Structural and optical properties of ZnO doped Mg thin films deposited by pulse laser deposition (PLD)

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Abstract

This paper reports the effect of Mg doping on structural and optical properties of ZnO prepared by pulse laser deposition (PLD). The films deposited on glass substrate using Nd:YAG laser (1064 nm) as the light source. The structure and optical properties were characterized by X-ray diffraction (XRD) and transmittance measurements. The films grown have a polycrystalline wurtzite structure and high transmission in the UV-Vis (300-900) nm. The optical energy gap of ZnO:Mg thin films could be controlled between (3.2eV and 3.9eV). The refractive index of ZnO:Mg thin films decreases with Mg doping. The extinction coefficient and the complex dielectric constant were also investigate.

Key words
Pulse laser deposition, zinc oxide, thin films.

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الخصائص التركيبية والبصرية لاغشية اكاسيد الزنك المطعم بالمغنيزيوم المرسبة بطريقة ترسيب الليزر النبضي

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الخلاصة

في هذا العمل درسنا تأثير التشويب المغنيزيوم على الخصائص التركيبة والبصرية لاغشية اوكسيد الزنك بطريقة التسريب باستخدام الليزر النبضي (PLD). رسبت اغشية اوكسيد الزنك على اساس من الزجاج باستخدام ليزر نيوديوم ياك (Nd:YAG) كمصدر ضوئي. تم فحص أغشيه اوكسيد الزنك بواسطة حيود الاشعه السينيه (XRD) و وجد ان تركيبها متعدد البلورات ذات تركيب سداسي. تم حساب فجوه الطاقه من طيف الامتصاص و وجد انها تزداد عند التشويب بالمغنيزيوم من (3.2 الى 3.9) الكترون فولط, كذلك وجد ان معامل الانكسار يتناقص عند التشويب.

Introduction

The ZnO has a wide direct band gap(~ 3.2 eV) semiconductor material [1]. The II-VI semiconductor Zinc Oxide (ZnO) has great potential for applications in short-wavelength optoelectronics, light-emitting diodes, lasers and detectors. It also has the potential to compete GaN, due to its promising properties such as a larger exciton binding energy, lower cost, and higher chemical etching rate [2], which gives it a high potential for room temperature light emission, more resistant to radiation, and multifunction as it has piezoelectric[3], dielectric, transparent, semiconducting oxide and optoelectronic applications in UV-Blue spectral range [4].

ZnO is a unique material that exhibits both semiconducting and piezoelectric properties. In the past decade, numerous studies have been made on both production and application of one dimensional ZnO compared to other semiconducting materials [4]. In addition, due to its direct band gap and its large photoresponse, ZnO is also very suitable for UV – photo – detector applications. [5].

The high cohesive energy of ZnO which is ~ 1.89 eV makes it a highly stable and perhaps most radiation hard material amongst the direct band gap semiconductor family, which ensures a long life and a high degradation threshold of ZnO based optoelectronic devices [6].

This paper presents study and characterization of pure and doped ZnO:Mg thin films using spectrophotometer (Sp-800) and X-Ray Diffraction (XRD) analysis, which was deposited by employing Pulsed Laser Deposition (PLD) technique. The quality of thin film deposited at room temperature via Pulsed Laser Deposition was studied. Crystalline of ZnO thin films can be improved by annealing of thin film after deposition.

Experimental details

ZnO and ZnO:Mg films were deposited on glass substrate by Pulsed laser deposited technique (PLD) as shown in Fig.1, where ZnO:Mg pellets prepared by solid state reaction route method which used as the target material. The films were deposited in a vacuum chamber using a 1064 nm Nd:YAG laser. The pulse repetition rate was set at (6) Hz and the energy density of the laser beam was (500) mJ/cm^2. The vacuum chamber was pumped down to a base pressure of (4 x 10^{-2})mbar and the partial pressure of oxygen was 4 x 10^{-1} mbar. The target to substrate distance maintained at (1cm). Crystalline quality and crystal orientation of prepared thin films were investigated by the X-ray diffraction technique. Ultra-violet visible absorption (UV-Vis) measurements were performed to determine the optical band gap.

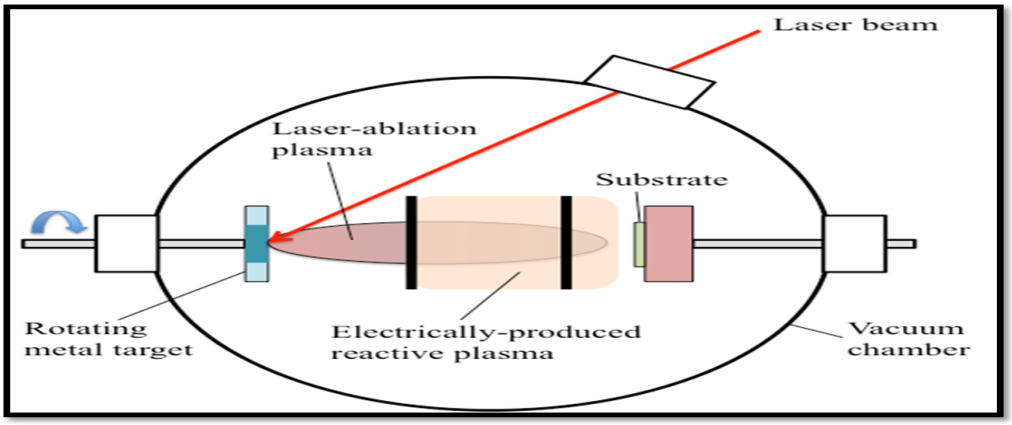

Fig. 1: Schematic diagram of a typical laser deposition set-up.

Results and discussion

1- Structural properties

The X-ray diffraction pattern (XRD) of the 300 nm average thickness ZnO film prepared by pulse laser deposition (PLD) technique shown in Fig. 2. The intensity of the diffraction peaks, their diffraction angles, and their indices are illustrated in Table1. It can be noticed from the X– ray diffraction spectra of ZnO that there are three sharp peaks and two other small. It means that the film is polycrystalline. The

strongest peak observed at Bragg's angle (2Θ= 31.699º) can be attributed to the (100) plane of the hexagonal ZnO **[7]**. The (002), (101), (012) and (110) peaks were also observed at 34.382°, 36.185° 47.468° and 56.578° respectively but these peaks are of lower intensity than the (100) peak. The effect of the Mg doped on the ZnO structure of the film is displayed in Fig. 2. The ZnO:Mg film shows a highly c-axis oriented (100) peak at 31.792º. The other peaks at 34.428º, 36.231º and 56.624º can be associated with (002), (101) and (110) peaks. the intensity of diffraction peaks decrease with doped by Mg **[8]**. The average crystallite size (D) was estimated using Eq.(1).

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

where, λ is the wavelength of the x-ray and β is the full width at half Maximum intensity in radians, θ_B is the Bragg angle and K is the shape factor of the average crystallite which equal to 0.9.

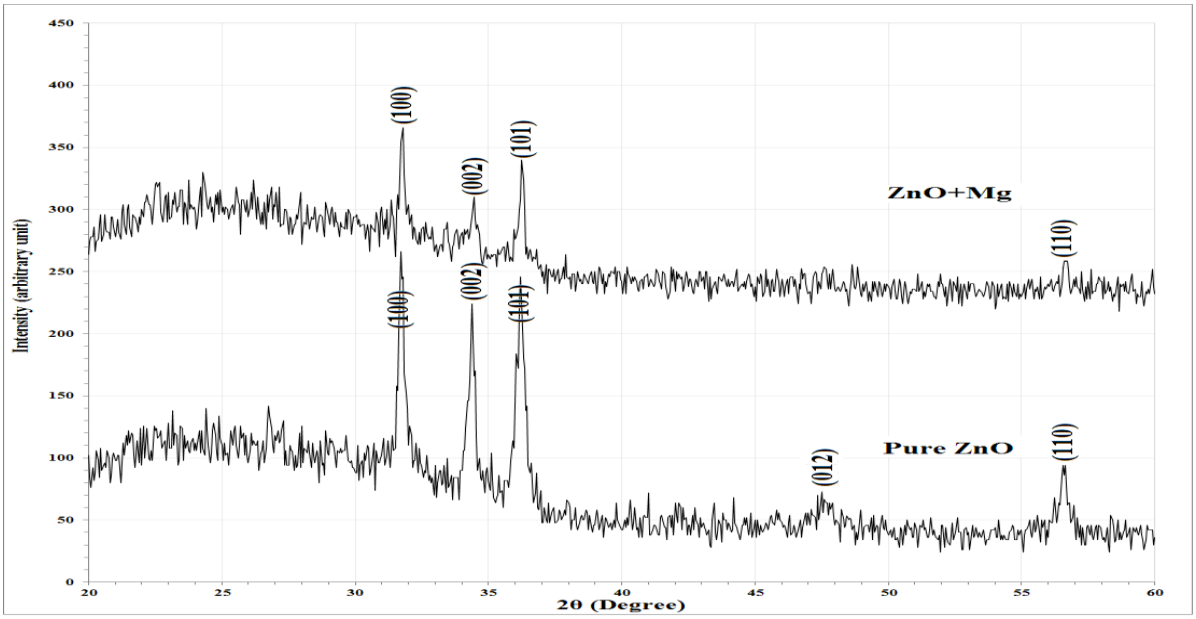

Fig.2: XRD patterns for thin ZnO pure and doped films.

Table 4-1: Average crystallite size of ZnO and doped ZnO:Mg thin films and roughness of thin ZnO pure and doped films.

y	2θ exp. (Deg.)	d Exp. (Å)	d Std. (Å)	Phase	(hkl)	Card No.	FWHM (Deg.)	G.S (nm)
ZnO	31.699	2.8204	2.8141	ZnO	(100)	96-230-0113	0.231	33.65
	34.382	2.6063	2.6027	ZnO	(002)	96-230-0113	0.324	24.20
	36.185	2.4804	2.4755	ZnO	(101)	96-230-0113	0.462	17.03
	47.468	1.9138	1.9107	ZnO	(012)	96-230-0113	0.601	13.60
	56.578	1.6254	1.6247	ZnO	(110)	96-230-0113	0.601	14.14
+Mg	31.792	2.8124	2.8141	ZnO	(100)	96-230-0113	0.231	33.65
	34.428	2.6029	2.6027	ZnO	(002)	96-230-0113	0.370	21.18
	36.231	2.4774	2.4755	ZnO	(101)	96-230-0113	0.277	28.38
	56.624	1.6242	1.6247	ZnO	(110)	96-230-0113	0.231	36.76

The optical properties of ZnO and ZnO:Mg

The optical transmittance as a function of wavelength in the range (300-800 nm) for ZnO pure and doped ZnO:Mg thin films prepared at room temperature and annealed at 450C^o with average thickness 300 nm was shown in Fig.3. It can be observed that the transmittance increases with doping by Mg and shifts to the shorter wavelength compared to the ZnO spectrum.[9]

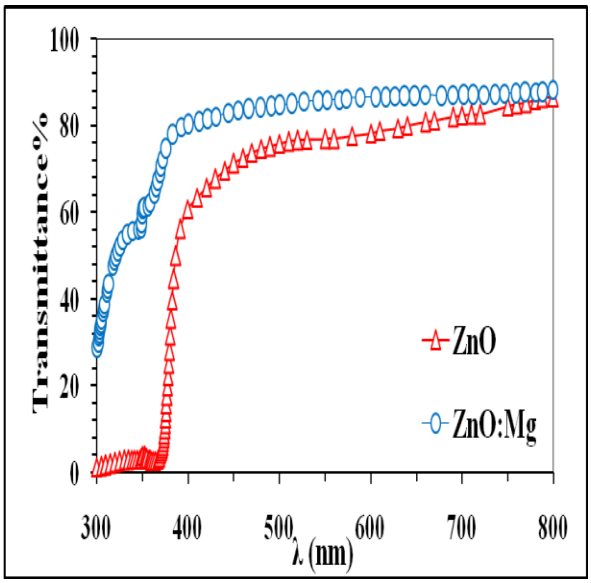

Fig.3: Transmittance as a function of wavelength for ZnO pure and doped thin films.

An extrapolation of the linear region of the plot of $(\alpha h\nu)^2$ versus photo energy hν (eV) on the x-axis gives the value of the optical band gap (E_g). The plot of $(\alpha h\nu)^2$ as a function of the energy of incident radiation of pure and doped ZnO deposited on glass substrate shown in Fig. 4. The figure shows the optical energy gap of ZnO which equal to 3.2 eV. It can be noticed that the optical band gap increases with doping and equal to 3.9 eV. This increasing may be attributed to the fact that new defects are introduced after Mg atoms substitute Zn atoms and enter into the ZnO lattice due to the electro negativity and ionic radius difference between Zn and Mg[10]. As a result, the exciton bond increases with an doped in Mg. Moreover, there are more electrons contributed by the Mg dopant due to the lower electron affinity of Mg compared with Zn, which take up the energy levels located in the bottom of the conduction band. Since the Pauli principle prevents states with doubly occupied and optical transitions from being vertical, the valence electrons require extra energy to be excited to higher-energy states in the conduction band [11].

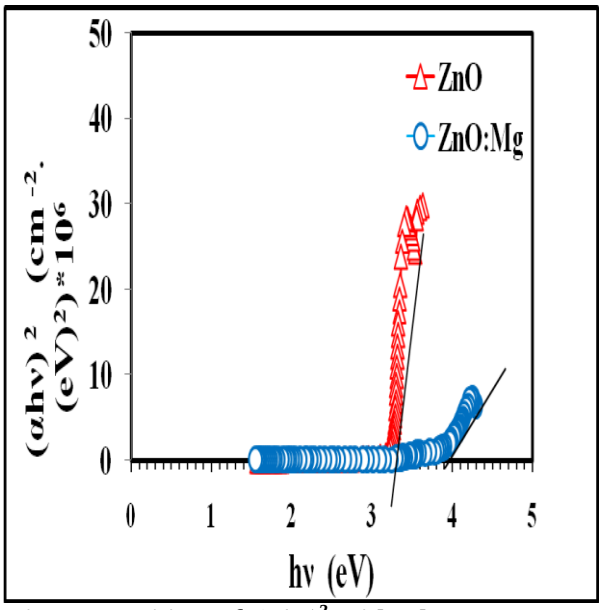

Fig.4: Varaition of $(\alpha h\nu)^2$ with photon energy (hν) of the ZnO pure and doped.

Fig. 5 show The variation of extinction coefficient (k) as a function of wavelength for ZnO pure and doped thin films. As shown in figure the k decrease with wavelength, in the UV visible regions, lower k can be originated from crystallographic flaws such as grain boundaries and voids. The voids act as optical scattering centers [12]. It is observed from these figure that the k decrease with dopeing.

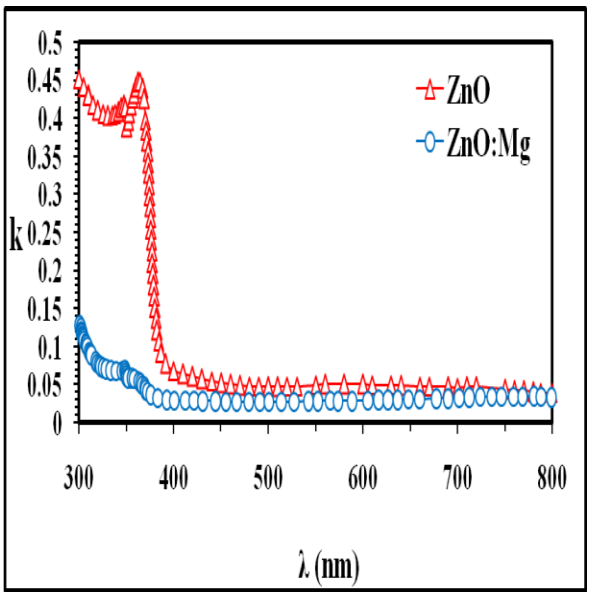

Fig.5: Variation of K as a function of wavelength of ZnO pure and doped.

Complex refractive index is the most desirable optical constants of photonic materials for the fabrication of quantum photonic devices. So, the variation in refractive index with wavelength for ZnO pure and doped with Mg film in the wavelength range of (300-800) nm was show in Fig.6. From this figure it can see that the refractive index decrease with doping by Mg [13].

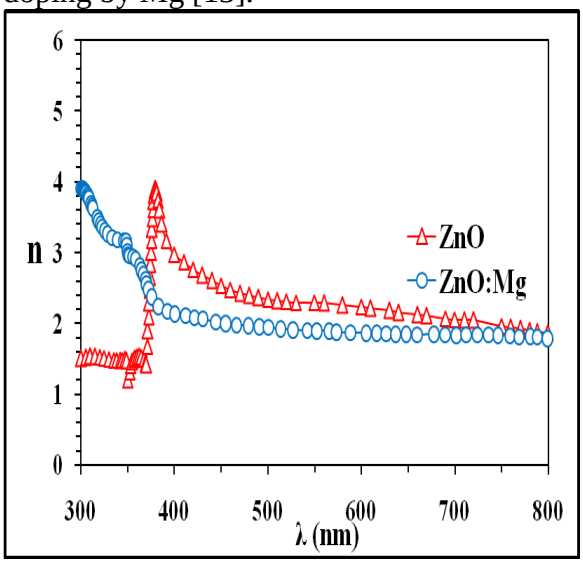

Fig.6: Variation of the refractive index (n) with wavelength of ZnO pure and doped.

Fig. 7 and 8 show the variation of real part (ε_r) and imaginary part (ε_i) of dielectric constants for ZnO pure and doped thin films with the wavelength. The real and imaginary parts Follow the same pattern and the values of real part are higher than imaginary part. It can be seen that the real and imaginary parts of the dielectric constant decreases with increasing wavelength in the visible region while increases in the ultraviolet region.

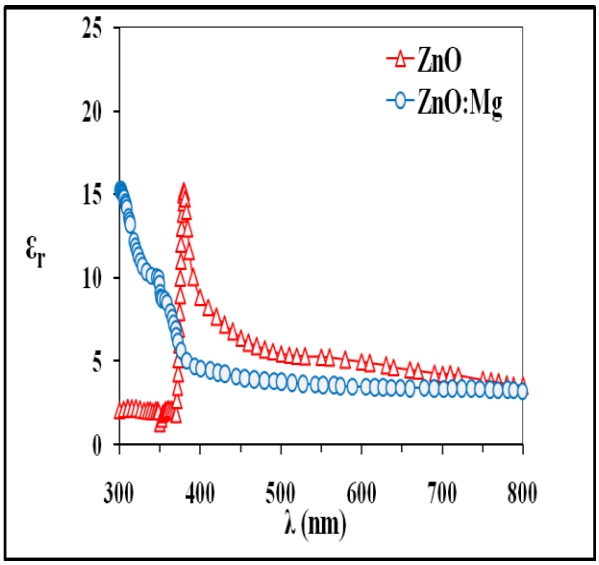

Fig.7:Variation of ε_r as a function of λ for ZnO pure and doped films.

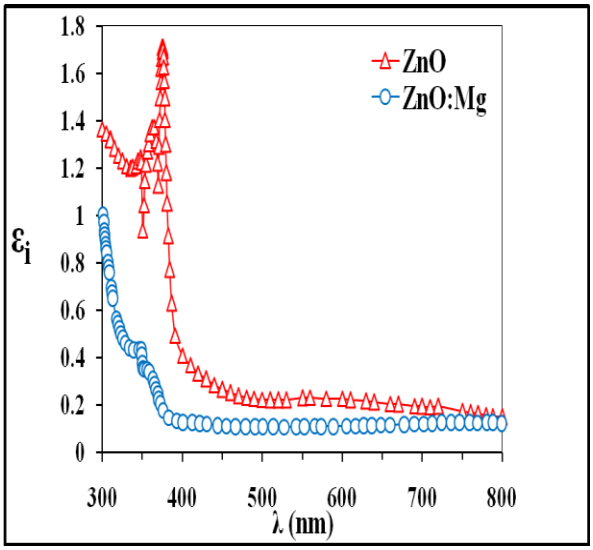

Fig.8:Variation of ε_i as a function of λ for ZnO pure and doped films.

Conclusions

ZnO and ZnO:Mg have been successfully prepared by plus laser deposition (PLD). X-ray diffraction results show that the structure of ZnO. films is polycrystalline with hexagonal wurtzite structure with preferential orientation in the (100) direction and intensity decrease with doped Mg. The optical transitions in ZnO are direct and the optical energy gap increases with doping from 3.2 to 4 eV.

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