



Study and Investigation of the Effects of the OTA Technique on the Physical Properties of the ZnO Thin Films Prepared by PLD

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Abstract

The polycrystalline thin films were deposited on glass substrate at room temperature by pulsed laser deposition PLD technique. The effects of annealing treatment by used the Oil Thermal Annealing (OTA) process on the structural, optical and electrical properties of ZnO thin film films were investigated. The film structure was investigated by X-ray diffraction to indicate that the heat treatment after the OTA process gives the optimized condition of crystalline. The transmission spectrum of the film was measured by UV-V is spectrophotometer, and the Urbach energy and forbidden band width were calculated. The surface topography of the film was observed by scanning electron microscopy (SEM) image of the ZnO thin film at the OTA process shows the changes in the shape and size of the grains. The atomic force microscopy (AFM) effect of heat treatment was demonstrated by the change in the surface roughness of the ZnO thin film. The electrical properties of thin film were optioned by Hall Effect technique. That these improvements in the ZnO thin film physical properties were annealing temperatures by OTA at 150 °C, 200 °C, 250 °C and 300 °C.

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1. Introduction

Zinc oxide is a binding energy semiconductor n-type with a direct bandgap of about (3.37 eV) and has interesting optical and electrical properties at room temperature It has been shown that ZnO thin films possess good electrical conductivity and high optical transmittance [1, 2]. ZnO thin film can be prepared at several preparation techniques, such as Pulsed laser deposition, chemical spraying, chemical vapor deposition, ion-beam assisted deposition, and reactive evaporation [1- 3]. There are many problems when using some of these techniques to prepare high-quality ZnO thin films. The pulsed laser deposition method was chosen as the preparation method. Pulsed laser deposition (PLD) is one of the best methods for growing high-quality, oriented c-axis ZnO thin film at low temperatures. The pulsed laser deposition technique is an ideal choice for the preparation of ZnO thin film on the glass substrate because of its high rate of good adhesion and easy control of the film thickness [4-6]. Because of the important features of the ZnO thin film, it has been preferred over silicon in the manufacture of solar cells, it has given good results [7]. ZnO thin film provides motivation advantages for a wide field of applications, gas sensors, displays, and photovoltaic devices [8-12]. Previous experiments have found that the physical properties of the ZnO thin film change significantly during the deposition process as well as the heat treatment. Therefore, physical properties such as structural, morphological, optical, and electrical are closely related to the preparation conditions and heat treatment [13-18]. The experiments in the previous studies showed that heat treatment has an important role in

improving the optical and structural properties of ZnO thin films [19]. This work aims to improve the physical properties of ZnO thin film through heat treatment. The heat treatment parameters were changed and verified to improve the physical properties of the ZnO thin film.

2. Theoretical

The pellet target of Zinc oxide powder was prepared by a hydraulic press. The material of powder ZnO (99, 99%) was cold-pressed by using a hydraulic press of 5 tons. The resulting pellet has homogenous surface on both sides with 25 mm diameter and 4 mm thickness of ZnO target. The Pyrex glass as substrate was used for deposits ZnO thin film. There are two steps before using the glass substrate at deposition process to preparing for work. Firstly, it was cut into small slides in (25×25) mm² dimensions. Secondly, it was cleaned with ethanol and ultrasonically and finally heated at 50 °C. ZnO thin film was prepared on the glass substrate by the manufactured system with PLD technique at parameters of Nd: YAG laser, wavelength $\lambda = 1064$ nm. And pulse power (400) mJ. The machine manufactured by Shenyang Scientific Instrument Research Institute. The substrate was Pyrex glass, Argon gas used as space surrounding the sample after vacuum obtained at 10⁻³ Torr at room temperature.

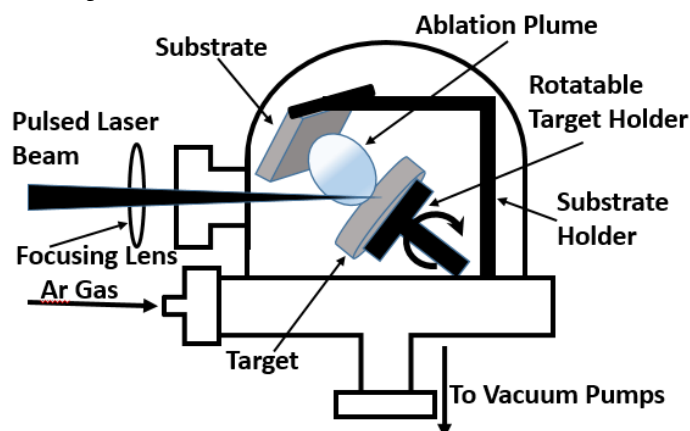


Figure 1: PLA Setup diagram with ZnO target during deposition on the glass substrate.

The thermal oil type used in the OTA technique in this work is DOWTHERM™. That's oil has a high heat transfer performance at temperatures from 15 °C to 400 °C. OTA process treatment stages start after the sample is placed inside the quartz container and filled with thermal oil, then heating until the desired temperatures reach are 150 °C, 200 °C, 250 °C, and 300 °C. After completing the heat treatment, the sample is left inside same the oil until cools, then extract the sample. The sample cleaned with n-Hexane C₆H₁₄, which has been chosen not to affect the physical properties of the film and its ability to good removes oil.

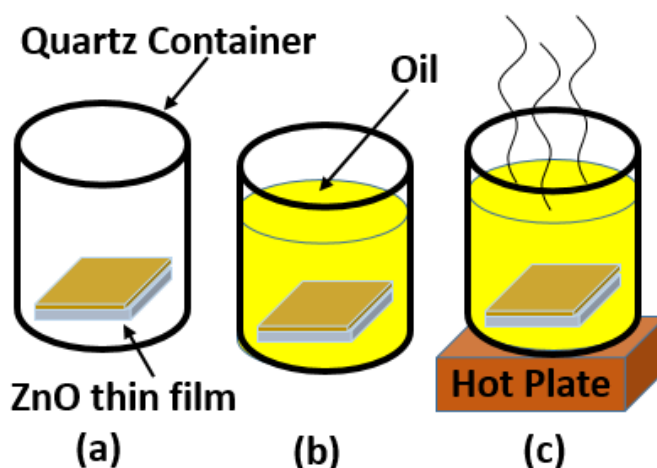


Figure 2: OTA process diagram of the stages treatment a) Putting sample inside the container b) Fill the container with oil c) Oil heat to the desired temperature.

The sample was XRD-tested by X-ray diffractometer, and the film thickness was 200 nm, measured by an XP-2 type step meter manufactured by AMBIOS, USA. The transmission spectrum of the sample was tested by a UV-2100 spectrophotometer manufactured by Shimadzu Corporation. The microscopic morphology of the sample was tested by scanning electron microscopy.

3. Results and Discussion

Physical properties study of ZnO polycrystalline thin films prepared by PLD technique, which are morphological, structural, optical and electrical. The properties of the ZnO thin films are closely related to the annealing temperature treatment. The treatment by OTA process was at four temperatures are 150 °C, 200 °C, 250 °C and 300 °C, which agree with [20].

3.1 Morphological Properties

3.1.1 SEM analysis

Figure 3 SEM images indicate the effect of annealing treatment by OTA process on the ZnO thin film compared with the as-deposited sample. The film deposited at room temperature then treatment annealed arrive about to 300 °C is fuller than the grain before annealing, the grain boundary is clear, the uniformity and compactness of the film are improved, and the film is smoother and denser. Where observed that annealing treatment a clearer topography as the increases temperature. The as-deposited sample compared with the annealing temperature at 150 °C observe little change. Change is gradually increasing very clearly when compared with other annealing temperatures 200 °C, 250 °C, and 300 °C respectively. That the surface of the deposited film at room temperature is rough, the bonding between the crystal grains is loose, the pinholes are large, and the grain shape is irregular. The ZnO thin film at 300 °C is a large change in the distribution of the dense grains. The properties are improved, although there is some grain size is not consistent. That the atoms in the film get higher energy when raising the temperature, for this reason, is migrate and recrystallize.

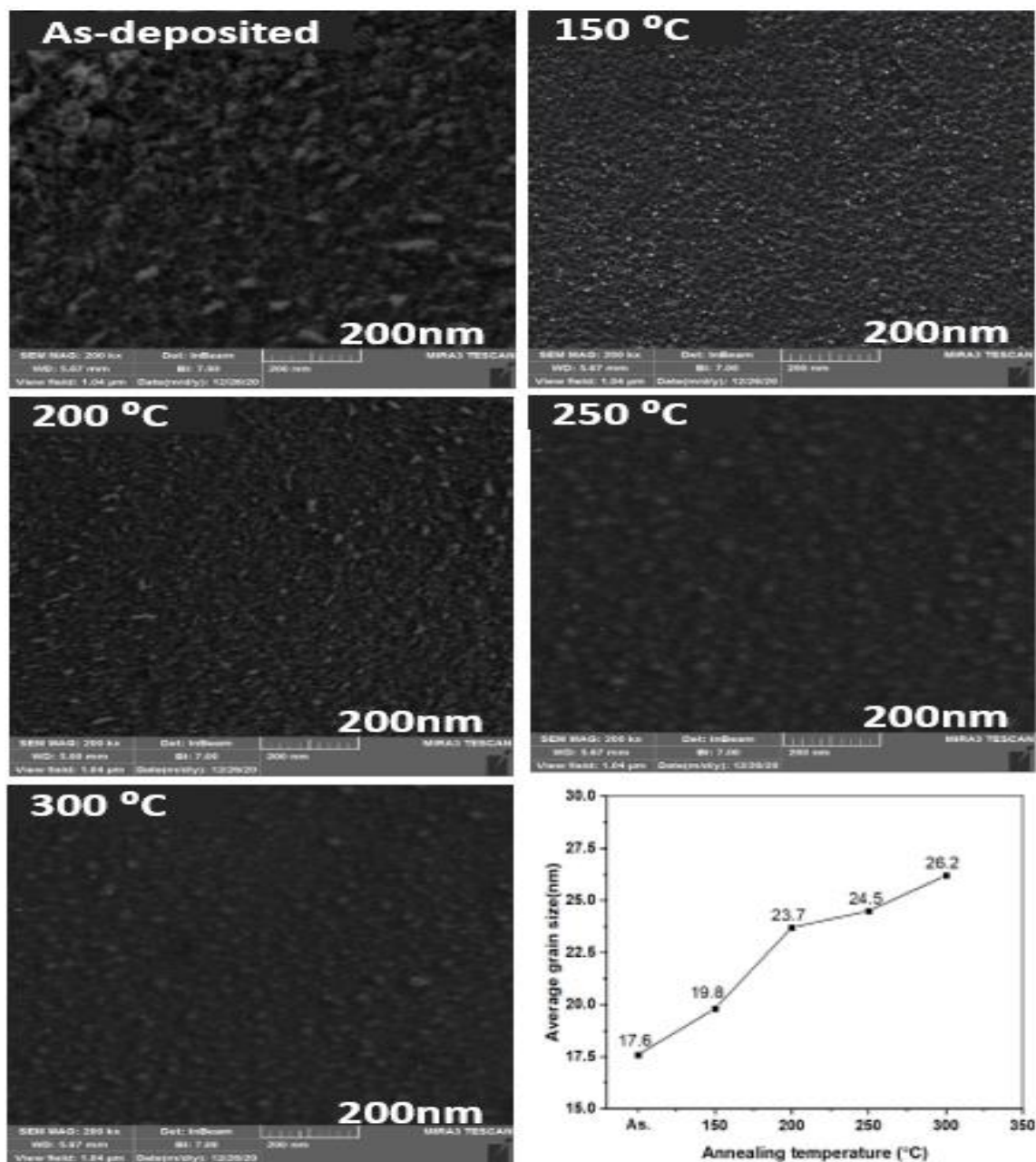


Figure 3: SEM images of the ZnO thin film before and after treatment by the OTA technique

3.1.2 AFM atomic Force microscopy analysis

Figure 4 shows three-dimensional AFM images before and after annealing by the OTA technique at temperatures 150 °C, 200 °C, 250 °C, and 300 °C respectively. The surface morphology of ZnO thin film, which has been verified by AFM, clearly indicates that polycrystalline. The roughness decrease on the ZnO thin film surface clear ranging from 30 - 59 nm depending on the increase of the annealing temperature. The film that was heat-treated at 300 °C shows ovals with layers' parallel to the surface and the small peaks that appear at temperatures of 150 °C, 200 °C and 250 °C cannot be found.

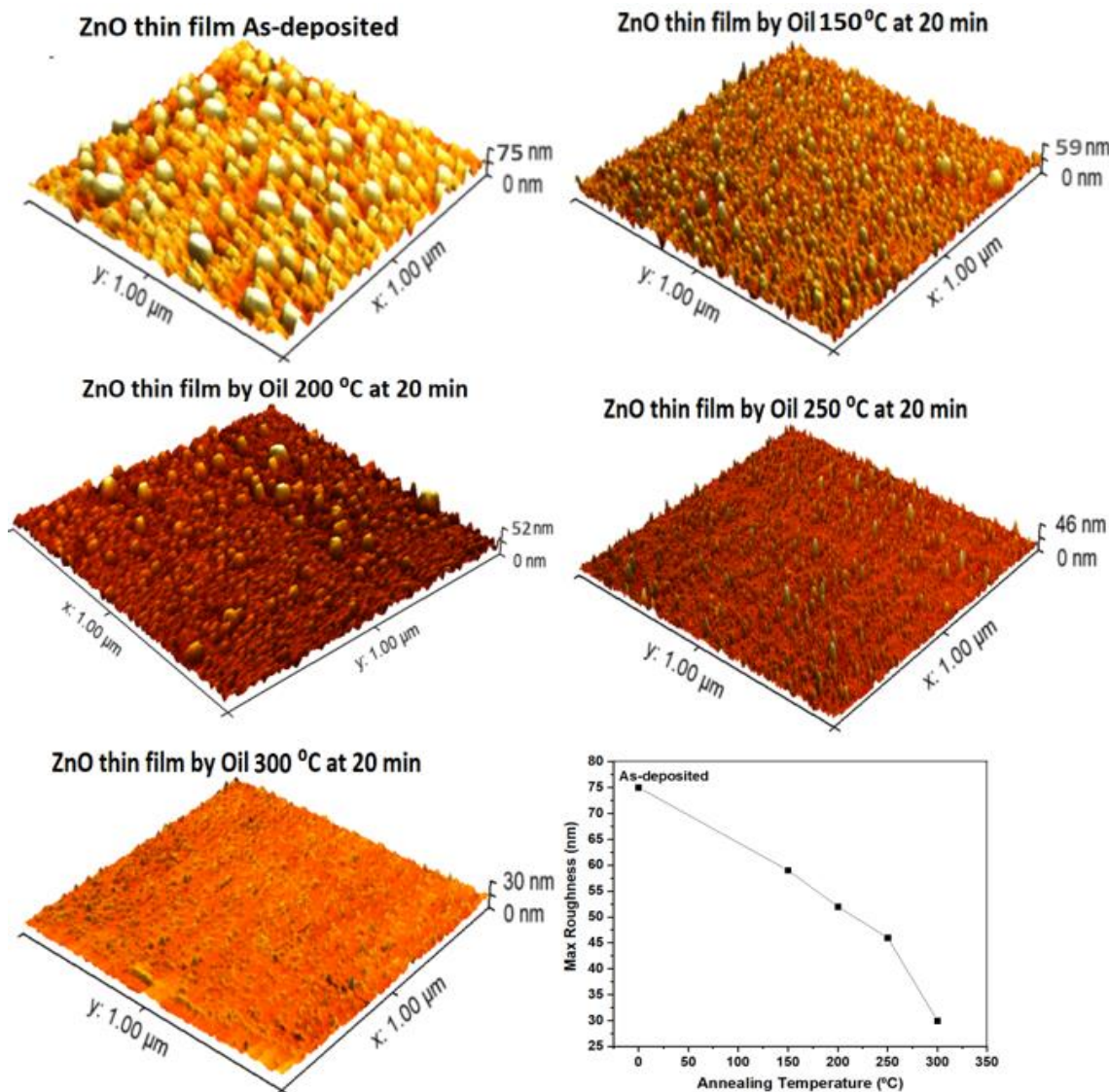


Figure 4: AFM images of the ZnO thin film before and after treatment by the OTA technique.

3.2. Structural Analysis

Figure 5 shows the X-ray diffraction spectrum of a ZnO thin film prepared at room temperature on the glass substrate by the PLD technique. The heat treatment was carried out through the OTA process to obtain an improvement in the structural properties. Heat treatment by the OTA process is under different temperatures at 150, 200, 250, and 300. The ZnO film observed is annealed at 300 °C within 20 mn defects, better microstructure. The ZnO crystal has two forms of wurtzite structure α -ZnO and sphalerite structure β -ZnO. It can be seen from Figure 1 that the films in this experiment are all hexagonal α -ZnO. There are three prominent diffraction peaks which are (002), (001), and (110). The film has a distinct preferred orientation in the (002) direction with increased annealing temperature. When increasing the heat treatment, the preferred orientation (002), (001), and (110) crystal plane increases. The diffraction peak intensity has a significant deviation at (002), (001), and (110), but the diffraction peak at other orientations weakened. This offset is related to the internal structure affected by the heat treatment.

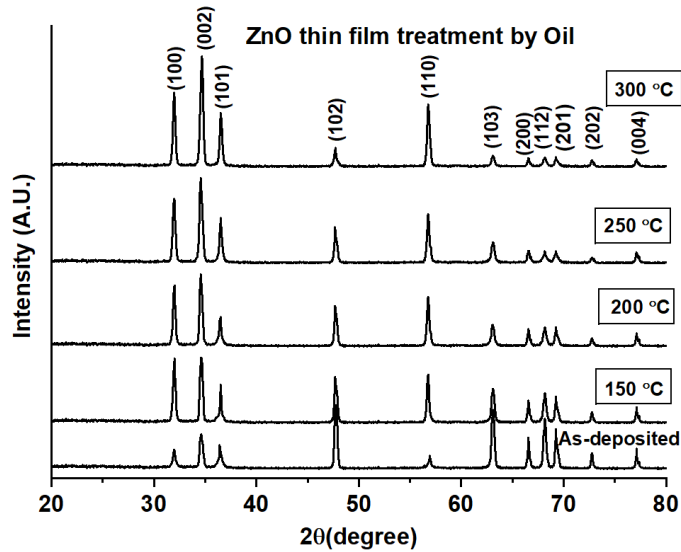


Figure 5: X-ray diffraction spectrum of the ZnO thin film before and after treatment by the OTA technique

Table 1 lists the ZnO film treatment by the OTA technique at temperatures 150 200 250 300. Diffraction peak angle position, crystal plane distance, full width at half maximum, and stress. The film sample has a certain shift from the peak position to the high diffraction intensity compared with the peak position of the As-deposited sample. As the working pressure increases, the offset angle increases, and the inter-planar spacing changes. It can be seen that the ZnO thin film has a certain shift from the peak position to the high diffraction intensity compared with the other peak of the As-deposited sample, and as the annealing temperature increases, the offset angle increases, and the inter-planar spacing changes. The peak position shift of the film sample indicates that the film has internal stress, which causes the crystal lattice to be stretched or compressed. According to the film property formula, the film stress can be calculated by measuring the crystal lattice distortion, which agrees with [10].

Table 1. Relationship between microstructure parameters and deposition pressure of ZnO thin films.

Annealing Temperature (°C)	Average Grain size (nm)	Orientation & 2θ (degree)
As.	17.6	
150	19.8	(100) _{31.96°} , (002) _{34.6°} , (101) _{36.4°} , (102) _{47.72°} ,
200	23.7	(110) _{56.92°} , (103) _{63.08°} , (200) _{66.6°} , (112) _{68.16°} ,
250	24.5	(201) _{69.24°} , (202) _{72.67°} , (004) _{77.12°}
300	26.2	

3.3. Optical Properties

3.3.1. Urbach with Band energy calculation

The lattice defects of the ZnO film can be reflected in the tail of the absorption band and can be characterized by the Urbach energy. The change of the energy of the Urbach is consistent with the change of the defect density of the film, and the density of the film is large. If the energy is small, the defect density is small. According to the Urbach rule, the absorption coefficient α of the film and the photon energy $h\nu$ are satisfied near the absorption edge.

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_u}\right) \quad (1)$$

Where E_u is Urbach energy, α_0 is a constant, and the absorption coefficient α can be calculated from the transmission spectrum.

$$\alpha = -\ln \frac{T}{d} \quad (2)$$

Where T is the transmittance and d is the film thickness. From (2), it can be seen that $\ln \alpha$ has a linear relationship with photon energy, and Urbach energy is the reciprocal of the slope of the linear part, as shown in Figure 6.

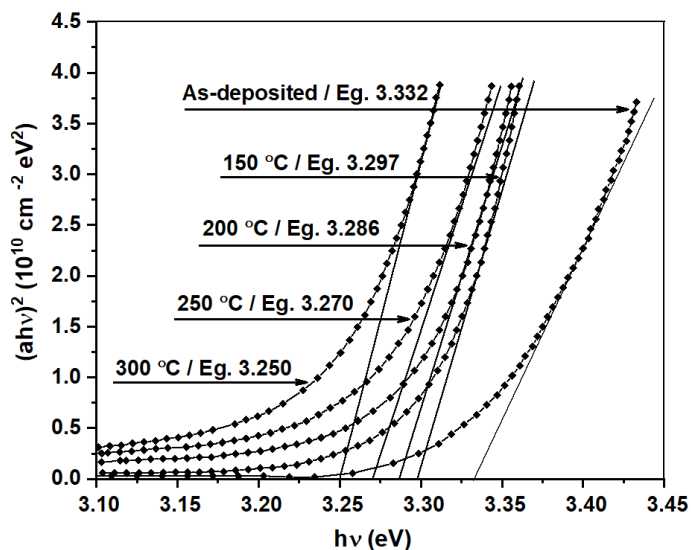


Figure 6: Determination of the ZnO thin film Band gap from the Urbach energy.

Figure 6 ZnO thin film $(\alpha h\nu)$ and photon energy curve compared with $(h\nu)$ at annealing temperatures 150 °C, 200 °C, 250 °C and 300 °C. The relationship between the bandgap and Urbach energy of ZnO thin film after annealing treatment show that the bandgap decreased with the annealing temperature. That confirms that as the annealing temperature increases, the film improvement increases, and defects decreased. The intercept of the absorption edge tangent on the abscissa is the optical energy gap. The annealed sample at 300 °C was the forbidden bandwidth $E_g = 3.28$ eV, which is consistent with the wurtzite ZnO.

Since ZnO is a direct bandgap semiconductor, its absorption coefficient and energy gap satisfy the Tauc formula.

$$(\alpha h\nu)^2 = A (h\nu - E_g) \quad (3)$$

Where $h\nu$ is the photon energy, E_g is the forbidden band width, A is a constant, and α is the absorption coefficient. A relationship diagram of $(\alpha h\nu)^2 - h\nu$ is made, as shown in Figure 7.

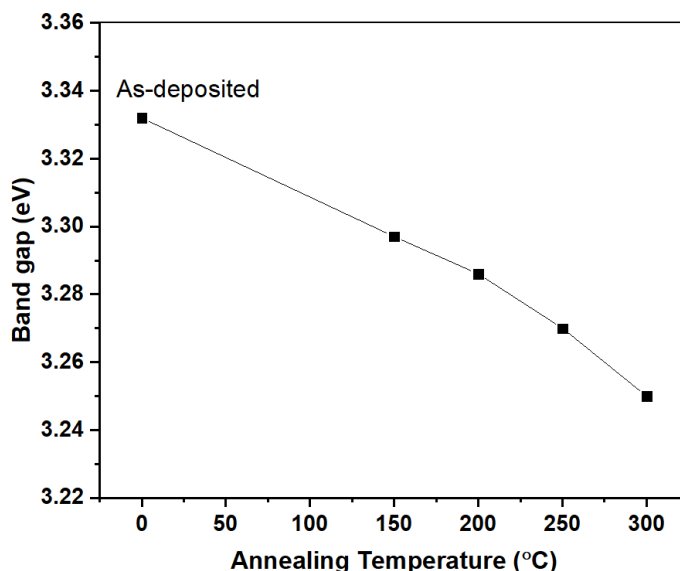


Figure 7: Variation of the bandgap of ZnO film with annealing temperature

3.3.2 Transmittance Spectrum Analysis

Figure 8 shows the transmission spectra of ZnO films at 200 nm thickness with heat treatment by different temperatures are 150 °C, 200 °C, 250 °C, and 300 °C. The film deposited by the PLD technique has a significant redshift in the absorption edge to the presence of defects caused during preparation, including the forbidden narrowed bandwidth. Some of these defects include the vacancies between the atoms caused by the molecule's vaporization and then deposited on the glass substrate. The thickness is at the lower deposition is larger than the upper this leads to interference phenomenon occurs because the thickness is smaller than the visible wavelength, there is no interference fluctuation. In addition, when the annealing temperature is 300°C, the absorption edge of the film is steep, indicating the film has good crystal quality. After annealing at 300 °C for 20 min, the transmittance is higher, and the transmittance is above 94% in the wavelength range of 450-900 nm.

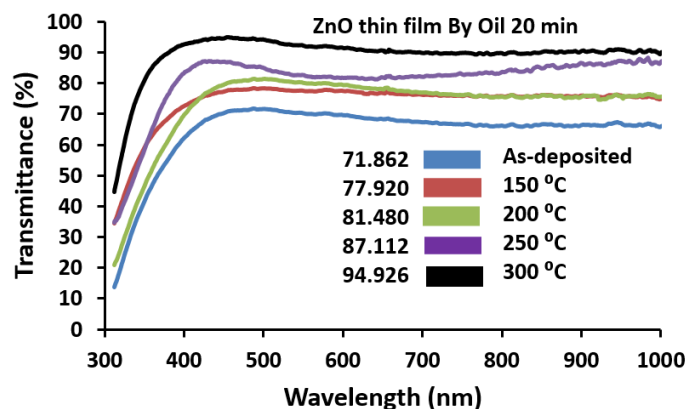


Figure 8: shows the Transmittance curve of ZnO film before and after annealing by OTA technique at 150 °C, 200 °C, 250 °C, and 300 °C.

3.4. Electrical Properties

Figure 9 shows the relationship between the effect of annealing temperature on resistivity and Hall mobility. It may be clear that the relationship of the annealing temperature with the resistivity is inverse proportioned, while with the Hall mobility it is a direct proportion. Hall's Effect theorem was used to measure the electrical properties of the film treated by the OTA technique. The Carrier concentration (n) and Hall mobility (μ) of the grown ZnO

thin films have been measure on the glass substrate, which electrical and temperature parameters as shown in table 2. The variation of electrical parameters explains a similar trend over a wide temperature shown in table (2), in which h eat treatment caused an order of magnitude in carrier concentrations. For as-deposited of the ZnO films, it is of the order of 5.65×10^{19} , whereas at the increase in temperature 150 °C, 200 °C, 250 °C, and 300 °C it increases to a value of the order of 1.95×10^{20} , 2.35×10^{20} , 3.11×10^{20} , and 3.92×10^{20} respectively. Found for each ZnO film that with increasing annealing temperature, the electron mobility and resistivity decreases, and carrier concentration increases.

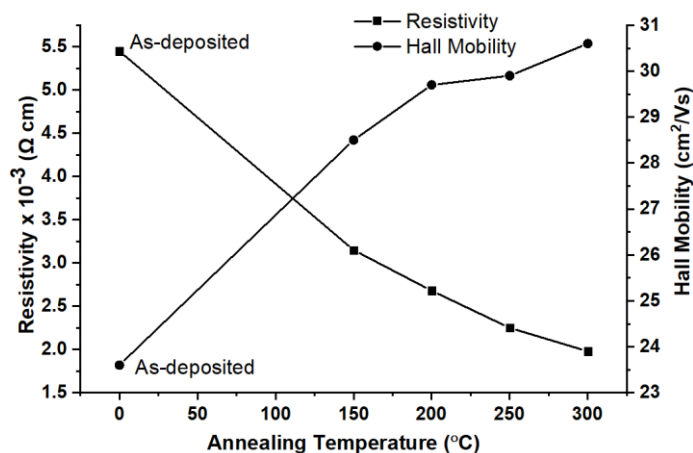


Figure 9: shown the resistivity of the ZnO thin film in the temperature range 150 °C, 200 °C, 250 °C, and 300 °C

Table 2. Carrier concentration, resistivity, and mobility of ZnO thin films with variant annealing temperature by OTA technique

Annealing Temperature °C	Resistivity $\times 10^{-3} (\Omega \text{ cm})$	Carrier concentration (cm^{-3})	Hall Mobility (cm^2/Vs)
As-deposited	5.45	5.65×10^{19}	23.6
150	3.15	1.95×10^{20}	28.5
200	2.68	2.35×10^{20}	29.7
250	2.25	3.11×10^{20}	29.9
300	1.98	3.92×10^{20}	30.6

4. Estimated cost

The economic cost is a term in which the sum of the value of materials, labor, and other direct and indirect costs of a given product is paid. The direct costs are that pay to trade off the product such as the ZnO material, the glass substrate, and the amount of gas. Indirect costs are the amounts paid to produce, such as the electrical current consumed in annealing processes and the consumption of devices. In general, indirect costs cannot be loading it to the value of the sample. Therefore, the purpose of the cost study is a compared with the sample cost at the same results of the physical properties for the different annealing processes.

There is no need to discuss the cost of preparing the ZnO thin film because it is a fixed cost. This study will be a focus on comparing the cost of the consumption power (watt) in the OTA technique with other annealing techniques. This study also includes the cost of the heat treatment processes only of the ZnO thin film sample. The ZnO thin film heat treatment process by the OTA technique is developed successfully at the required temperatures. The transparency and resistivity of the samples treated by OTA processes compared with those of other researchers. Tables 3 and 4. Show compares electrical and optical properties at the thermal annealing process with

other techniques at 300 °C. The resistivity of the ZnO thin film changing after heat treatment by the OTA technique from 5.45 $\Omega\cdot\text{cm}$ to 1.98 $\Omega\cdot\text{cm}$. While the transmittance of ZnO thin films changing after heat treatment by the OTA technique from 71.86 % to 94.92 %. The heat treatment by the OTA technique compared to others is very simple.

Table 3. Show the resistivity of the ZnO thin film before and after treated by OTA processes at 300 °C compared with those of other researchers.

Technique type	Consumption power (watt)	Resistivity x 10 ⁻³ ($\Omega\cdot\text{cm}$) before heat treat	Resistivity x 10 ⁻³ ($\Omega\cdot\text{cm}$) after heat treat	Reference
OTA	800	5.45	1.98	Our study
Quartz furnace in nitrogen gas	2500	1.26	1.05	[13]
Quartz furnace in air	2000	6.7	5.5	[16]
Quartz furnace in vacuum	2500	3.68	2.85	[18]
Quartz furnace in ambient atmosphere	2000	3.20	2.90	[19]

Table 4. Show the transparency of the ZnO thin film before and after treatment by OTA processes at 300 °C compared with those of other researchers.

Technique type	Consumption power (watt)	transmittance % before heat treat	transmittance % after heat treat	Reference
OTA	800	71.86	94.92	Our study
Quartz furnace in air	2000	63	67	[14]
Quartz furnace in vacuum	2500	85	87	[15]
Quartz furnace in air	2000	80	90	[16]
Quartz furnace in air	2000	70	86	[17]

5. Conclusion

In this paper, ZnO thin films were deposited by the PLD technique. The effects of heat treatment by the OTA technique on the physical properties of the ZnO thin films were investigated. The results show that prepared ZnO

film has a hexagonal structure, and the film deposited at room temperature grows preferentially along the (002) crystal plane. As the annealing temperature increases, the physical properties improving. The characteristics of the ZnO film are best improving when the annealing temperature at 300°C, compared with others temperatures. The heat-treated effect on the ZnO film by the OTA technique gave crystal quality and transmittance characteristics to be flat and transparent. In Addition, the improvement of electrical properties through a decrease in the resistivity and the forbidden bandwidth is 3.28 eV.

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Conflict of Interest:

The authors declare that they have no conflict of interest.

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