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# Optical and Structural Properties of Mg Doped ZnO Thin Films

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## Abstract

Thin films of ZnO and Mg doped ZnO were prepared by chemical spray pyrolysis. . The optical energy gap was increased from (3.27-3.54) eV as the Mg content increases, while all the optical parameters show a reverse behavior, that n, k, $\varepsilon_1$, $\varepsilon_2$ and σ decrease as the Mg content increases. These films were characterized through the use of XRD technique. The results are found to be corresponding to polycrystalline and show a wurtzite hexagonal crystal structure, with a preferred orientation along the ZnO (002) plane.

**Keywords:** chemical spray pyrolysis, optical constants , ZnO Thin film, Mg doping

## الخصائص البصرية والتركيبية لاغشية اوكسيد الخارصين الرقيقة المشوبة بالمغنيسيوم

**سرور ابراهيم صالح**
هيئة المعاهد الفنية / المعهد الطبي التقني- اربيل / قسم الاشعة

## الخلاصة

باستخدام تقنية الترسيب الكيمياوي استطعنا تحضير اغشية رقيقة لكل من اوكسيد الخارصين و اوكسيد الخارصين المشوب بالمغنيسيوم. ازدادت فجوة الطاقة البصرية بازدياد محتوى المغنبسيوم من ( 3.27 – 3.54 ) eV, بينماابدت بقية الثوابت البصرية سلوك عكسي, اي ان كل من معامل الانكسار, معامل الخمور, ثابت العزل بجزئيه الحقيقي و الخيالي و التوصيلية البصرية جميعها قلت بزيادة محتوى المغنيسيوم. كشفت نتائج حيود الاشعة السينية على ان الاغشية المحضرة ذات طبيعة متعدد التبلور ومن النوع السداس المتراص و بالاتجاه السائد لاوكسيد الخارصين لمستوي (002)

**الكلمات المفتاحية**: التحلل الكيميائي الحراري ، الثوابت البصرية ، الاغشية الرقيقة ،اغشية اوكسيد الخارصين الرقيقة ، التشويب بالمغنيسيوم .

## Introduction

ZnO has attracted considerable attention due to its unique properties such as, high conductivity, chemical stability, wide and direct gap, exciton binding energy up to 60 meV, non toxic, high material availability, ease in doping, high transmittance, high refractive index [1-3]. ZnO is a promising material for several technological applications like gas sensors [4], varsitors [5], dilute magnetic semiconductors [6], solar cells [7], short wavelength light emitting device [8], and field emission device [9]. Several deposition techniques are used to grow ZnO thin films. These include sol-gel method [10], reactive Co-sputtering [11], pulse laser deposition [12], chemical dipping technique [13], atomic layer deposition [14] and chemical spray pyrolysis [15]. In this work, the preparation of undoped and Mg-doped ZnO deposited on a glass substrate by chemical paralysis was reported. The structural and optical properties of these films were studied.

## Experimental work

ZnO and Mg doped ZnO thin films were obtained by spray pyrolysis technique in air atmosphere. Homogenous solution was prepared by dissolving zinc chloride (0.1 M) and Mg $(CH_3COO)_2\ 2H_2O$ (0.1 M) in redistilled water individually at room temperature. The glass substrates were cleaned with ethanol, rinsed in distilled water, and subsequently dried before deposition. Deposition was done using an automated spray machine in which the spray rate was 5ml/min, deposition time 10 sec lasted by 2 min to avoid excessive cooling. The substrate temperature was adjusted to be 450ºC during deposition. The atomic ratio of Mg in the spray solution was varied from x = 0 to 4%. The grown films had good adhesion to the substrate surfaces.

The thickness of the films was measured by gravimetric method and was around 0.3µm. The XRD data of the films were taken using Shimadzu x-ray diffractometer system (XRD-6000) with CuKα radiation $\lambda = 1.5418$ Á over the range $2\theta = 20\text{-}50^0$ at room temperature (Ministry of science and technology –Baghdad). The absorption and transmission spectra were measured using UV/VIS double beam spectrophotometer (Shimadzu UV-1600) in the wavelength range (300-900nm).

## Results and Discussion

The XRD patterns of $Zn_{1-x}Mg_xO$ with different Mg content are shown in figures (1, 2, and 3). XRD analysis reveals that the films show highly intensives (002) diffraction peak, which corresponds to the hexagonal wurtzite ZnO structure without any impurity phase. We observed that (101) peaks become more intense as the Mg content increases, no peak originating from MgO was detected at least to the X-ray diffraction detection limit.

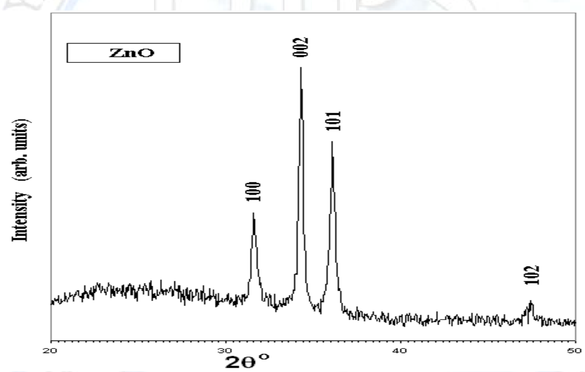


**Figure (1): XRD pattern for undoped ZnO**

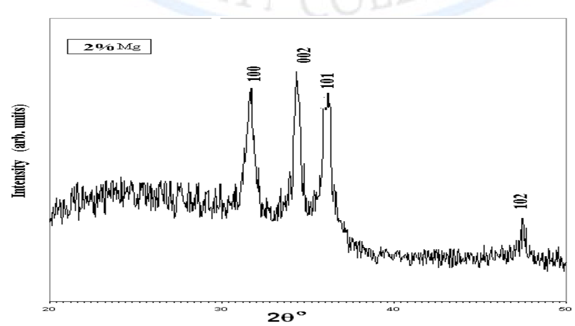


**Figure (2): XRD pattern for ZnO: 2% Mg.**

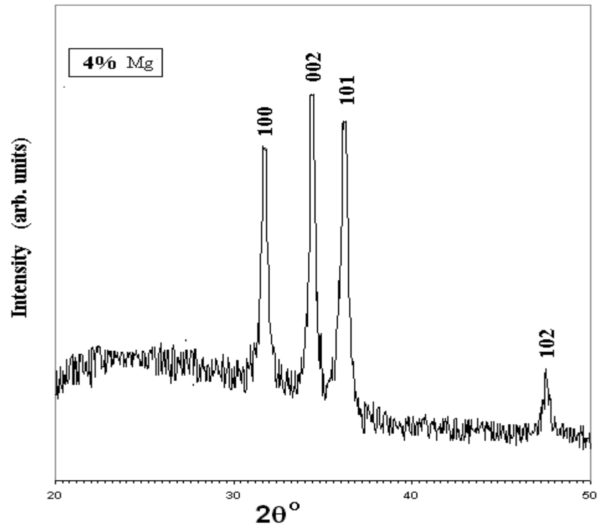


**Figure (3): XRD pattern for ZnO: 4% Mg.**

This result clearly indicates that $Mg^{+2}$ can be incorporated into the ZnO lattice by chemical spray pyrolysis. Also we observe that the full width at half maximum decreases as the Mg content increases which means , that the average grain size increases with Mg content.

Figure (4) shows transmission as a function of wavelength (λ) for undoped and Mg doped ZnO, where the optical absorption edge shifts to lower wavelength side with increasing Mg content, indicating that the optical band gap increases by Mg doping.

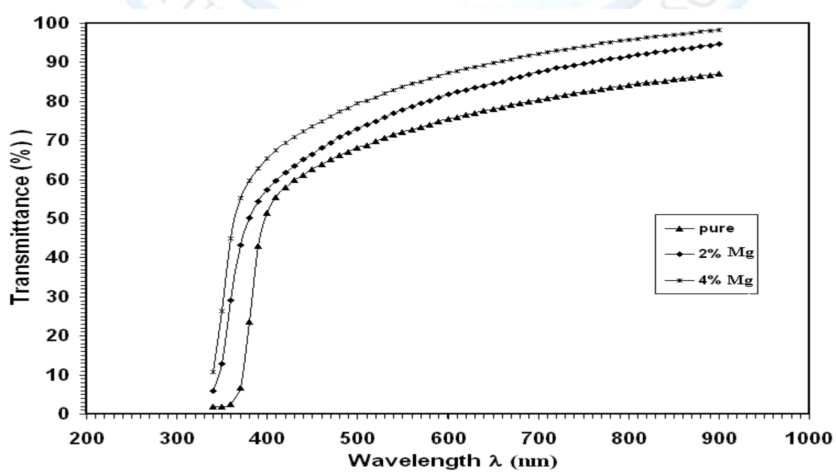


**Figure (4): Transmission as a function of wavelength (λ) for ZnO and ZnO: Mg**

The direct band gap of the films was estimated by utilizing the relation introduce by Tauc [16].

$\alpha h\nu = A\,(h\nu - Eg)^{1/2}$---------------------- (1)

Where $\alpha$ is the absorption coefficient, $h\nu$ the photon energy, Eg the optical energy gap. Figures (5), (6), and (7) show the variation of $(\alpha h\nu)^2$ as a function of photon energy, and from these figures ,by extrapolating the linear parts of the absorption edge one can find the intercept with $h\nu$ axis.

The value of Eg was found to increase from 3.27 eV to 3.54 eV with corresponding increase in Mg content. This increase could be attributed to the higher band gap energy of MgO [17].

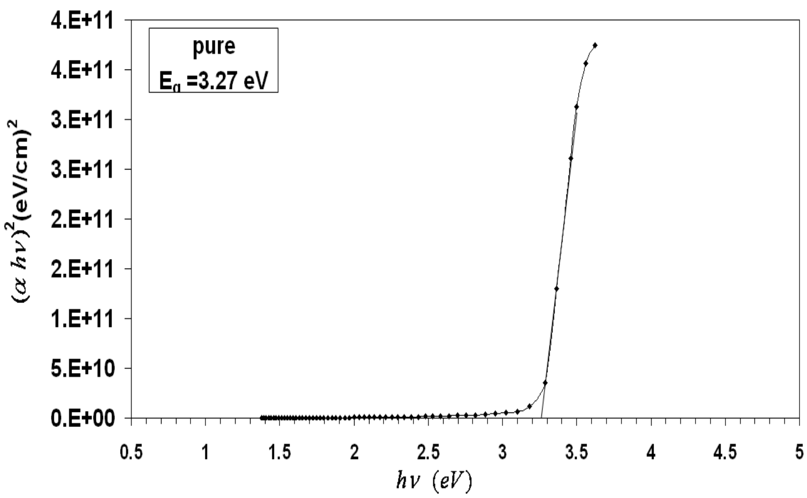


**Figure (5): Direct transition as a function of photon energy for undoped ZnO**

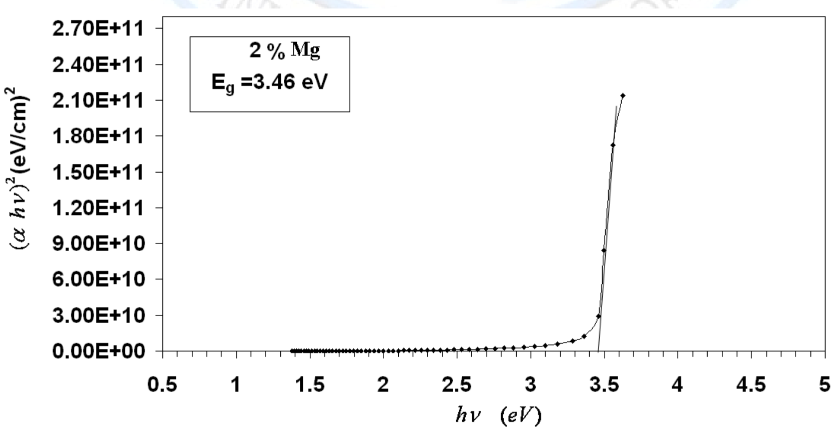


**Figure (6): Direct transition as a function of photon energy for ZnO: Mg**

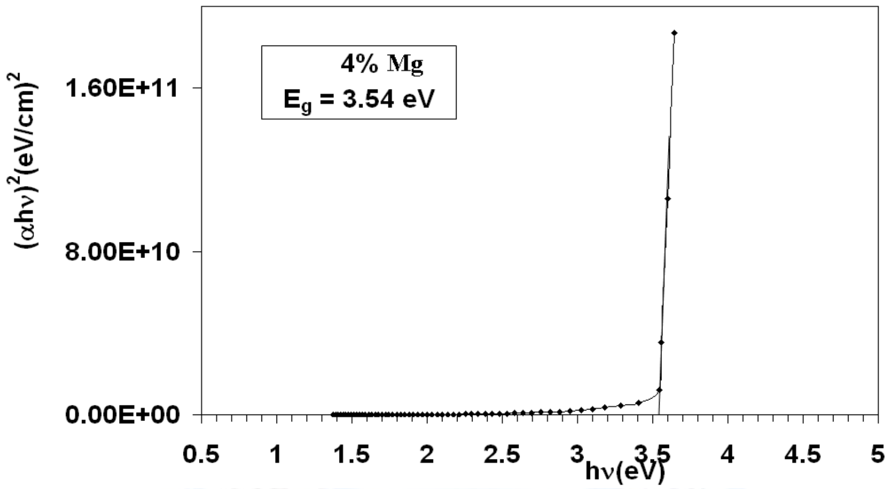


**Figure (7): Direct transition as a function of photon energy for ZnO: Mg**

The refractive index (n) is an important parameter for optical materials, thus it is important to determine optical constants of the films using the following relation [18].

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - K^2} \quad \text{-------------- (2)}$$

Where R is the reflectance which can be determined from the equation (R=1-T-A), k is extinction coefficient given by the equation ($k = \frac{\alpha\lambda}{4\pi}$) where $\alpha$ represents the absorption coefficient and $\lambda$ is the wavelength of the incident X-ray, (n) and k values dependence of the wavelength are shown in figures (8) and (9) respectively.

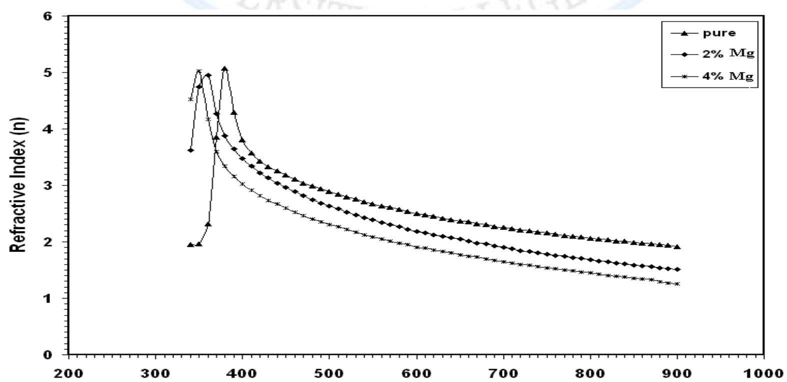


**Figure (8): Refractive index as a function of wavelength for ZnO and ZnO: Mg**

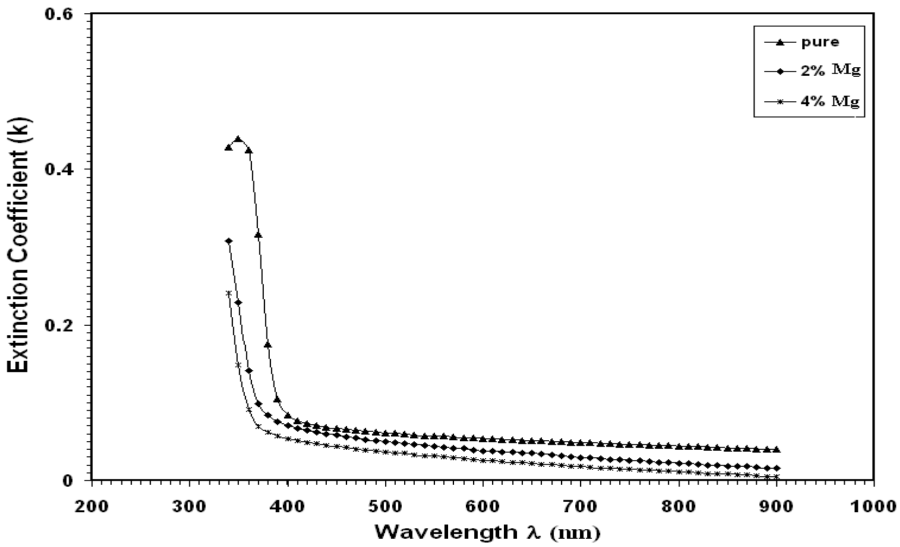


**Figure (9): Extinction coefficient as a function of wavelength for ZnO and ZnO: Mg**

As seen from the figures, the (n) and K value decreases with increasing the Mg content. The decrease of refractive index could be attributed to the decrease of the optical absorption as the Mg content increases. The complex dielectric constant $\varepsilon$ of semiconductor materials is defined as [19].

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 \text{ ----------------------------------------- } (3)$$

Where $\varepsilon_1$ and $\varepsilon_2$ are the real and imaginary parts of the dielectric constant respectively, these parameters are related to the (n) and K values as:

$$\varepsilon_1 = n^2 - K^2 \text{ ---------------------------------- } (4)$$

$$\varepsilon_2 = 2nK \text{ ------------------------------------ } (5)$$

The calculated wavelength dependence of $\varepsilon_1$and $\varepsilon_2$ are shown in figures (10) and (11) respectively...

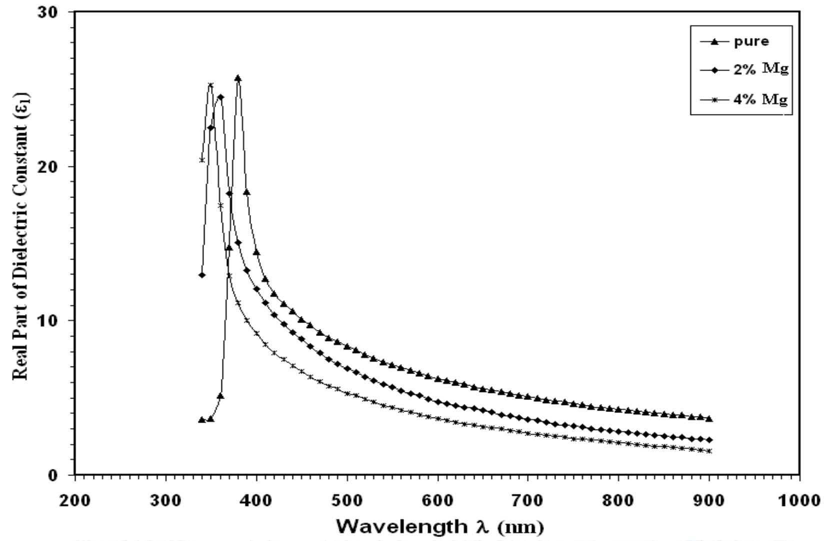


**Figure (10): Real part of dielectric constant as a function of wavelength for ZnO and ZnO: Mg**

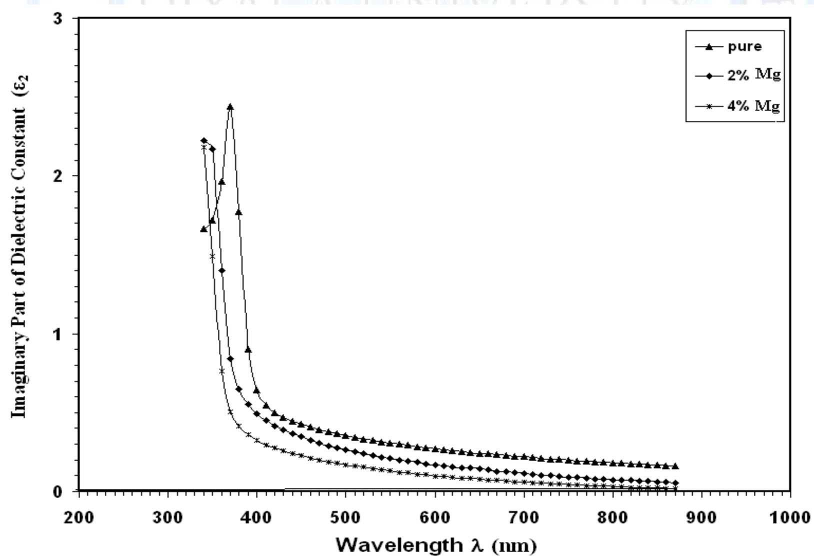


**Figure (11): Imaginary part of dielectric constant as a function of wavelength for ZnO and ZnO: Mg**

The real part $\varepsilon_1$ values are higher than the imaginary part $\varepsilon_2$ values. Both $\varepsilon_1$ and $\varepsilon_2$ are decreasing as the Mg content increased .

The optical conductivity (σ) was calculated from the relation [20].

$$\sigma = \frac{\alpha n c}{4\pi} \quad \text{------------------------------} \quad (6)$$

Where (c) is the velocity of light. Figure (12) shows the calculated wavelength dependence of optical conductivity on the wavelength. The increase in the optical conductivity at low wavelength is due to the low absorbance of ZnO thin films in that region, also the behavior of the graphs seems to be the same as all the studied parameters, that σ decreased as the Mg content increased.

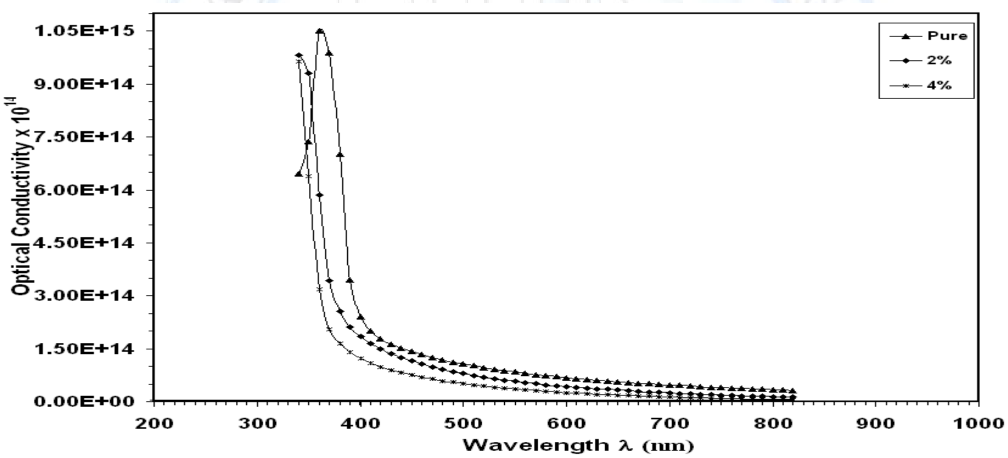


**Figure (12): Optical conductivity as a function of wavelength for ZnO and ZnO: Mg**

## Conclusions

Undoped and Mg doped ZnO was deposited by chemical spray pyrolysis technique. The value of direct band gap increased with increasing Mg content. The optical constants (refractive index, extinction coefficient, real and imaginary parts of dielectric constant and optical conductivity) were also calculated. Optical parameters values tend to decrease with increasing doping concentration.. The x-ray diffraction patterns indicate that all films are polycrystalline in nature.

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