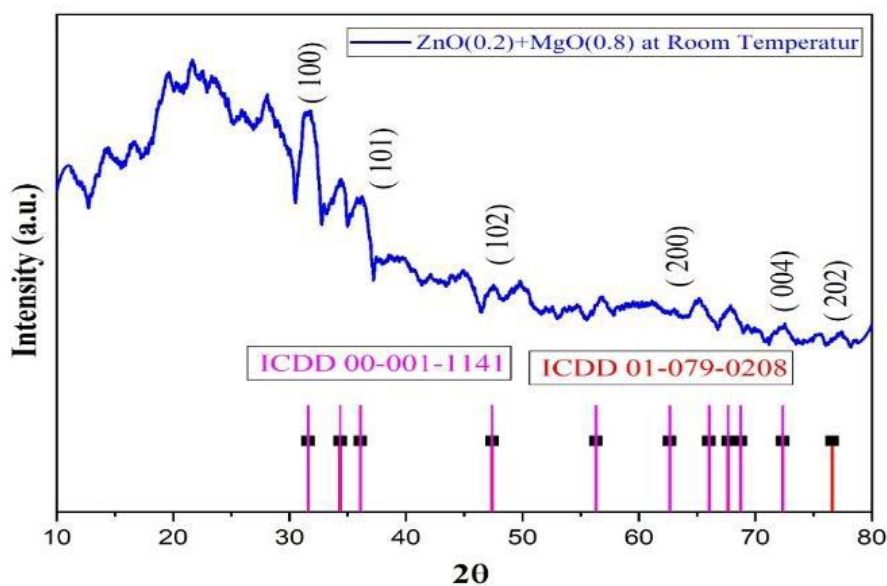


Figure 14: The crystalline structure of the grafted films (MgO40% ZnO60%) ICDD

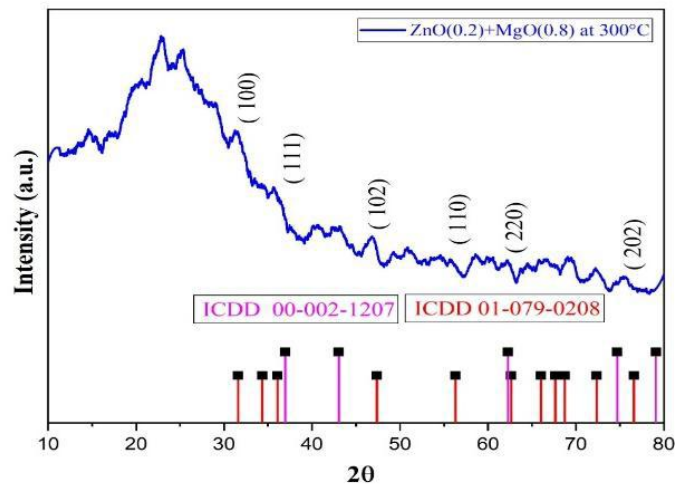


Figure 15: The crystalline structure of the grafted films T=350°C (MgO40% ZnO60%)

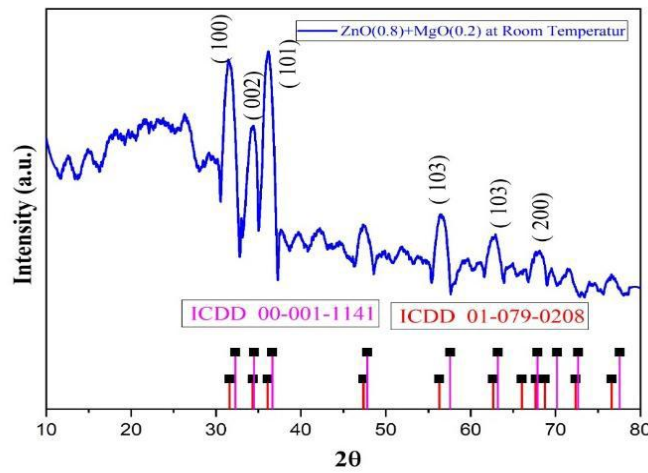


Figure 16: The crystalline structure of the grafted films T=350°C (MgO60% ZnO40%) ICDD

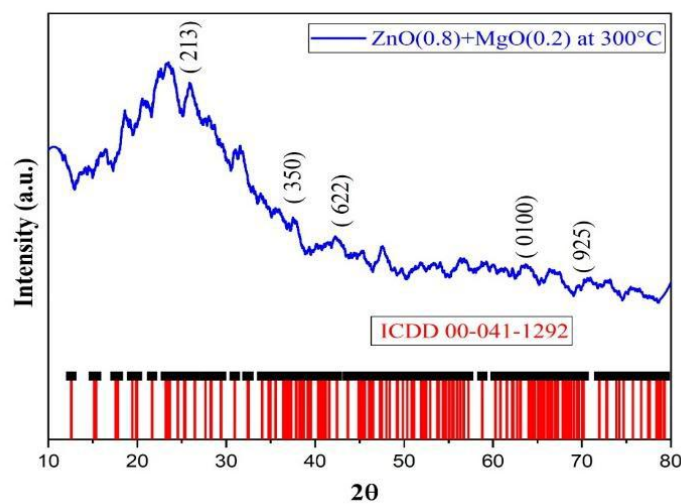


Figure 17: The crystalline structure of the grafted films T=350°C (MgO60% ZnO40%)

Conclusions

- 1) It has been observed that the grafting process of films reduces the optical properties (reflective transmittance, refractive index and energy gap).
- 2) All the prepared membranes were of polycrystalline and hexagonal structure.
- 3) X-ray diffraction measurements and scanning electron microscope images showed that the granular structures of the prepared films fall within nanostructures.
- 4) The prepared films have preferred grain growth directions at (111)(110)(002)(112)(102).
- 5) Optical properties increase with the annealing process.
- 6) The optical energy gap increases with increasing annealing.

REFERENCES

- [1] Lee, G.-H., Morphology and luminescence properties of ZnO micro/nanostructures synthesized via thermal evaporation of Zn-Mg mixtures. *Ceramics International*, 2015. 41(7): p. 8475-8480.
- [2] Wan, Q., et al., Fabrication and ethanol sensing characteristics of ZnO nanowire gas sensors. *Applied physics letters*, 2004. 84(18): p. 3654-3656.
- [3] Ilican, S., Y. Caglar, and M. Caglar, Preparation and characterization of ZnO thin films deposited by sol-gel spin coating method. *Journal of optoelectronics and advanced materials*, 2008. 10(10): p. 2578-2583.
- [4] Chen, D., et al., N-ZnO nanorod arrays/p-GaN light-emitting diodes with graphene transparent electrode. *Journal of Luminescence*, 2019. 216: p. 116719.
- [5] Wu, J.J. and S.C. Liu, Low-temperature growth of well-aligned ZnO nanorods by chemical vapor deposition. *Advanced materials*, 2002. 14(3): p. 215-218.
- [6] Nasih, S., et al., The effects of thermal power and deposition time on the structural characteristics of ZnO nanorods and their optical properties for photovoltaic applications. *Applied Physics A*, 2020. 126(9): p. 1-10.
- [7] Yun, E.-J., et al., Development of ZnO-based thin-film transistors with top gate structures. *Journal of the Korean Physical Society*, 2012. 60(1): p. 55-58.
- [8] Bhatia, D., et al., A novel ZnO piezoelectric microcantilever energy scavenger: Fabrication and characterization. *Sensing and bio-sensing research*, 2016. 9: p. 45-52.
- [9] Vittal, R. and K.-C. Ho, Zinc oxide based dye-sensitized solar cells: A review. *Renewable and Sustainable energy reviews*, 2017. 70: p. 920-935.
- [10] Myoung, J.-M., et al., Effects of thickness variation on properties of ZnO thin films grown by pulsed laser deposition. *Japanese Journal of Applied Physics*, 2002. 41(1R): p. 28.
- [11] Hu, J., et al., Characterization of zinc oxide crystal whiskers grown by thermal evaporation. *Chemical Physics Letters*, 2001. 344(1-2): p. 97-100.
- [12] Yang, S., et al., Investigation of annealing-treatment on structural and optical properties of sol-gel-derived zinc oxide thin films. *Bulletin of Materials Science*, 2010. 33(3): p. 209-214.
- [13] Kathirvel, P., et al., Spectral investigations of chemical bath deposited zinc oxide thin films-ammonia gas sensor. *Journal of Optoelectronic and Biomedical Materials*, 2009. 1(1): p. 25-33.
- [14] Selvamani, T., et al. (2010) "Easy and effective synthesis of micrometer-sized rectangular MgO sheets with very high catalytic activity." *Catalysis Communications* 11.6: 537-541.
- [15] Tigunta, S., et al., Effect of gas atmospheres on degradation of MgO thin film magnetic tunneling junctions by deionized water. *Thin Solid Films*, 2020. 709: p. 138185.
- [16] Taşer, Ahmet, Muhammed Güldüren, and Harun Güney. (2021) "Cr Dopant Effect on MgO Thin Film Structural, Optical and Morphology Properties." *Erzincan University Journal of Science and Technology* 14.1: 284-291.
- [17] Chayed, n. F., badar, n., rusdi, r., kamarudin, n. &kamarulzaman, n.2011 .Optical band gap energies of magnesium oxide (Mgo) thin film and spherical nanostructures. *Aip conference proceedings*,. American institute of physics, 328-332.
- [18] Fahmy, h., el-hakim, m., nady, d., mostafa, y., mohamed, f., yasien, a., moustafa, m., elmsery, b. &yousef, h. 2022. Review on mgo nanoparticles multifunctional role in the biomedical field: properties and applications. *Nanomedicine journal*, 9, 1-14.
- [19] Zribi, a. F. J. B. 2009. Functional thin films and nanostructures for sensors synthesis, physics and applications.
- [20] Kale, R. & Lokhande, C. 2004. Room Temperature Deposition Of Znse Thin Films By Successive Ionic Layer Adsorption And Reaction (Silar) Method. *Materials Research Bulletin*, 39, 1829-1839.
- [21] Zhi, Z., Liu, Y., Li, B., Zhang, X., Lu, Y., Shen, D. & Fan, X. 2003. Effects Of Thermal Annealing On ZnO Films Grown By Plasma Enhanced Chemical Vapour Deposition From Zn (C₂H₅)₂ And Co₂ Gas Mixtures. *Journal Of Physics D: Applied Physics*, 36, 719.

Citation of this Article:

Manea Mohammed Khlaif, “Study of the Effect of Annealing on the Optical and Structural Properties of ZnO Films Doped with Magnesium and Prepared Using Chemical Bath Deposition (CBD) Technique”, Published in *International Research Journal of Innovations in Engineering and Technology - IRJIET*, Volume 8, Issue 3, pp 185-193, March 2024. Article DOI <https://doi.org/10.47001/IRJIET/2024.803025>
