Study on physical properties of nanostructured ZnO prepared by pulse laser deposition

Raied K. Jamal, Mohammed A. Hameed, and Kadhim A. Adem
University of Baghdad, Collage of science, Department of physics, Baghdad Iraq

Abstract
Zinc Oxide thin film of 2 μm thickness has been grown on glass substrate by pulsed laser deposition technique at substrate temperature of 500 °C under the vacuum pressure of 8×10^{-2} mbar. The optical properties concerning the absorption, and transmission spectra were studied for the prepared thin film. From the transmission spectra, the optical gap and linear refractive index of the ZnO thin film was determined. The structure of the ZnO thin film was tested with X-Ray diffraction and it was formed to be a polycrystalline with many peaks.

Keywords: ZnO thin film, pulse laser deposition.

Introduction

The ZnO nanostructures have many applications in gas sensors, UV detector and solar cell (1-3). This material has some additional advantages compared to other large band-gap semiconductors; for example, its large exciton binding energy (about 60 meV) which is three times the binding energies of ZnSe and GaN (4). This allows a stable exciton distribution and achieves efficient excitonic emission at room temperature. The optical and electrical properties of ZnO nanostructures are study at different preparation techniques and at different substrate materials (5-6). Many different techniques, Such as sputtering, chemical vapour deposition, ion-beam assisted reactive deposition, pulsed-laser deposition, chemical spraying, sol-gel and reactive evaporation have been employed in the growth of ZnO thin film. Recently there are many applications of laser one of these applications in a thin film preparation field that called Pulsed Laser deposition (PLD). There many studies done in this filed (7-10). With the pulsed laser deposition method, thin films are prepared by the ablation of one or more targets illuminated by a focused pulsed-laser beam. This technique was first used by smith and Turner in 1965 (11) for the preparation of semiconductor and dielectric thin films and was established due to the work of Dijkkamp and coworkers (12) on high-temperature superconductors in 1987. Their work already showed main characteristics of PLD, normally the stoichiometry transfer between target and deposited films, high deposition rate of about 0.1 nm per pulse and the occurrence of droplets on the substrate surface. The advantage of using PLD then other sputtering techniques is that PLD is quite easy to produce multilayered films of different material by sequential ablation of assorted targets. Besides, by controlling the number of pulses, a fine control of film thickness down to atomic monolayer can be achieved. The most important feature of PLD is that the stoichiometry of the target can be retained in the deposited film. In the said advantages of PLD, some short comings have been identified in using this deposition technique. In This paper ZnO nanostructure film have been fabricated by pulsed laser deposition (PLD) method, which I widely used for the growth of oxide film because it allows for the stoichiometry of the synthesized material. The optical and structure of ZnO was studied.

Experimental details

A typical set-up for Pulse Laser Deposition (PLD) is schematically shown in Figure 1. In this study, ZnO was used as targets with diameter of 2 cm and thickness of 1cm was fixed at the top chamber. Glass substrate was used as substrate material to study the optical. The cleaning of the substrates was very necessary to ensure surface free from contamination films such as grease, absorber water. The glass substrates were cut into standard sizes of 10 x 10 mm, were ultrasonically cleaned in acetone and dried into oven until it was. ZnO thin films were produced by Pulse Laser Deposition (PLD). In order to optimize the best location of the substrates on holder, the influence of the substrate to target distance on the structural and optical properties of ZnO thin films produced by Pulse Laser Deposition (PLD) in argon atmosphere was studied. The ZnO films were grown during 5 min onto glass microscope slides diametrically on the top plate substrate holder. The base pressure in the chamber and the working pressure were 2.0×10^{-5} mbar and 8×10^{-2} mbar, respectively. Pulse Laser Deposition (PLD) has become a preferred method for metal and semiconductors deposition. Providing high deposition rates and uniform coverage, dc magnetron sputtering provides the ability to quickly deposit large amounts of material, the optimums position on substrate holder of the substrates with respect to the target distance was determined. A series of films were synthesized under argon atmosphere with power 500 mJ and the working pressure (P_W) were kept constants and equal, $P_W = 8.0 \mathrm{x} 10^{-2}$ mbar. In this study, a variety of characterization techniques were used to evaluate the structural, optical and electrical properties of the thin films. Of particular interest was the determination of the structure from X-ray diffraction, the film thicknesses from optical interference fringes. Optical parameters from UV-Visible absorbance spectrum in the spectral range (200 -850) nm. For determination of the thicknesses of films we can use optical interference fringes measurements can be rapid, accurate, and non-destructive. Interferometer is used as a quantitative method for the determination of certain optical parameters is very important in the characterization of the investigated films. Optical method was used for thickness measurements and in the flowing is explained in details:

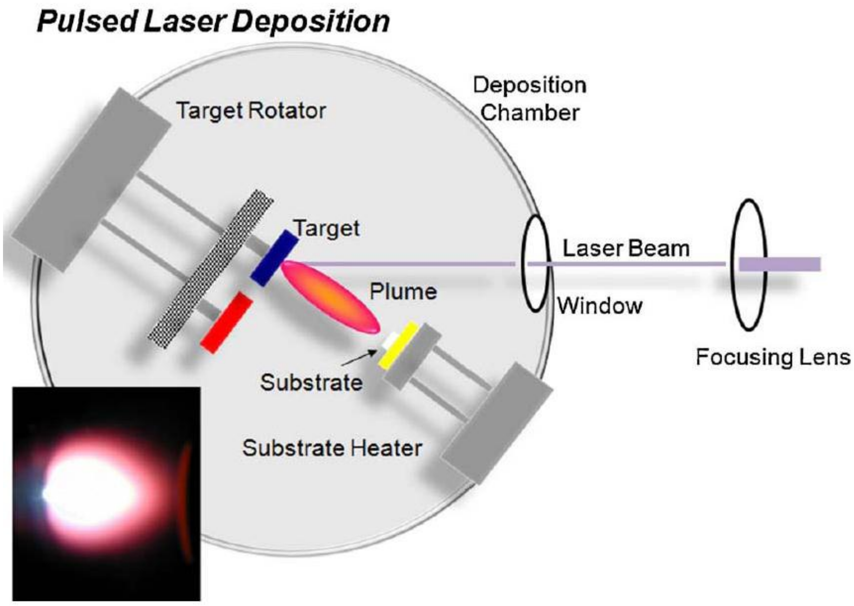

Figure (1): Schematic diagram of a typical laser deposition set-up.

The thickness of ZnO thin film was measured by using an optical interferometer method employing He-Ne laser 0.632 µm with incident angle 45° as shown schematically in Figure 2. This method depends on the interference of the laser beam reflected from thin film surface and then substrate, the films thickness t was determined using the following formula:

$$t = \frac{\lambda}{2} \cdot \frac{\Delta X}{X} \qquad (1)$$

Where: X= is the distance between the fringes.

ΔX= the shifting distance between the fringes.

λ= wavelength.

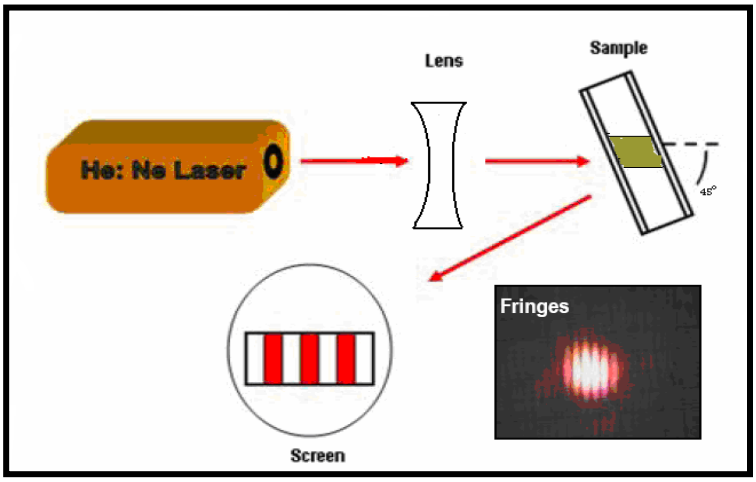

Figure (2): The schematic diagram of the film thickness

X-ray diffraction (XRD) is one of the most powerful techniques for qualitative and quantitative analysis of crystalline compounds. This experimental technique has long been used to determine the overall structure of ZnO thin films, including lattice constants, grain size identification of unknown materials, orientation of single crystals, and orientation of polycrystals. In this study thin films have been examined by X-ray diffraction (XRD) technique under the conditions power diffraction system with Cu-Kα X-ray tube (λ = 1.54056 Å) was used. The X-ray scans were performed between 2θ values of the X-ray diffraction (XRD) was recorded at a scanning rate of 0.08333° s^{-1} with the diffraction angle 2θ, range (20°-60°).

Optical measurements on the ZnO thin films were performed on a UV mate SP-8001 double beam spectrophotometer covering the wavelengths range (190-1100 nm) supplied by Metertech Corporation (Taipei, Taiwan). During scanning, a blank glass slide was placed in one of the beam's direction and another glass slide with film deposit was in the other beam's direction. Thus, the absorption spectrum displayed by the UV mate SP-8001 double beam spectrophotometer was as a result of the films deposited on the glass slide substrates.

Results and Discussion

X-ray diffraction investigates the structural type of the ZnO thin films prepared by pulse laser deposition. The XRD pattern for films deposited at room temperature showed that they are polycrystalline structure takes place. The XRD patterns for this ZnO films are presented in figure (3). The table 1, showed many dominant strongest peaks with their d spacing, FWHM, and diffraction angle values. The mean grain size of thin film calculated using the Scherrer's equation (13):

$G = 0.94\,\lambda / \beta \cos\theta$ (2)

Where *G* is the average crystalline grain size, λ is the wavelength, β represents the full- width at half maximum (FWHM) in radian and θ is the Bragg diffraction angle in degree. The calculated values of grains size for ZnO thin film are shown in table 1.

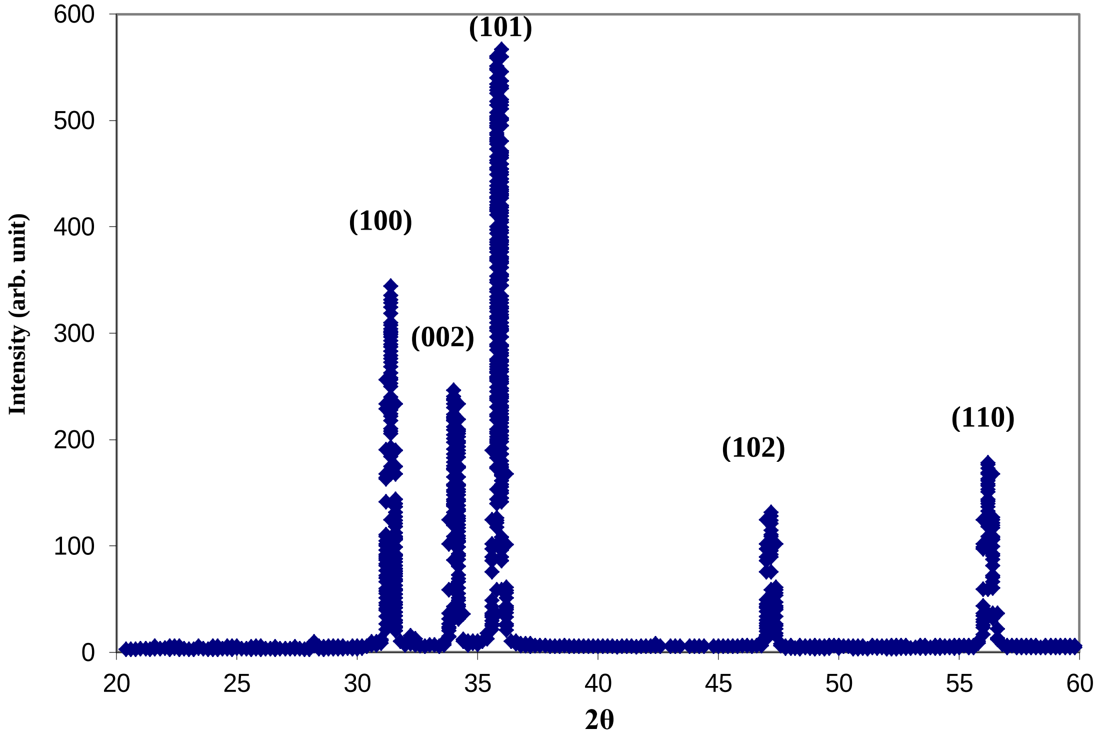

Figure (3): XRD pattern of ZnO thin film despite of glass substrate

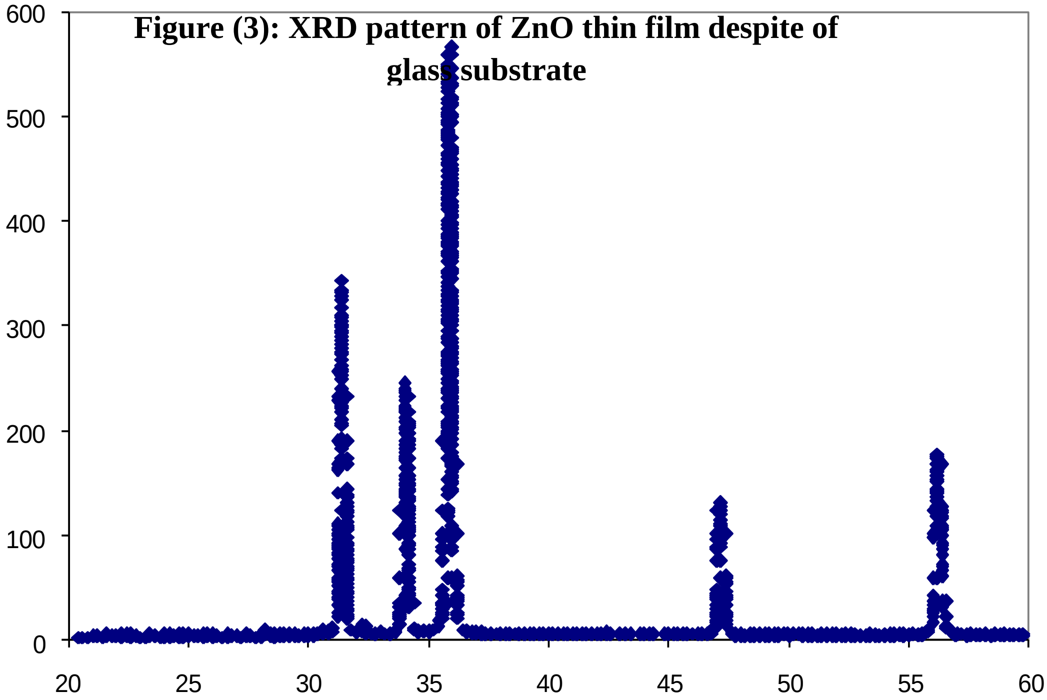

Table (1): All peaks and its Bragg's angle, interplanar distance, and full width half at maximum

peak No.	(hkl)	2 Theta (deg)	d(A°)	FWHM (deg)	G (nm)
1	(100)	31.47	2.84	0.4	21.5
2	(002)	33.94	2.67	0.1	86.8
3	(101)	36	2.49	0.6	14.5
4	(102)	47.07	1.92	0.4	22.64
5	(110)	56.39	1.63	0.4	23.54

The optical characteristics which involve the absorption coefficient, the optical energy gap E_g, and the optical constants (i.e. refractive index n, extinction coefficient k, real dielectric constant ε_r and imaginary dielectric constant ε_i), were studied within the range (200-800) nm for ZnO thin deposited by PLD technique. The absorbance spectra for ZnO thin films are shown in figure (4). This spectrum reveals that the maximum absorption peak at (200-250) nm range.

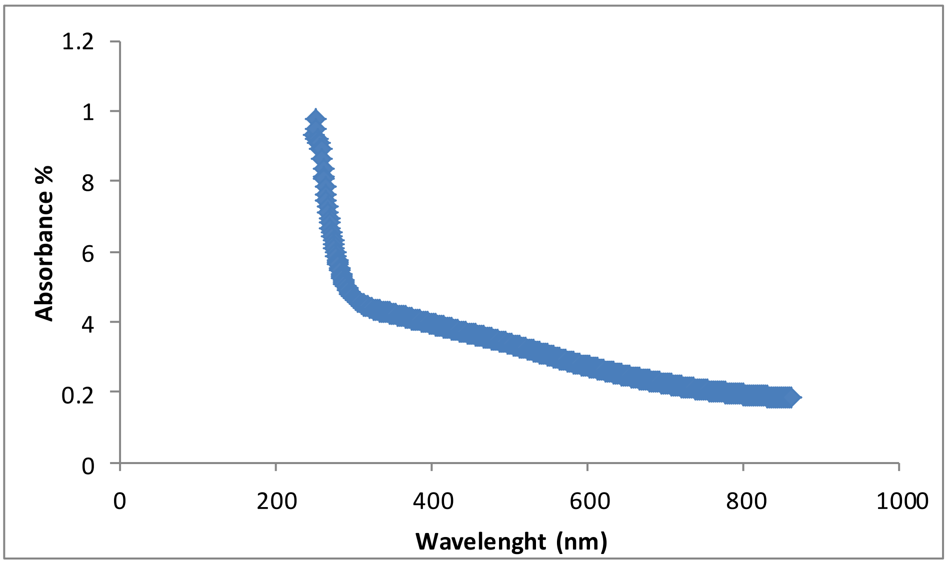

Figure (4): The optical absorbance of ZnO thin films

Figure (5) showed the variation of $(\alpha h\upsilon)^2$ as a function of $(h\upsilon)$ for ZnO thin films. It can be observed from this figure that the energy gap equal to 3.8 eV. Figure (6) showed the optical reflectance spectra of ZnO thin films. The reflectance spectrum represents the interference between the rays that are reflected from the film faces. As shown from figure (6), the reflectance of the film in visible region where wavelength (400-450) nm.

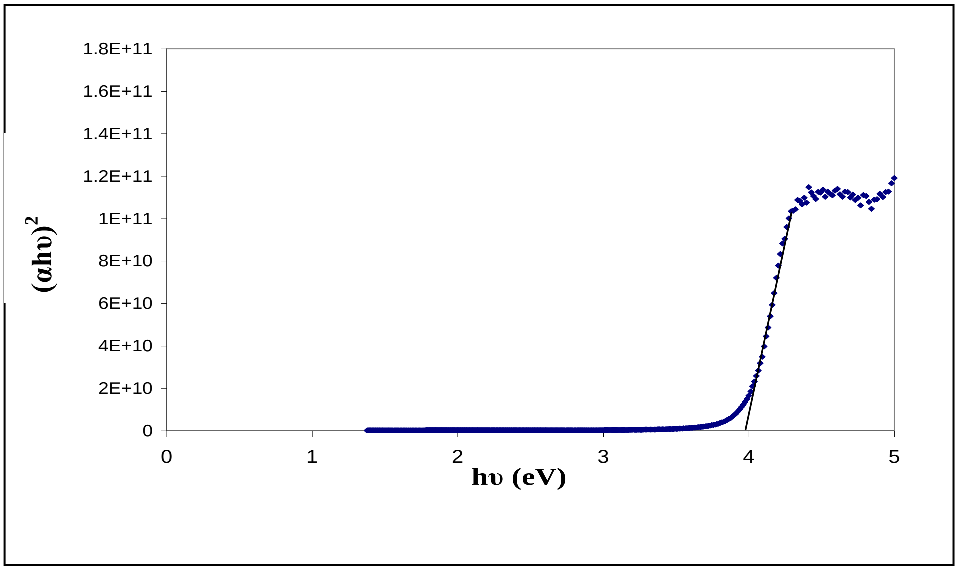

Figure (5): Variation of $(\alpha\ h\upsilon)^2$ versus hυ for ZnO thin films

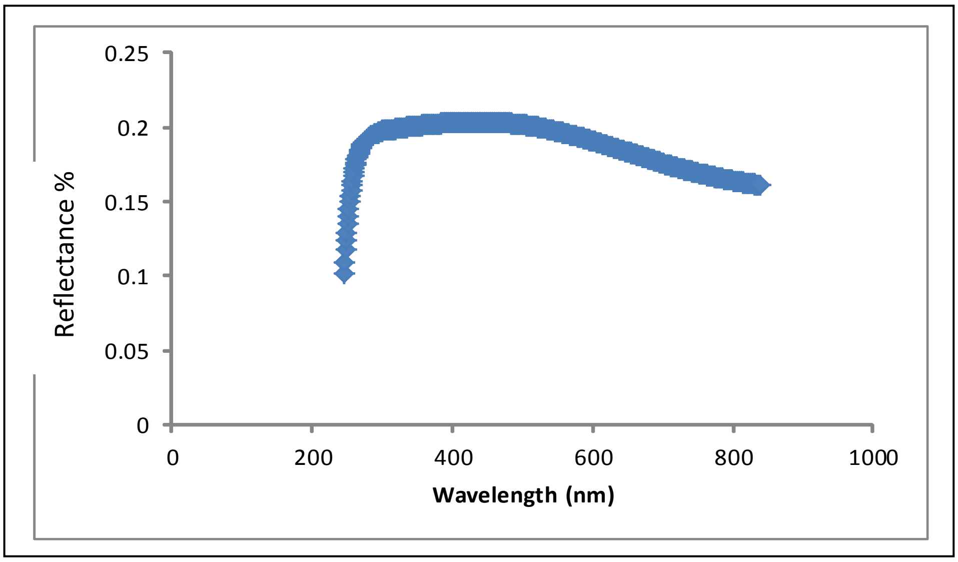

Figure (6): The reflectance spectra for ZnO thin films room temperature

The optical constants which are include the of refractive index n, extinction coefficient k, the real E_r, and imaginary E_i parts of dielectric constants were determined from transmission and absorption spectra within the range (200 -800) nm for ZnO thin films prepared by PLD. Figure (7) showed the variation of the refractive index as a function of the wavelength for ZnO thin films. It indicates that the refractive index almost constant at range (350-600) nm, and decrease with increasing wavelength.

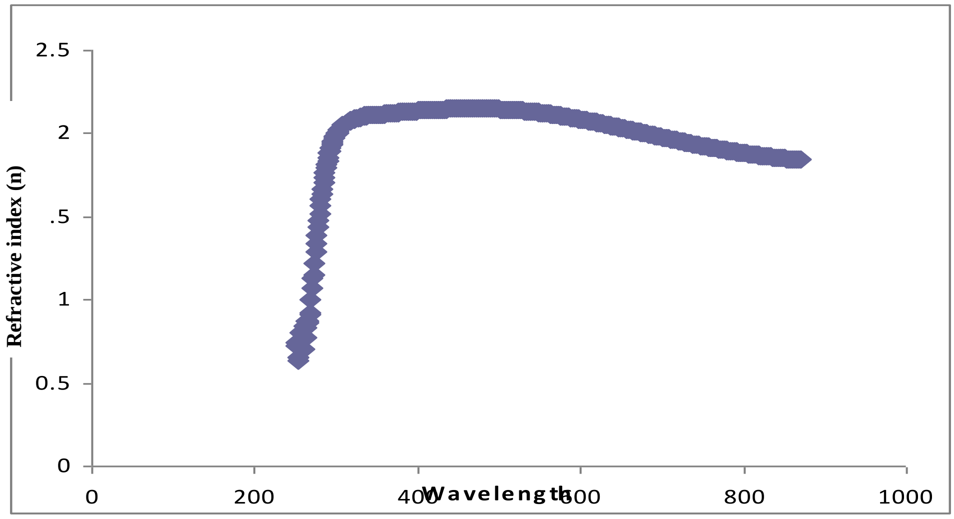

Figure (7): The refractive index (n) for ZnO thin films at room temperature

Figure (8) showed the variation of extinction coefficient as a function of wave length for ZnO Thin films. It is observed from this figure that the extinction coefficient almost constant at visible range. Also, it is observed from this figure that the extinction coefficient at wavelength 200 nm decreases with the wavelength, opposite to the variation of the refractive index, and this is due to the reason mentioned before. But the less values of extinction coefficient at 200 nm are due to the improve of the structure. Figures (9, 10) showed the variation of real ($\in_r$) and imaginary ($\in_i$) dielectric constants for ZnO thin films. One can observed that the variation of ε_r is similar trend to that of the refractive index because of the smaller value of k^2 in comparison with n^2, while the variation of ε_i mainly depends on the *k* value, which are related to the variation of absorption coefficient. ε_i represent the absorption of radiation by free carriers. It is observed from the figures that the real and imaginary dielectric constants increase with the increase of the wavelength of the incident radiation and this behavior is due to the change of reflectance and absorbance.

Conclusions

In this work we have reported the optical characteristic of ZnO thin films prepared by PLD. The optical absorption measurement shows that the ZnO film has a flat surface, a high average absorption over 80 % in (200-250) nm region and a direct band gap of 3.8 eV. The optical constants absorption coefficient, extinction coefficient and optical dielectric constant, of these films were determined using transmittance and refraction spectra.

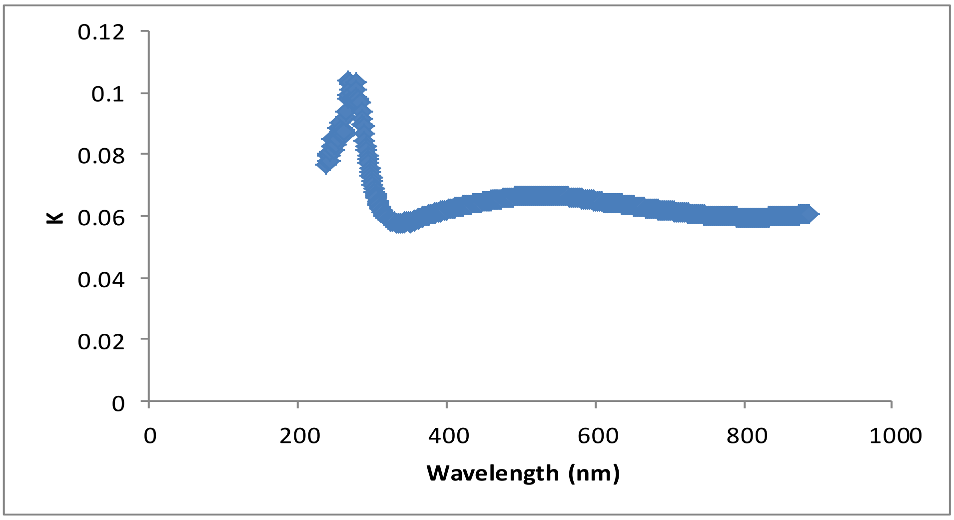

Figure (8): The extinction coefficient for ZnO thin films at room temperature

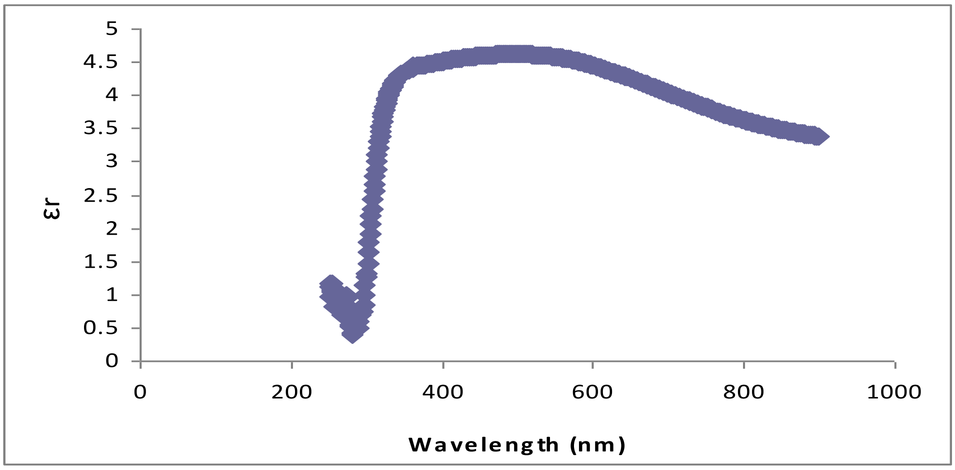

Figure (9): Real dielectric constant ε_r for ZnO thin films.

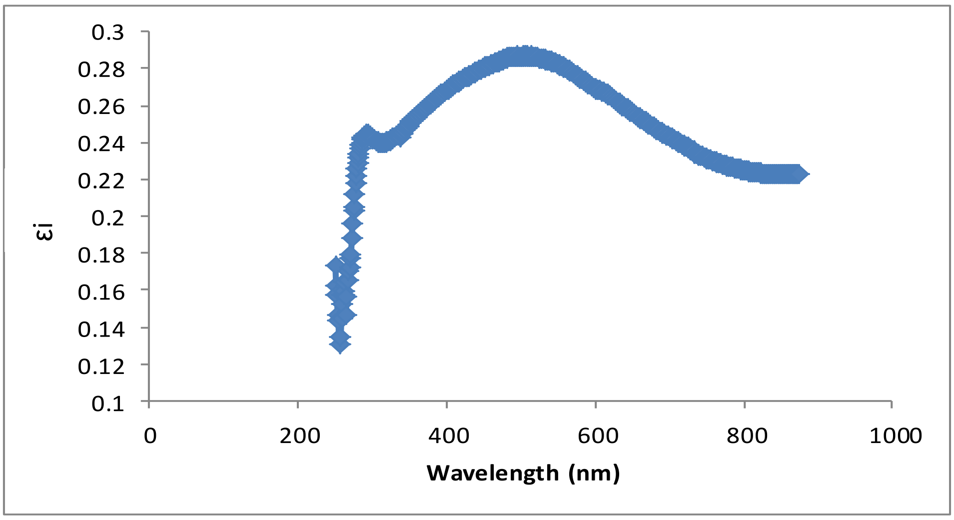

Figure (10): Imaginary dielectric constant ε_i for ZnO thin films

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