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Investigation in Optical Properties of Magnesium Doped Nanostructure Zinc Oxide Films by Pulsed-Laser Deposition Method

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Abstract
In the present work, films have been grown under various deposition conditions in order to understand the effect of processing on the film properties and to specify the optimum condition, namely substrate at temperatures of 400°C, oxygen pressure (2×10^{-1}) mbar, laser fluence 0.4 J/cm^2, and with different Mg contents (x=0, 0.02, 0.04, 0.06), using double frequency Q-switching Nd:YAG laser beam (wavelength 532nm), repetition rate (1-6) Hz and the pulse duration of (10 ns), to deposit $Mg_xZn_{1-x}O$ films glass substrates with thickness of about 200 nm for all $Mg_xZn_{1-x}O$ films at different deposition condition and the number of laser pulses was 100 pulses. The optical properties were characterized by the transmittance and absorption spectroscopy at room temperature, measured in the range from 300 to 900 nm. For all the films, the average transmittance in the visible wavelength region λ = (400 - 800) nm is greater than 70%. The maximum value of the transmittance (greater than 95%) was obtained for these films. E_g values of $Mg_xZn_{1-x}O$ thin films were (3.37, 3.59, 3.82, and 4.00) eV corresponding to the Mg-content (x = 0, 0.02, 0.04 and 0.06), respectively. In other word, the optical band gap of $Mg_xZn_{1-x}O$ thin films become wider as Mg-content increases and can be precisely controlled between 3.37 and 4.00 eV. The refractive index of the films ranged from 2.1-2.8 between 350nm to 900nm. The extinction coefficient and the optical conductivity of the films increases with doped. The real dielectric constant and the imaginary part increases when the doped rate increasing.
Keywords: Optical properties, Pulsed-laser deposition, $Mg_xZn_{1-x}O$ Nanostructures.

1. Introduction

Zinc Oxide (ZnO) is one of the most promising materials from the view point of its exceptional optical and physical properties. Such unique properties of ZnO make it a good candidate for short wavelength photonic devices. Success of ZnO as a semiconductor also depends on the possibilities of band gap engineering [1]. ZnO has ability to make alloys with MgO and CdO. In particular, alloys made from MgO and ZnO give wide band gap semiconducting material with a highly tunable band gap which can be easily controlled over a wide range by making $Mg_xZn_{1-x}O$ alloy thin films [2-4]. Thus MgZnO alloys have been increasingly investigated due to UV luminescence ranging from 150-400 nm or alternatively wide band gaps from 3.3 eV to 7.8 eV. [5].

Nanomaterials, especially metal oxides have received a considerable attention over the last few years due to their distinguished performance and potential applications in various fields. Among them, ZnO exhibits the most diverse and abundant configurations of nanostructures [6-8]. ZnO is considered to be one of the best metal oxides that can be used at a nanoscale level. ZnO itself has normally a hexagonal or wurtzite structure and it is well-known as an n-type II–VI semiconductor with a wide direct band-gap of about 3.37 eV and a large exciton binding energy of 60 meV [9]. They have many applications in solar cells, luminescent, electrical and acoustic devices, chemical sensors, catalysis, electronics, gas sensor devices, optoelectronics, transducers and biomedical devises [10,11]. Numerous applications have made the ZnO as wonder material for material scientists and the quantity of ZnO used in different application is also increasing. Hence, its production is ever increasing and a suitable method for preparing ZnO possessing less operating cost, working at ambient temperature, less time with narrow size range and better properties is a challenge for scientists [12]. In the present study, we have investigated the structural and optical properties of $Mg_xZn_{1-x}O$ thin films with different Mg concentrations prepared by pulsed laser deposition technique, as this enables the growth of good quality films. The employed methodology is supposed to cause different structural properties, different surface morphology of the obtained nanostructures in addition to different optical properties.

2. Experimental

$Mg_xZn_{1-x}O$ thin films were synthesized by pulsed laser deposition system using a second harmonic Nd:YAG laser. Thin films were grown in a vacuum chamber with background pressure of (2×10^{-1}) mbar. The Nd:YAG laser was operated at λ=533 nm with the repetition rate of (10Hz) and pulse duration of 7ns. The target to substrate distance was (3cm). Mg-ZnO composite targets with $Mg_xZn_{1-x}O$ for (x=0, 0.02, 0.04, 0.06), were used

during the deposition. The composite targets were obtained by the standard pressing and sintering method. Mg and ZnO powders were first weighted and mixed with corresponding concentrations in methanol by magnetic blender for 1 hour. After the liquid was evaporated, the mixed powder was blended mechanically again so that the mixture is uniformly distributed. The mixture was then calcined at 100 °C in flowing oxygen for 6 hours. The resultant powder was ground again and then pressed into round pellets with two-inch diameter. The targets were finally obtained after the pellets were sintered in oxygen at 200 °C for 12 hours. Glass (thickness of 1 mm) was used as substrates for growing these $Mg_xZn_{1-x}O$ thin films. Before loaded into the vacuum chamber, substrates were cleaned with standard chemical method, first with acetone followed by methanol for 10 min in ultrasonic bath. Thin films were grown in oxygen environment with O_2 partial pressure of (10^{-1} mbar) at substrate temperature of 400 °C. Laser energy density focused on the target was about (0.4) J/cm^2. The deposition time was typically 10 min. After the deposition, thin films were cooled down to room temperature.
The optical transmittance of $Mg_xZn_{1-x}O$ thin films with different doping concentrations (x = 0, 0.02, 0.04, 0.06) on glass substrates with different deposition condition, was measured using UV-Vis spectrophotometer (SHIMADZU UV-1650 PC) from 300 nm to 900 nm. The optical properties were calculated from these optical measurements.

3. Results and Discussion

3.1 Optical Properties

The optical properties of the pure $Mg_xZn_{1-x}O$ films deposited by pulsed laser deposition technique are measured by UV-VIS spectrophotometer on glass substrate at 400 °C temperature in the range from 300nm to 900nm. The laser fluence energy density is 0.4 J/cm^2, the pressure of oxygen was maintained at 2×10^{-1} mbar at various Mg-content (x = 0, 0.02, 0.04 and 0.06) with film average thickness equals 200 nm. The absorbance and transmittance of the prepared films were then measured. Also the optical energy gap and optical constants were determined.

3.1.1 Transmittance (T)

Figure 1 shows the UV-Visible transmittance spectra of $Mg_xZn_{1-x}O$ thin films deposited on glass substrate with different Mg-contents. The transmittance spectra of the films can be analyzed as follows:

1. For all films, the average transmittance in the visible region (λ: 400-800 nm) is greater than 80%. The maximum value of the transmittance, which was greater than 95 %, was at Mg content level of 0.06.
2. There is an obvious shift in the absorption edge towards shorter wavelength with increasing Mg-content. This observed shift towards the blue region clearly reflects the incorporation of Mg in the ZnO lattice, indicating that the optical band gap was enlarged by Mg doping regardless of crystallinity which is in agreement with the reported literature data [13].
3. The transmittance of the $Mg_xZn_{1-x}O$ thin films increased with increasing Mg-content. The increase in the observed transmittance of the prepared films was accompanied by a decrease the grain size which is consistent with the published data in [14].

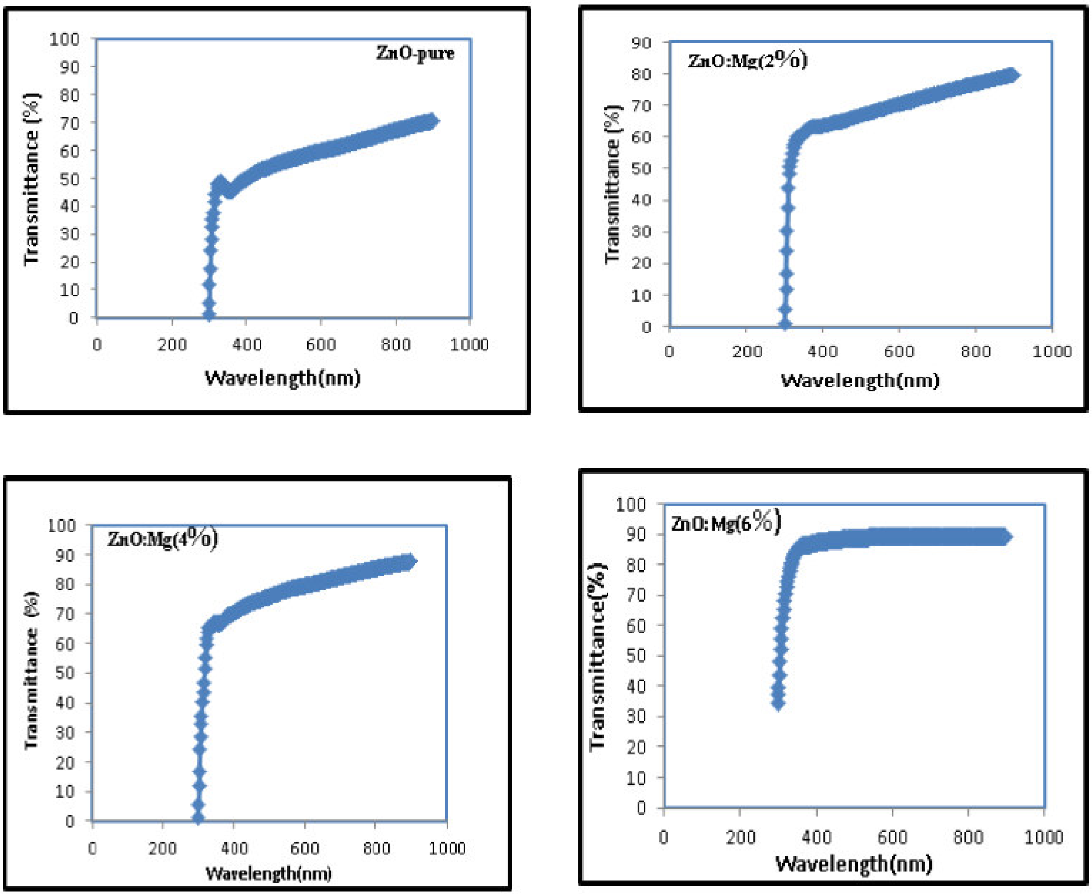

Figure 1: The optical transmission of ZnO thin films with various Mg-content (x= 0, 0.02, 0.04 and 0.06)

3.1.2 Optical Absorption (A)

The absorbance spectra of the $Mg_xZn_{1-x}O$ thin films deposited on glass substrate at a growth temperature 400 °C, measured at room temperature are shown in Figure 2. The spectra, in the high energy spectral range where the film is strongly absorbent, clearly indicated that the absorbance of $Mg_xZn_{1-x}O$ films decreased as a function of increasing Mg-content [15].

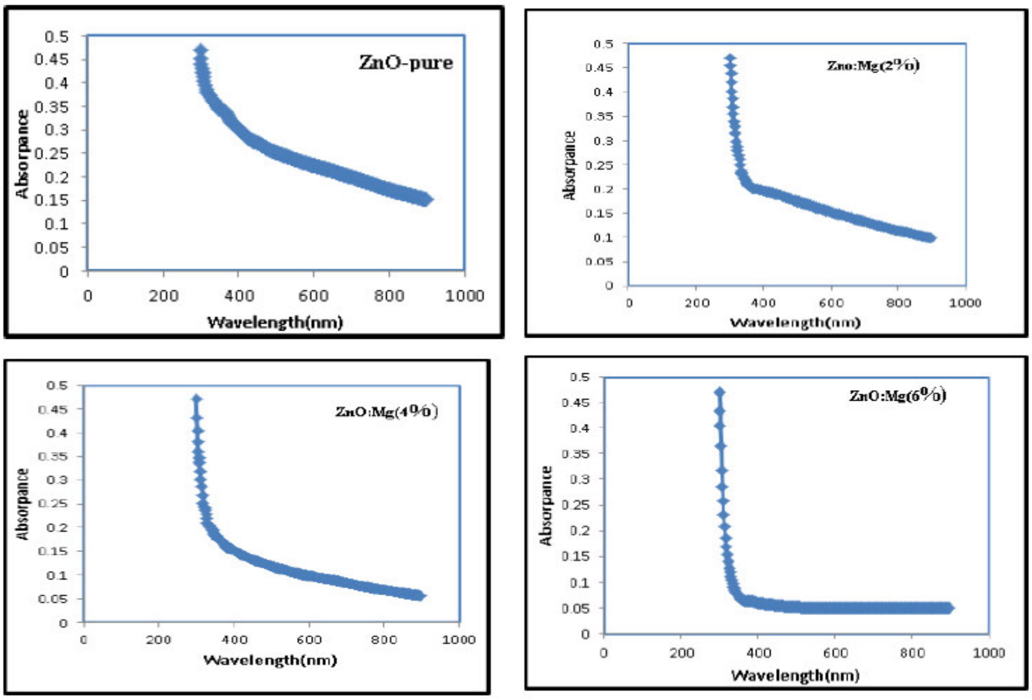

Figure 2: The optical absorption of ZnO thin films with various Mg-content (x=0, 0.02, 0.04 and 0.06)

3.1.3 Optical Absorption Coefficient (α)

Figure 3 shows the absorption coefficient (α) of the $Mg_xZn_{1-x}O$ thin films with different Mg-contents as determined from absorbance measurements. The absorption coefficient of $Mg_xZn_{1-x}O$ thin films decreased sharply in the UV/VIS boundary, and then decreased gradually in the visible region because it is inversely proportional to the transmittance. It is noticed that the absorption coefficient decreased as a function of increasing Mg-concentration, its value is larger than (10^4 cm^{-1}). This could be attributed to the decrease in the grain size in addition to the light scattering effect for its low surface roughness [16].

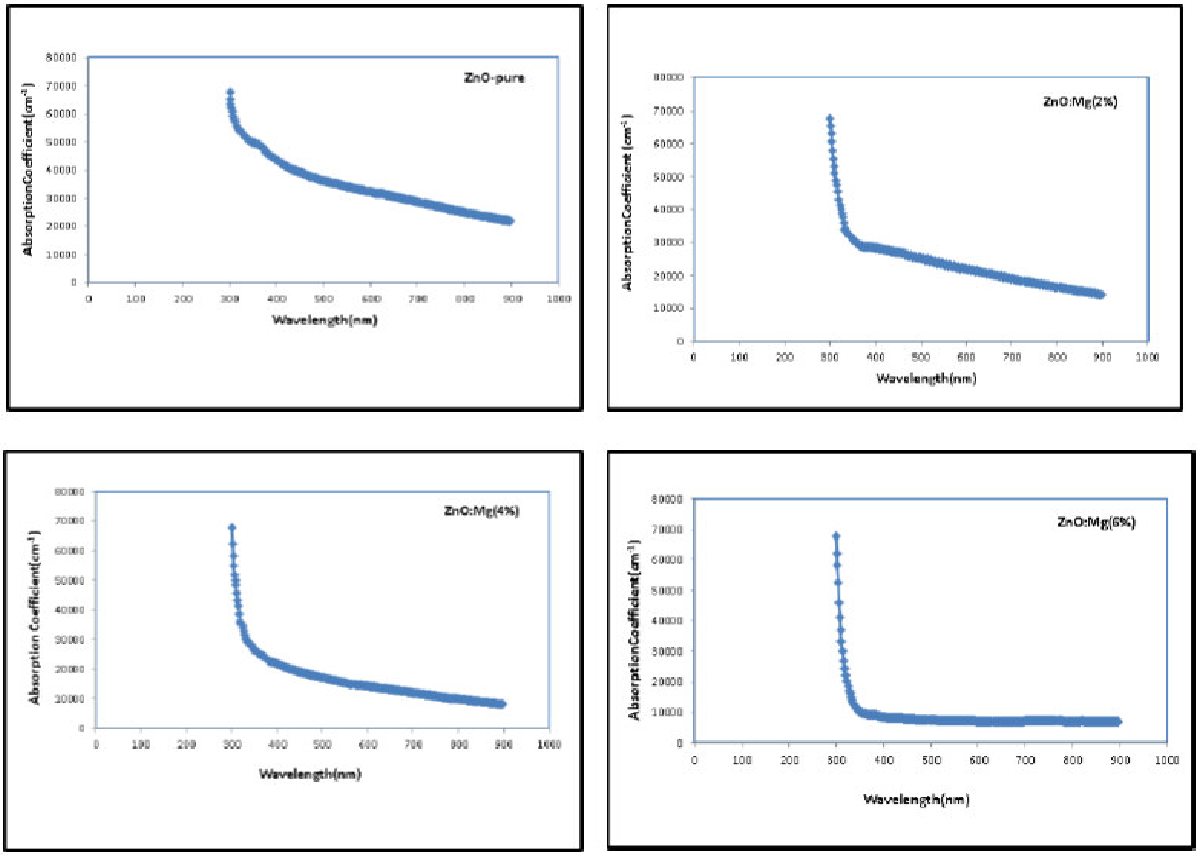

Figure 3: Absorption coefficient as a function of wavelength of $Mg_xZn_{1-x}O$ thin films at different Mg-content

3.1.4 Optical Energy Gap (E_g)

The optical band gap (E_g) of the $Mg_xZn_{1-x}O$ thin films was evaluated from the transmission (or absorption) spectra and the optical absorption coefficient (α) near the absorption edge for allowed direct transitions. The characteristics of $(\alpha h\nu)^2$ vs. $h\nu$ (photon energy) were plotted for evaluating the band gap (E_g) of the $Mg_xZn_{1-x}O$ thin films, and extrapolating the linear portion near the onset of absorption edge to the energy axis as shown in Fig. (4).

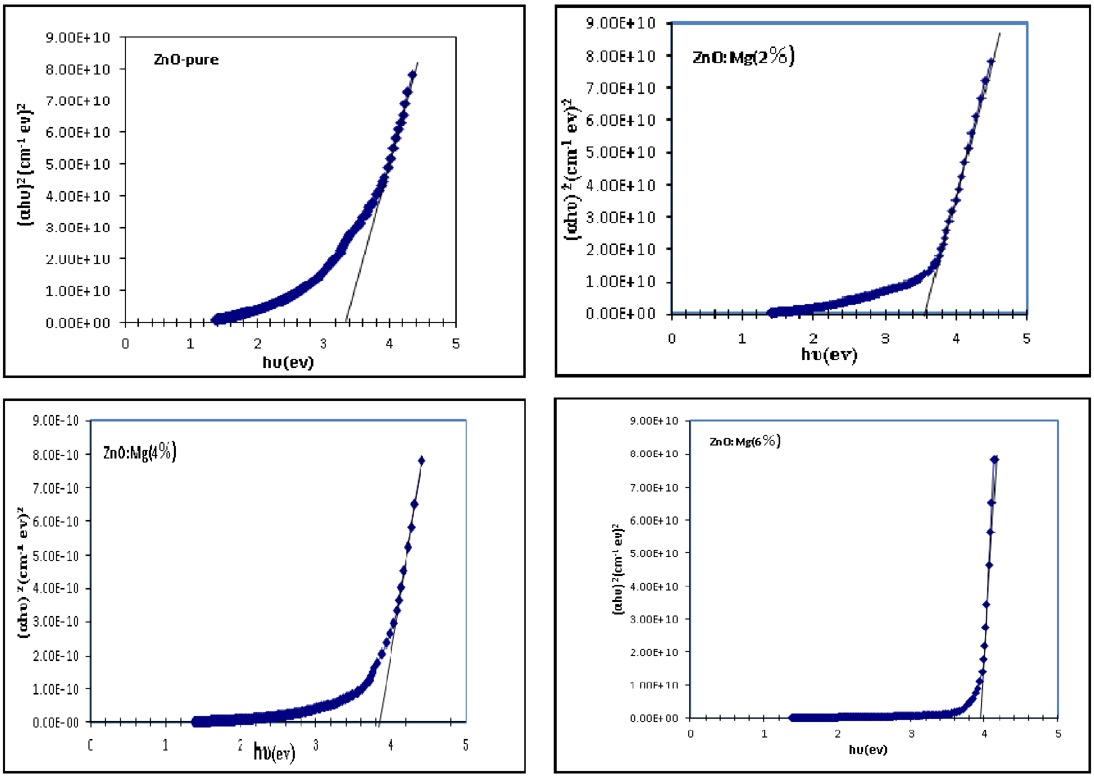

Figure 4: Variation of $(\alpha h\nu)^2$ vs. photon energy $(h\nu)$ for ZnO:Mg thin film.

As can be seen clearly, E_g values of $Mg_xZn_{1-x}O$ thin films are (3.37, 3.59, 3.82 and 4.00) corresponding to the Mg-concentrations (x = 0, 0.02, 0.04 and 0.06) respectively (Table 1). In other word, the optical band gap of $Mg_xZn_{1-x}O$ thin films became wider upon increasing Mg-content and can be precisely controlled between 3.37 and 4.00 eV, which is consistent with the reports [17-22].

Table 1. The values of optical energy gap for $Mg_xZn_{1-x}O$ thin film.

Mg-content	E_g (eV) at T=400°C, E=400mJ
ZnO	3.37
$Mg_{0.02}Zn_{0.98}O$	3.59
$Mg_{0.04}Zn_{0.96}O$	3.82
$Mg_{0.06}Zn_{0.94}O$	4.00

3.1.5Reflectance (R)

Figure 5 shows the reflectance spectra of $Mg_xZn_{1-x}O$ thin films measured at room temperature. The reflectance of $Mg_xZn_{1-x}O$ films decreased with the increase of Mg-concentration in the films and especially at concentration increasing of doping (x=0.06).

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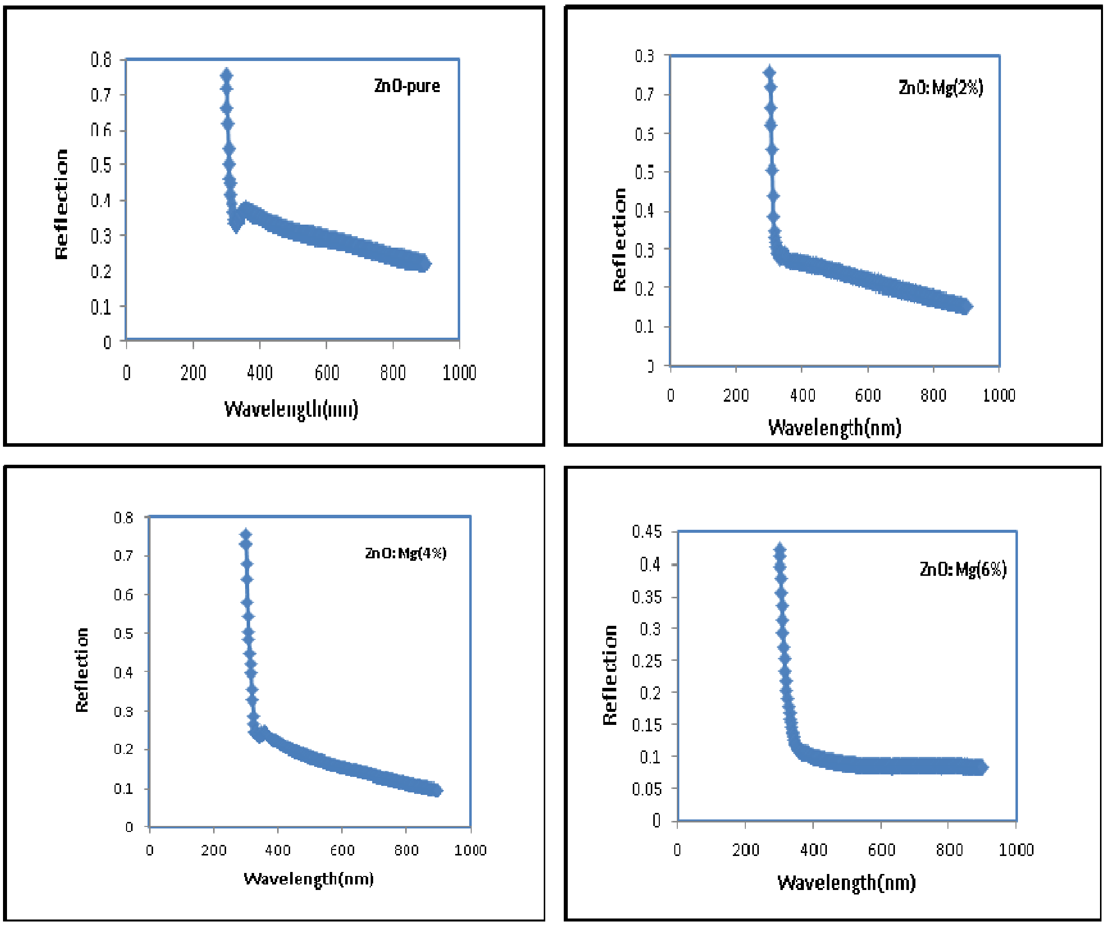

Figure 5: The optical Reflectance of ZnO thin films with various Mg-content (x=0, 0.02, 0.04 and 0.06)

3.1.6 Refractive Index (n)

The refractive indices (n) of the $Mg_xZn_{1-x}O$ thin films, as shown in Figure 6, were also found to be influenced by Mg-content. The refractive indices decreased as a function of increasing Mg-content in the range of (1.5 - 2.6), respectively. The results showed that the decrease in grain size was generally accompanied by a decrease in the measured refractive index of the studied films. The decrease in both, the refractive and absorption indices could be attributed to the improvement of stoichiometry [14], the decrease in grain size and the increase in micro strain, which is consistent with the data reported previously in the literature [23, 24].

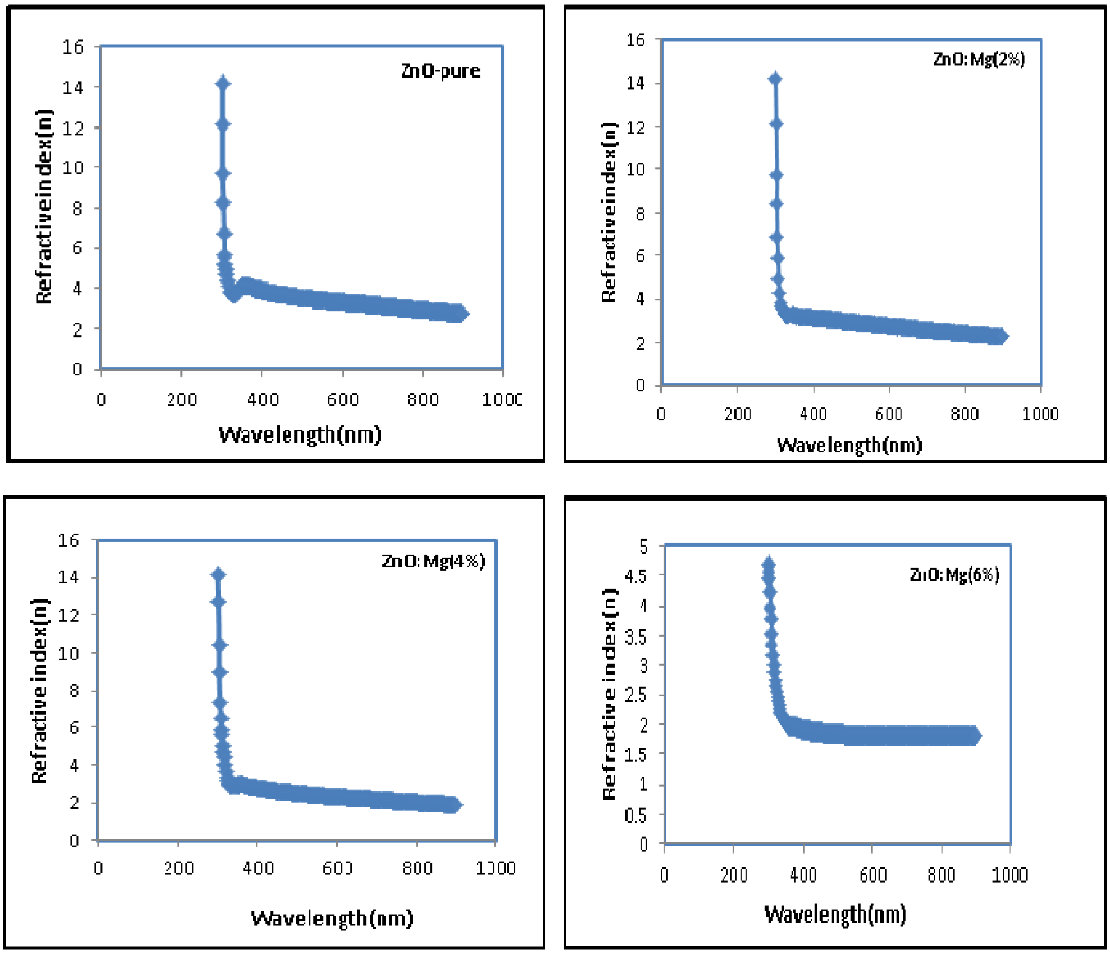

Figure 6: Refractive index as a function of wavelength for $Mg_xZn_{1-x}O$ thin films at different Mg-content

3.1.7 Extinction Coefficient (K_o)

Figure 7 shows the extinction coefficient (K_0) as a function of wavelength for different Mg-content. Generally, the extinction coefficients of the prepared films decreased with increasing concentration of Mg. the same trend was observed upon increasing wavelength. Both results were in total agreement with those reported previously [4, 24].

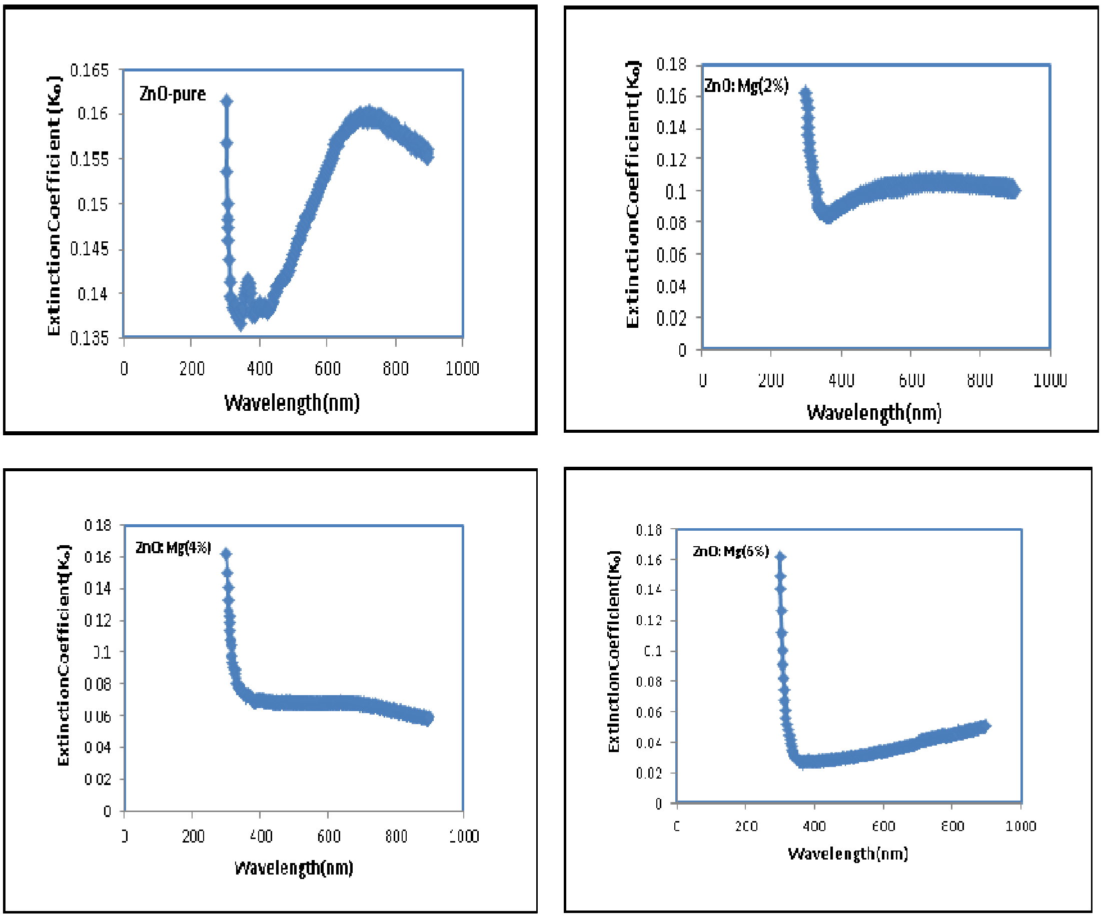

Figure 7: Extinction coefficient as a function of wavelength for $Mg_xZn_{1-x}O$ thin films at different Mg-content.

3.1.8 Real and Imaginary Part of Dielectric Constant (ε_r), (ε_i)

An absorbing medium is characterized by a complex dielectric constant. The real and imaginary part of dielectric constant of the $Mg_xZn_{1-x}O$ thin films deposited on glass substrate by Pulse laser deposition technique are shown in Figures 8 and 9. The variation of (ε_r), (ε_i) with wavelength for percentage of both types of pure ZnO and ZnO:Mg films. The current results indicated that for $Mg_xZn_{1-x}O$ thin films, the values of the real and imaginary part of dielectric constants decreased as a function of increasing wavelength, especially it decreased with rate of increasing concentration doping (x=0.06).

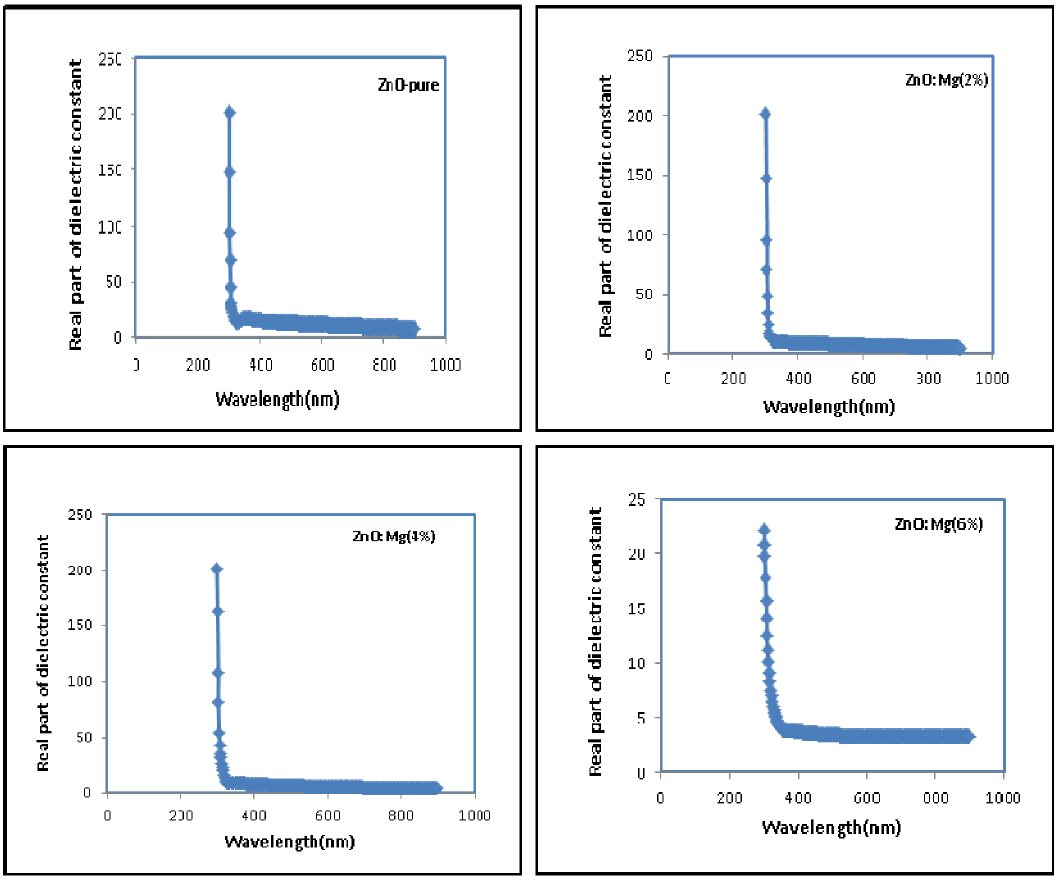

Figure 8: Real part of dielectric constant of the $Mg_xZn_{1-x}O$ thin films.

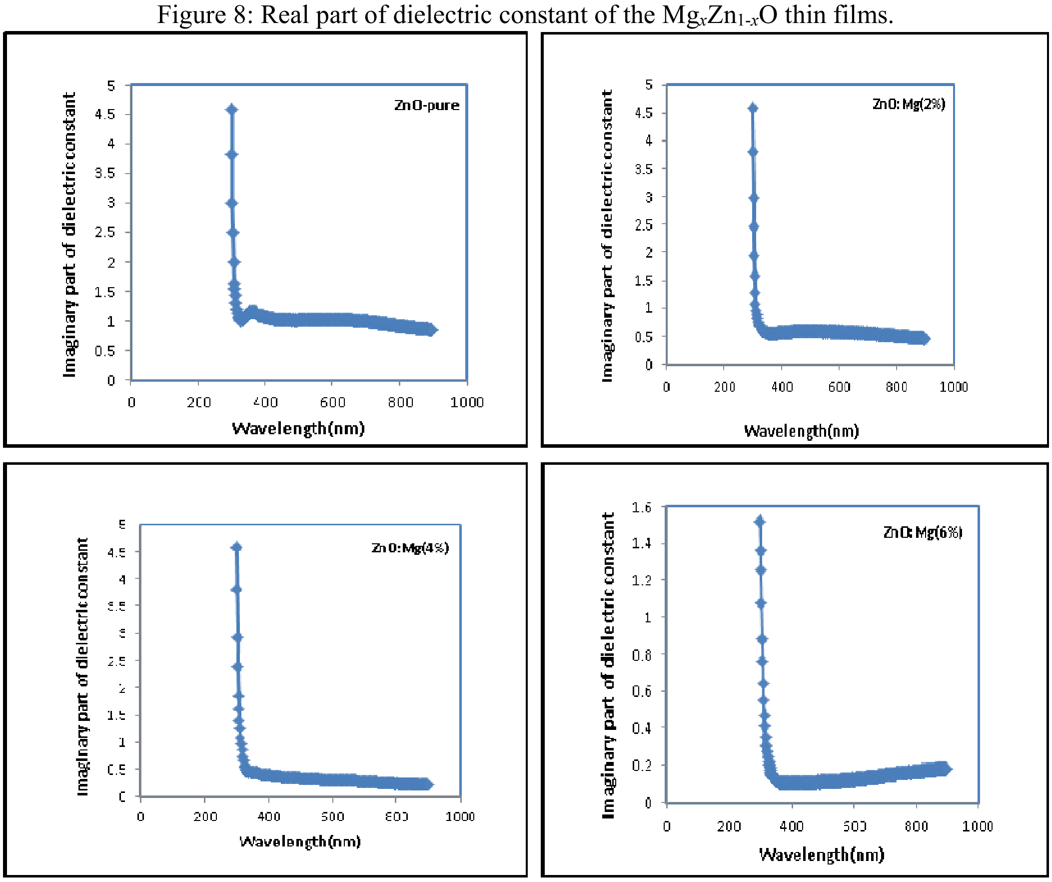

Figure 9: Imaginary part of dielectric constant of the $Mg_xZn_{1-x}O$ thin films.

3.1.9 Optical Conductivity (σ)

The variation of optical conductivity as a function of wavelength, measured for the different Mg-content of the $Mg_xZn_{1-x}O$ thin films are shown in Figure 10. The results indicated that the optical conductivity of the prepared films increased with increasing photon energy. This suggests that the increase in optical conductivity is due to electron exited by photon energy, and the optical conductivity of the films increases with increasing Mg-content in the films.

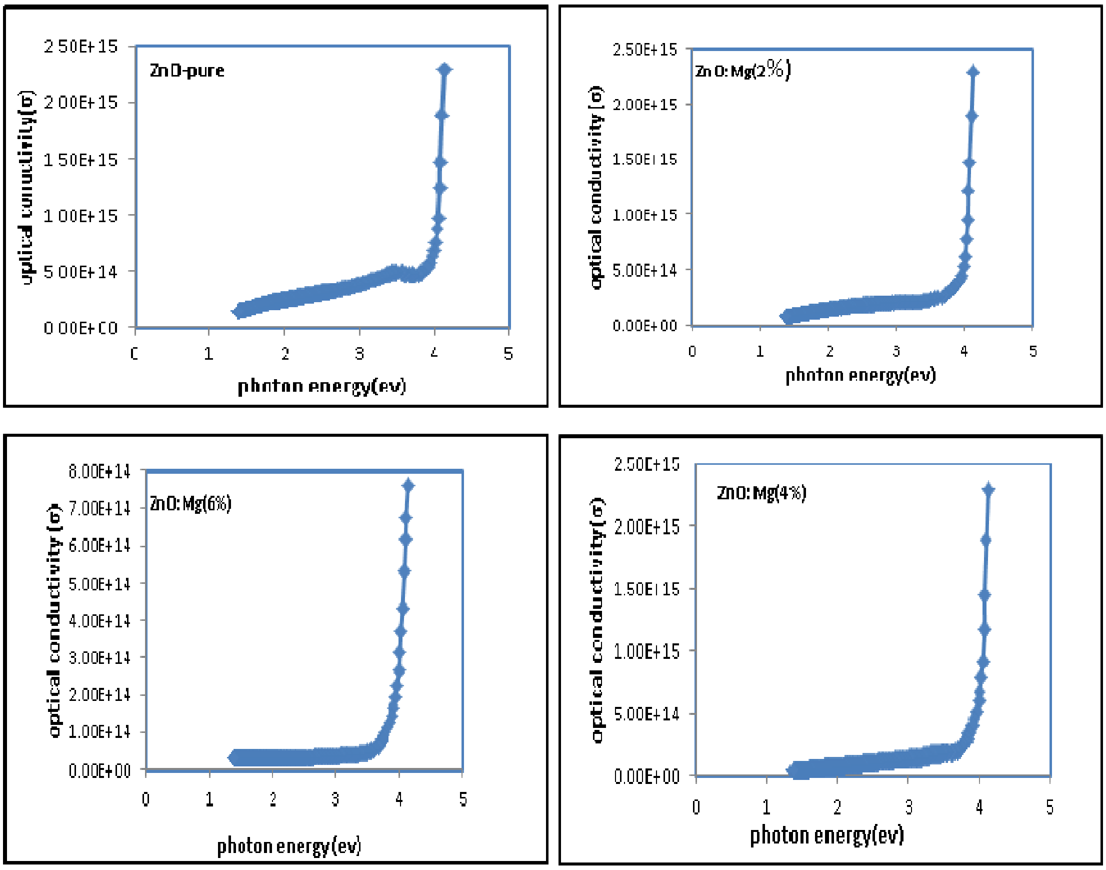

Figure 10: Optical conductivity as a function of photon energy for $Mg_xZn_{1-x}O$ thin films.

4. Conclusions

The current investigation describes the preparation of nanostructure zinc oxide thin films on glass substrate by pulsed laser deposition techniques. The effect of doping on the optical properties of $Mg_xZn_{1-x}O$ thin films were then studied by UV-VIS measurements. The variation of doped has a great influence on the optical properties.

- The increase of dopant concentration into the target caused an increase in the the toughness of the deposited films.
- The optical properties of $Mg_xZn_{1-x}O$ thin films revealed that the films have allowed direct transition, with an average transmittance over 90% for all films and in the wavelength range extending from 300 to 900 nm. The transmittance in the UV region increases with the increase of films doped. The optical band gap is dependent on the films doped, increasing in the doping percentage for Mg caused an increase in the optical band gap value and an increase in the optical constants (ke, n, ε_r and ε_i). Moreover, refractive index (n) values of $Mg_xZn_{1-x}O$ films had values in the range (1.5 - 2.6) and indicating the possible use of these films as anti-reflection coating materials. These films are also suitable for solar cell applications.
- The films deposited from pure ZnO and 6 wt % Mg doped ZnO targets at oxygen pressure of (2×10^{-1}) mbar, 400°C substrate temperature and laser fluency 400 mJ are good candidates for structural, morphology and optical properties.

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