

Spectroscopic ellipsometry, optical, structural and electrical investigation of sprayed pure and Sn-doped ZnO thin films

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Abstract: in this work, we report the transparent pure and Sn-doped zinc oxide (ZnO). The films were deposited onto microscope glass substrate which was heated at $350 \pm 5^\circ\text{C}$ by ultrasonic spray pyrolysis (U S P) deposition technique. The concentrations of Sn were selected within the range of 0-3% by step of 0.5% and the time deposition is kept at 5 min. A (002)-oriented wurtzite crystal structure was confirmed by X-rays patterns; and grain size varied within the range 7.37-14.84nm, and cristanillity is calculated goes from 14.4 to 45.9%. Based on UV-VIS-IR analysis, the results revealed the high transparency of the sprayed films which exceeds 90%. The band gap energy was of 3.26-3.30 eV. The film thickness was estimated by spectroscopy ellipsometry and the found values were of 165-270nm. The refractive index is in the range of 2.75. The obtained electrical parameters were around 10^{18} cm^{-3} , $3.6 \text{ cm}^2/\text{Vs}$, $1.6 \Omega \cdot \text{cm}$; $5.8 \text{ cm}^3/\text{C}$. finally the Sn-doping has influenced the physical parameters of as-ground ZnO films

Keywords:

ZnO; ultrasonic spray pyrolysis; Sn-doping; X-rays patterns; optical properties; electrical properties; spectroscopy ellipsometry; refractive index.

1. Introduction

Zinc oxide (ZnO) is an n-type semiconductor which it's recently gained much attention due to many advantages over other oxide thin films with its direct wide band gap of 3.30-3.39 eV [1]; and the large exciton binding of 60 meV [2]. ZnO is mechanically and chemically stable with wurtzite structure and the lattice parameters are $a=3.25 \text{ \AA}$ and $c=5.19 \text{ \AA}$ [3]

The resistivity value of ZnO can be tuned between 10^{-4} and $10^{12} \Omega \text{ cm}$ which it can be controlled by adjusting doping and preparation parameters [1].

Pure and Sn-doped ZnO has been used in many applications as gas sensors, solar cells windows, transparent electrode [1], [2], [3].

ZnO films can be produced by several techniques such as sol-gel process [4]. chemical vapor deposition [5], sputtering [6], pulsed laser ablation [7] and ultrasonic spray pyrolysis (USPD) [8].

USPD is a facile, unobstructive, low cost and non-toxic deposition technique.

Up to our knowledge, few works on Sn-doped ZnO films fabricated by USPD have been achieved. In this work, structural, optical, spectroscopic ellipsometry and electrical properties of as-deposited ZnO films produced by USPD were investigated and the role of Sn-doping on physical properties of ZnO films was emphasized.

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2. Experimental procedure

2.1 Preparation of sprayed ZnO films

ZnO films were deposited by USPD route from zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) used as precursor. 0.1 mol of zinc acetate was dissolved in 100 ml of methanol. Tin doping was added from the tin chloride (SnCl_2) to the precursor with different concentrations from 0 to 3% by step of 0.5%.

The used substrates were the microscope glass which they were chemically successively cleaned by methanol for 15min and distilled water for 20min. We deposit our films at fixed substrate temperature of 350 °C and the time deposition was 5min and the distance nozzle-substrate was around 5cm. The substrate must be placed under nozzle before the temperature reaches 50C° to avoiding the thermal chock as shown in figure 1.

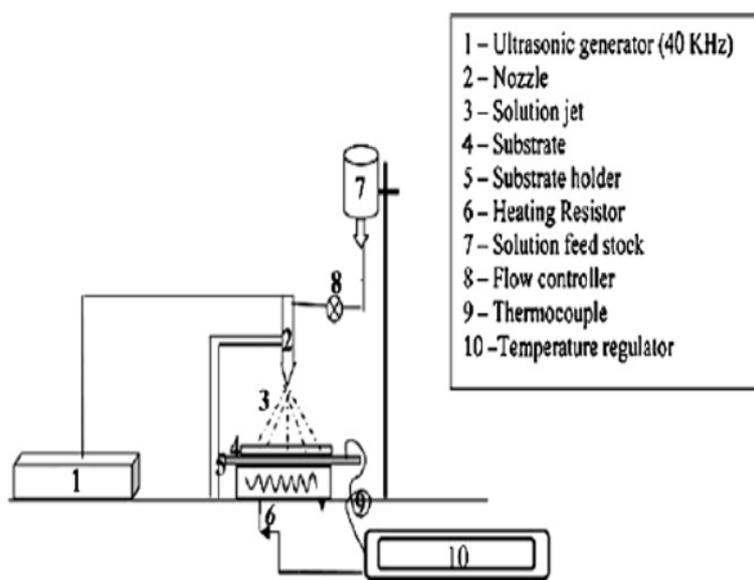


Fig.1: Schematic diagram of USP system set-up

2.2 Characterizations of as-grown films

Room temperature X-rays diffraction pattern of pure and Sn-doped ZnO films were carried out by Bruker (D8 ADVANCE with DAVINCI design) diffractometer in 2θ range of 20-80°.

The transmittance and absorbance were calculated by two beams Shimadzu spectrophotometer (UV-VIS-IR spectrophotometer Shimadzu UV-3600).

The thickness of films were taken by spectroscopic ellipsometry (we use Ellipsometer PHE-102) which is an optical technique used for analysis and metrology. The light beam is reflected by the sample which will be detected by a sensor and then analyzed to see what the sample did to the light beam and finally we draw conclusion about the simple (as thickness show in table 1).

Sn/Zn (%)	Thickness (nm)	Eg (eV)
0	262	3.26
1.5	221	3.28
2	165	3.29
2.5	236	3.28
3	270	3.28

Table1: Thickness and optical band gap of pure and Sn-doped ZnO films

The electrical parameters such as bulk density, resistivity and mobility were measured by Hall measurement system (HMS)

Results and discussion

In this work, the films selected were those grown from 0.1 M at 350°C during a deposition time of 5min.

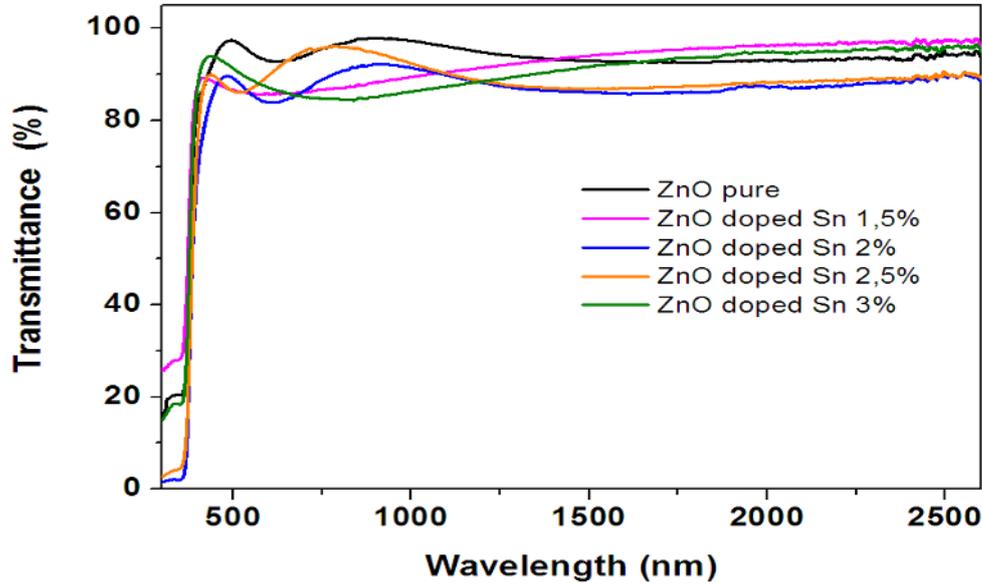


Fig. 2: transmittance spectra of Sn-ZnO thin films

We note that the films are highly transparent in the visible region and low in ultraviolet region. The transmittance is higher than 90% with an absorption edge between 380nm and 420nm depending on the deposition parameters.

The interference fringes of the transmittance curves revealed that the films surface is smooth and highly reflecting, there is no match scattering or absorption loss in the films.

It has observed that the absorption edges of doped ZnO are slightly shifted to the shorter wavelength (blue shift); this is mainly attributed to the Burstein-Moss effect [9].

The variation of $(\alpha h\nu)^2$ as a function of the photon energy $h\nu$ of the pure and Sn doped ZnO are sketched in Fig.3 the optical band gap for as-grown films is obtained by the intercept of the straight line on the horizontal axis.

2.1 optical properties

The transmittances of prepared thin films were collected by using UV-VIS-IR spectrophotometer. The value of transmittances spectra were measured by taking a similar glass as a reference to compare it with our films, hence the spectra were from the film only.

The thicknesses of as-deposited films were calculated by using spectroscopy ellipsometry.

The obtained results range within 160 and 270 nm depend strongly on doping level.

The results are plotted in Fig.2 as a function of wavelength λ from 300nm to 2500nm.

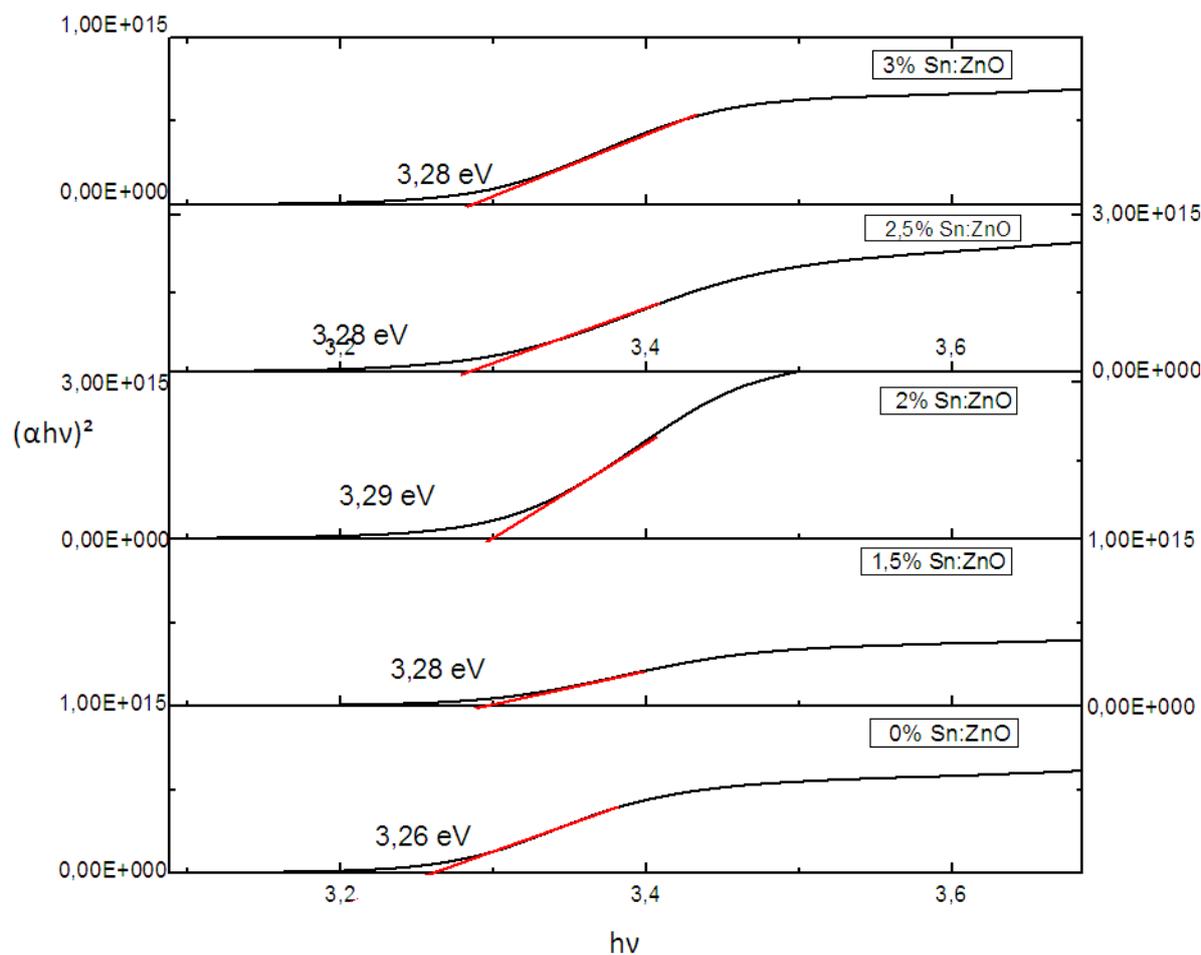


Fig 3: plot of $(\alpha hv)^2$ vs $h\nu$ of pure ZnO and doped Sn

2.2 structural properties

The crystallinity and the preferred crystal orientation of the undoped and Sn doped ZnO films were analyzed by XRD method by Bruker D8 ADVANCE with DAVINCI design diffractometer as shown in Fig.4

Films Sn/Zn (%)	2θ ($^\circ$)	$\Delta\theta$ ($^\circ$)	d (A°)	Cristallinity (%)	Grain Size (nm)
0	33.48	0	2.65	31.1%	14.84
1.5	34.00	-0.52	2.60	45.9%	7.37
2	33.27	0.21	2.70	28.3%	9.19
2.5	33.36	0.12	2.68	42.3%	11.33
3	33.01	0.47	2.71	14.4%	9.81

Table 2: 2θ -angle, lattice spacing, and cristallinity of pure and doped ZnO according to (002) orientation

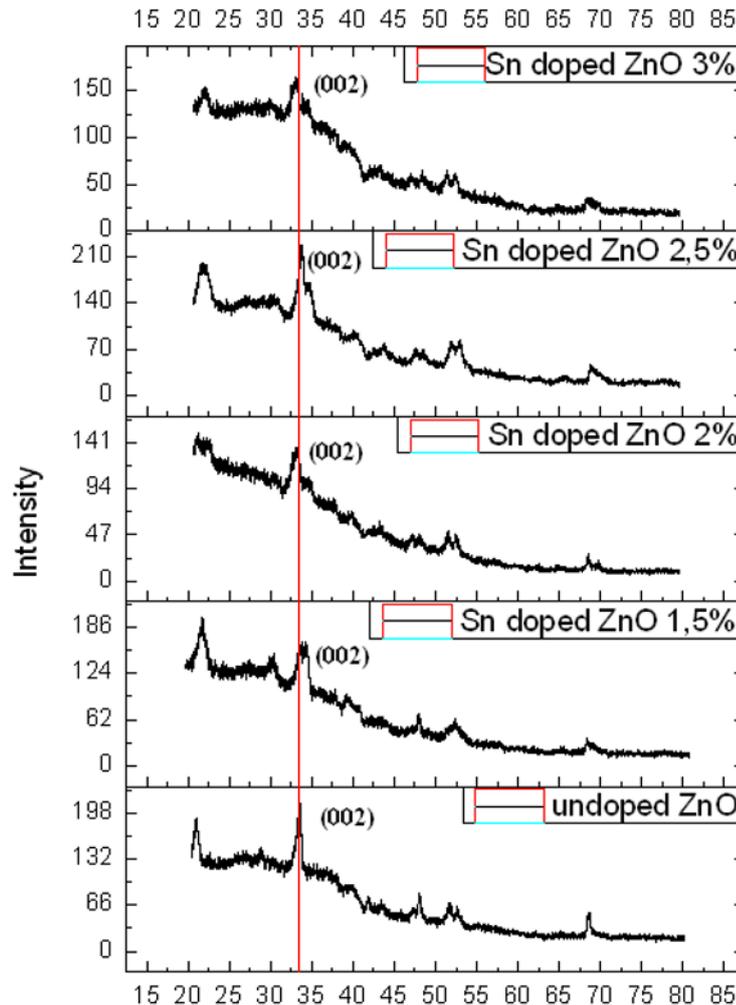


Fig.4: XRD spectra of undoped and Sn doped ZnO

Fig.4 shows that the films are polycrystalline with a hexagonal wurtzite type structure (ASTM 89-1357). And shows a high diffraction intensity for (002) peak hence the films exhibit preferential orientation along the (002) plane.

The lattice spacing, Bragg angle and percentage of crystallinity and the angle shift $\Delta\theta$ is determined as 2θ (pure ZnO)- 2θ (doped ZnO) are listed in table 2.

The first peak located at $\sim 22^\circ$ corresponds to amorphous carbon comes from zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), amorphous carbon's peak is sited in Zhou Kong's work [25]

The lattice spacing was calculated by the Bragg law [3]:

$$n \lambda = 2 d \sin \theta \quad (1)$$

Where θ is half of Bragg angle, d is the lattice spacing, n is diffraction order and λ is the X-ray wavelength.

The grain sizes were calculated by Scherer's formula:

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

Where β is the full width at half maximum.

It is observed that doping include a shift angle for the main orientation of the ZnO films. JCPDS card of ZnO shows that (002) is peaked at 34.46° .

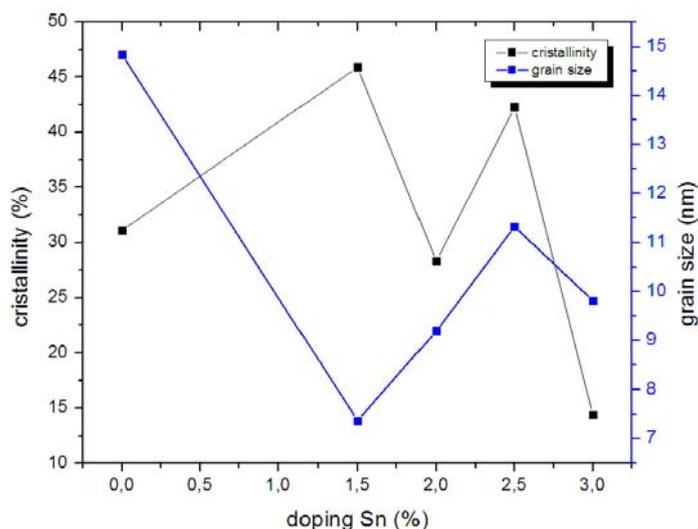


Fig.5: show the grain size versus doping Sn

Fig.5 show the graphs of crystallinity and grain size versus percentage of Sn as dopant. If we take undoped ZnO film as an example we can say that the film is 31.1% crystallized in groups of grain size ± 14.84 nm.

We observe that the grain size of doped ZnO 2% and 3% films is bigger than 1.5% 2.5% films with lower crystallinity as table 2 shown, its maybe due to the influence of thickness of films and/or the influence of the lattice spacing $d(\text{\AA})$. The crystallinity increase with decreasing of lattice spacing as it's shown in Fig.6.

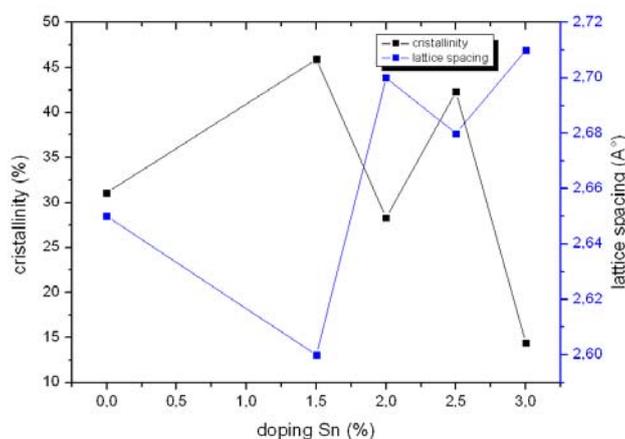


Fig.6: plot of crystallinity, lattice spacing versus doping Sn

2.3 Electrical properties

The current-voltage (I-V) measurements of all films have been carried out by using four-probe method at room temperature (300K), which the sample was held between four gold contacts as sketched in Fig.7.

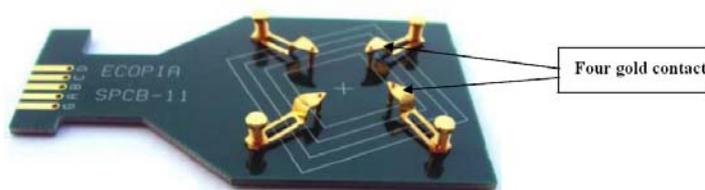


Fig.7: gold contact used in the measurement of electrical properties

ZnO has a wide range of electrical conductivity which it can be controlled by doping. The variation of electrical conductivity with doping Sn is shown in Fig.8.

It is shown that the conductivity increase with increasing of doping Sn, it can be explained by the substitution of Zn^{+2} by Sn^{+4} in ZnO crystal structure which resulting in two more free electron to contribute to the electrical conduction.

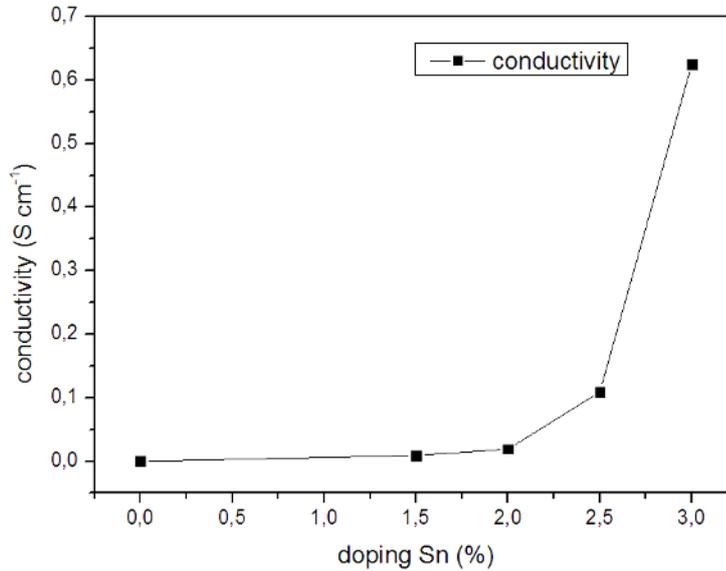


Fig.8: plot of electrical conductivity versus doping Sn

Table3 show the electrical parameters as bulk density, mobility, resistivity, hall coefficient.

Sn/Zn %	N_b (cm ⁻³)	μ (cm ² /Vs)	ρ (Ω .cm)	R_H (cm ³ /C)	Type	V_H sign
0	-7.54E12	35.36	2.34E4	-8.276E5	<i>n</i>	<i>negative</i>
1.5	3.627E15	15.85	1.086E2	1.721E3	<i>p</i>	<i>positive</i>
2	-1.47E16	8.215	51.64	-424E2	<i>n</i>	<i>negative</i>
2.5	-2.95E17	2.312	9.149	-21.15	<i>n</i>	<i>negative</i>
3	1.064E18	3.67	1.599	5.869	<i>p</i>	<i>positive</i>

Table3: bulk density, mobility, resistivity, hall coefficient.

2.4 Spectroscopy ellipsometry

Spectroscopy ellipsometry (SE) known for its precision and non-destructive, by measuring the change in the light polarization state as ψ (ψ) and Δ (Δ) which represent the amplitude ratio and phase difference between p- and s-polarization respectively of the reflected light off the surface of the film. [10.11.12]

SE was used to measure the optical constant at an incidence angle of 70° as it's shown at Fig.9 and It's found that the calculated ψ and Δ are consistent with the experimental data for all films.

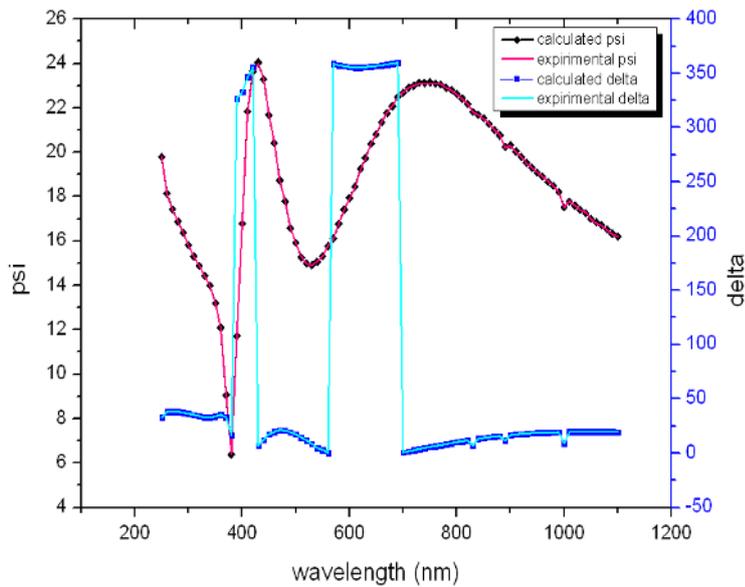


Fig.9: ellipsometry spectra of undoped ZnO

The optical constants are very important to designing the optical devices, because of their relation to the electronic polarizability of ions and the local field inside materials [12]. Thus it's important to determine the refractive index (n) and extinction coefficient (k) of the films. The dielectric function can be determined from the optical parameters (n) and (k) by:

$$\epsilon_1 = n^2 - k^2 \quad (3)$$

$$\epsilon_2 = 2nk \quad (4)$$

Fig.11 show (n) and (k) of the rest of films which has same reaction with doping Sn.

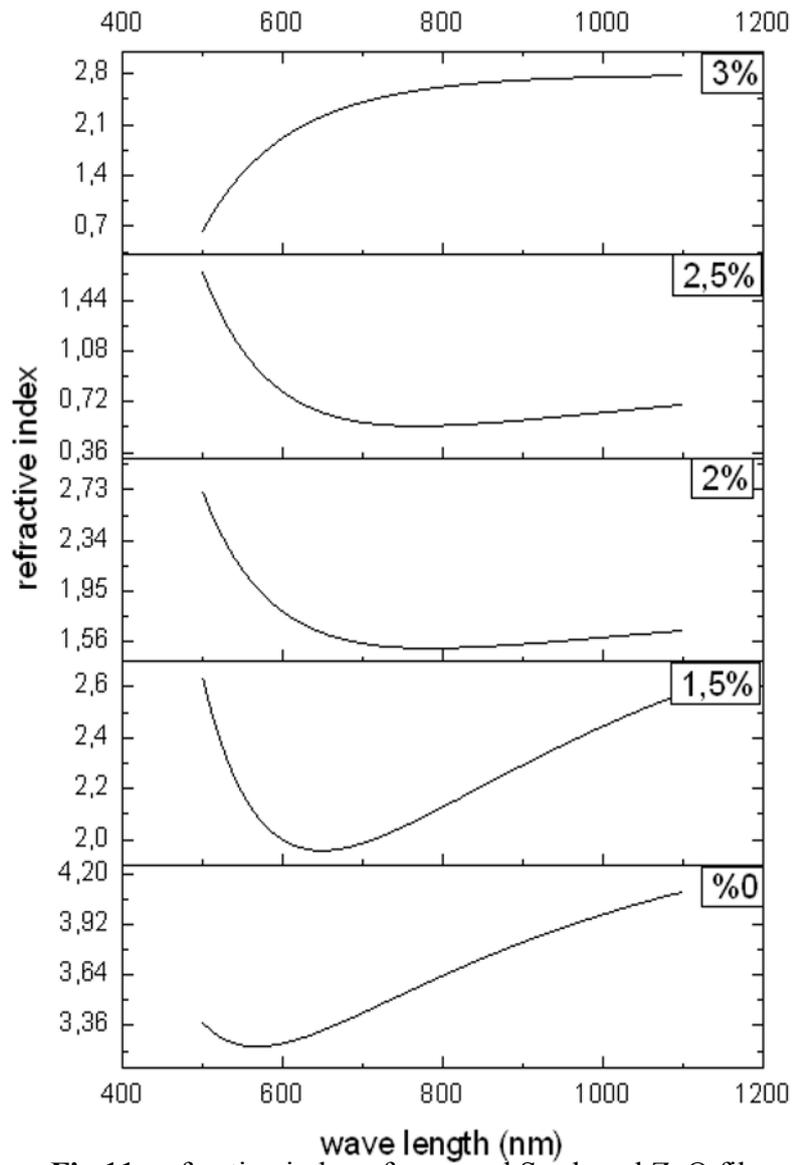


Fig.11: refractive index of pure and Sn-doped ZnO films

Fig.12 and Fig.13 show the variation of the real and imaginary values of dielectric function.

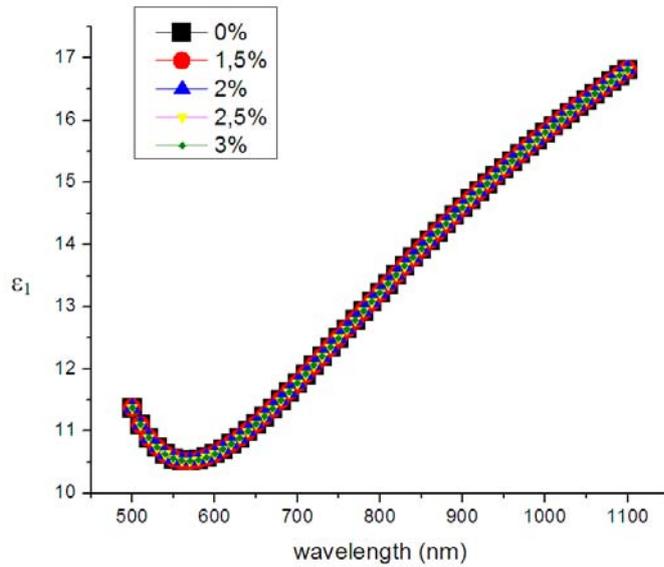


Fig.12: real part of dielectric function of undoped and doped ZnO

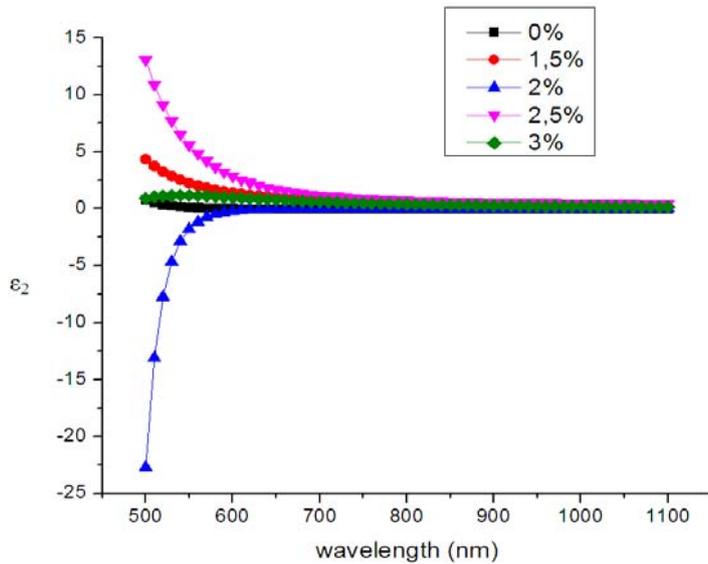


Fig.13: imaginary part of dielectric function of undoped and doped ZnO

We observe that we have the same values of ϵ_1 for all films, it means that the films of pure and Sn-doped ZnO films have the same real part of the dielectric function.

The imaginary part of the dielectric function are shown in Fig.13 which we can observe the reaction of dielectric function with Sn-doping.

Conclusion

The impact of tin doping on optical, structural, electrical and spectroscopy ellipsometry of Zinc oxide by ultrasonic spray pyrolysis deposition are investigated.

The optical parameter shows that the films of undoped and doped ZnO are highly transparent and the band gap energy was shifted from 3.26eV to 3.28eV by Burstein-Moss effect due to the introduction of Sn impurity which leads to.

The structural characterization revealed that the films prefer plan (002) as a preferential orientation with best crystallinity is for ZnO doped Sn a 1.5%. which is due to the lowest value of spacing lattice.

The electrical studies show the possibility to get p-type zinc oxide and reveals that the decrease of resistivity due to the increase of the bulk density.

Spectroscopy ellipsometry reveal the optical parameter of ZnO and show that the refractive index decrease with doping increase and that's due to the change of structure of ZnO by introduction of Sn as impurity. The data of SE reveal that the doping doesn't affect the real part of dielectric function but the imaginary.

Acknowledgements

The work is included in the **PNR** project under contract number **8/U311/R77**, supported by "agence thématique pour la recherche scientifique et technologique" (ATRST) <http://www.atrst.dz>, and national administration of scientific research (NASR) www.nasr.dz. This work is a part of CNEPRU project n° **D01920120039** supported by Oran university of sciences and technology USTO-MB. The first and second authors are grateful for the assistance of Dicle University-Diyarbakir-Turkey, Mentouri University of Constantine and the virtual library of SNDL <https://www.sndl.cerist.dz>

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