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Optical Properties of Sn Doped ZnO Thin Film Prepared Using Sol-Gel Method for Optical Limiting Application

Marwa Mudfer Alqaisi[1,*] and Alla J. Ghazai[2]

Department of Physics, College of Science, Al-Nahrain University, Baghdad-Iraq

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Abstract

In this work, pure Zinc oxide and tin doped Zinc oxide thin films nanoparticles with various volume concentrations of 2, 4, 6, and 8 V/V% were prepared by using the sol-gel method. The optical properties were investigated by using UV-Visible spectroscope, and the value exhibits the direct allowed transition. The average of transmittance was around ~(17-23) % in visible region. The optical energy band gap was calculated with wavelength (300-900) nm for pure ZnO and Sn doped ZnO thin films which decreases with increasing concentration from 3.4 eV to 3.1 eV respectively and red shift. The real dielectric (ε_r) and the imaginary dielectric ε_i are the same behavior of the refractive index(n) the extinction coefficient (k) respectively. The optical limiting properties were studied by using an SDL laser with a wavelength of 235 nm. Pure ZnO and doping thin films an found efficient as optic limiting and depend on the concentration of the all samples.

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*Corresponding author: marwaalqaisi966@gmail.com

1. Introduction

Tack transparent conducting oxides (TCOs) researchers have paid considerable attention to the peculiar characteristics of the material advantage of other materials, such as thin film oxides with high optical transmission in the visible region and high reflectivity in the infrared region [1,2]. Among these, Zinc oxide (ZnO) thin films are attractive in the field of semiconductors due to their good optical properties, excellent electrical properties and high stability. In addition, the number of ZnO publications was increased annually in the last decade and ZnO became the second most common semiconductor after Si in 2007 [3, 4]. Zinc oxide is known as n-type oxide that belongs to the semiconductors in II-VI groups, whose covalence is on the boundary between semiconductors that are ionic and covalent. A wide energy band (3.37 eV), high binding energy (60 meV), non toxiaity, high chemical, high stability in thermal and mechanical conditions at room temperature due to attractive for potential applications in optoelectronics, electronics, and laser technologies [5,6]. It has been used in many applications, such as gas sensor [7], solar cells [8], magnetic transparent conducting films [9], light emitting diodes [10], chemical sensors [11], laser system [12]. In addition, zinc oxide may be prepared in the different methods such us, chemical vapor deposition (CVD) [13], Pulse laser deposition (PLD) [14], spray paralysis [5], magnetron sputtering [16], piezoelectrical [17], sol-gel [18-20], etc. Sn doped ZnO was the remarkable material transparent conducting oxide, and it's widely used in various types of devices as the transparent electrode. Impurity doped Zinc oxide, such as (Sn, Al, In) may improve optical, electrical, structural, etc.; for ZnO thin film properties [6]. Sol-gel can give prepared a wide and small area coating of ZnO thin film at low-cost [21], and used these films as optical limiting.

In this paper we prepared pure Zinc oxide and Tin doped Zinc oxide thin film nanoparticles using sol-gel method because of the compositional control and high level of homogeneity due to the lower crystallization temperature and simultaneous liquid precursor mixture,

2. Theoretical Part

In this section, all the mathematical backgrounds of optical constants were introduced based on the UV-Vis measurements. Determining the absorption coefficient (α) is the first quantity that is calculated by the following [22]:

$$\alpha = 2.303/(A/t) \quad (1)$$

where α is absorption coefficient, A is absorbance, and t is thickness of sample.

The energy band gap value is measurement by the tauc formula [23]:

$$A h\nu = A(h\nu - Eg)^n \quad (2)$$

where A is a constant, h is the Planck's constant, ν: is the frequency of incident light, Eg is the energy gap, and n is

the index linked to the density of states (n = 1/2 for the direct transition and n = 2 for the indirect transition).

The refractive index, n, of the prepared thin films can be evaluated as a function of various wavelengths according to the spectrophotometric measurement of reflectance R(λ). [24]:

$$R = \frac{(n-1)^2+K^2}{(n+1)^2+K^2} \quad (3)$$

After performing a simple algebraic manipulation for Eq. (3), the refractive index is expressed via the absolute values of the reflectance using the following relation [24]:

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

where K is the extinction coefficient, R is the reflectance.

The extinction coefficient of films were calculated by [20]:

$$k = \frac{\alpha\lambda}{4\pi} \quad (5)$$

The values of n and k were used to determine the both real ε_r and imaginary part ε_i of the dielectric constant [25]:

$$\varepsilon_r = n - k \text{ and } \varepsilon_i = 2nk \quad (6)$$

3. Experimental

The sol-gel spin coating method was used to prepare pure ZnO and Sn doped ZnO thin films. Zinc acetate dihydrate $Zn(CH_3COO)_2 2H_2O$, tin chloride as a material, 2-methoxyethanol as a solvent and monoethanolamine (MEA) as a stabilizer. Zinc acetate to MEA has a molar ratio of one.

First, zinc acetate added to 2-Methoxyethanol, with 1 M of (HCL) and dropped (MEA) slowly to the solution, were dissolved to create pure ZnO, and then the solution was stirred for 1 hour at 60 °C to obtain a transparent yellow solution. Then Sn added into a ZnO solution with a various concentrations of 2, 4, 6 and 8 V/V% were stirred for 30 minutes at 60 °C to create a homogeneous ZnO aqueous solution that has been left at room temperature for 24 hours prior to the deposition process.

Secondly, pure ZnO and Sn doped ZnO solution, were deposition on a glass substrate by using spin coating method with spin speed of 2000 rpm for (60) sec after that, they were dried for 20 minutes at 200 °C on a hot plate. Finally, the films were annealed in a furnace for 1 hour at 400 °C to achieve ZnO crystallization.

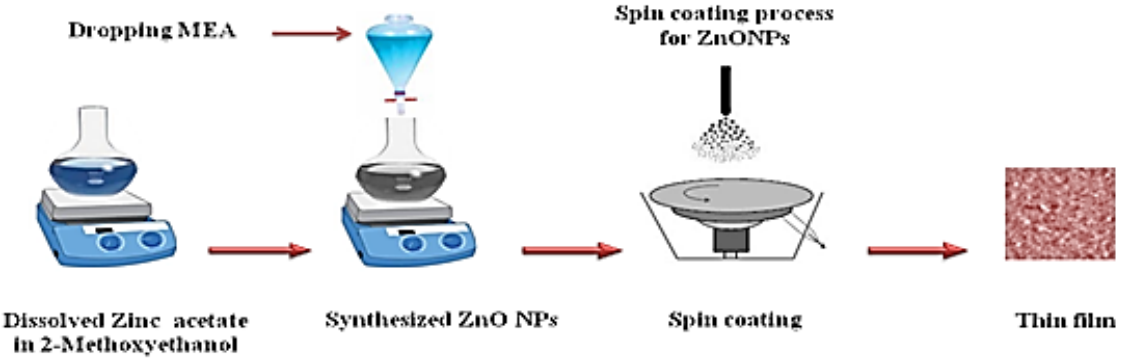

Figure 1. Experimental process of prepared pure and Sn doped ZnO thin film.

4. Result and Discussion

4.1 Optical properties

The optical transmittance spectra T for pure and Sn doped ZnO thin films with a various concentrations of 2, 4, 6, and 8 V/V%, are shown in Figure 2 recorded on the wavelength range of (300–900) nm for all samples. The average transmittance is around ~(17-23)% in the visible range, the transmittance value for doped films exhibited increase at concentration of in Sn 2% and then decrease at Sn 4% and at Sn 6-8% increase to be close to the pure ZnO value. The observed deterioration of transmittance with increased doping concentration could be attributed to increased photon scattering by crystal defects as well as a higher metal to oxygen ratio [15].

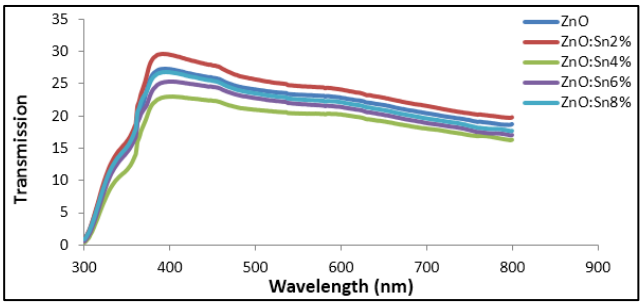

Figure 2. Transmission of pure and Sn doped ZnO with various concentrations.

The absorbance of the all samples shown in Figure 3 were highest value at the edge of the primary absorption (short wavelengths) in the visible area then it decreases with increasing wavelength, and for doped films the absorbance increases with increasing Sn concentration.

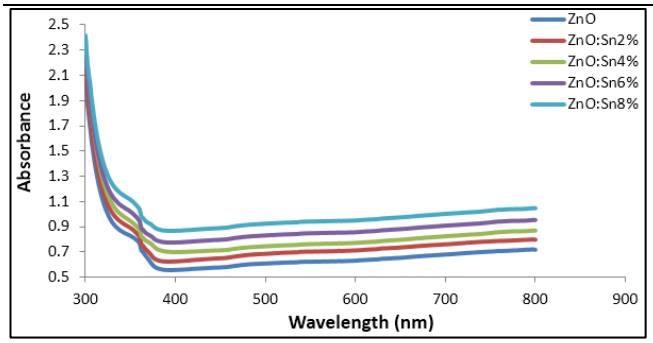

Figure 3. Absorbance of pure and Sn doped ZnO with various concentrations.

The absorption coefficient α of the all samples calculated by using Eq. (1), As shown in Figure 4 that the spectra decrease with increasing wavelength, for pure ZnO film, but for doping ZnO films with Sn the absorption coefficient increased with increasing Sn concentration.

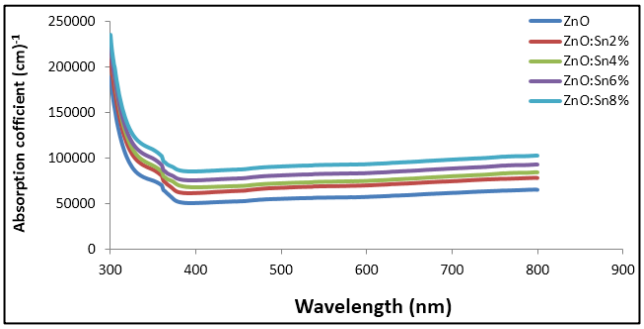

Figure 4. Absorption coefficient of pure and Sn doped ZnO with various concentrations.

The band gap of the all samples calculated by using Eq. (2), for pure ZnO was 3.4 eV and the value of Sn doped ZnO films were decreased slightly with increasing concentration of Sn from (3.4 to 3.1) eV as listed in Table 1 and shown in Figure 5 [18]. This decreases due to the shrinkage effect because of the increasing in carrier concentration. This decrease in band gap leads to increased efficiency in the fabrication of nano-scale devices using these materials.

Table 1. Energy band gap value of pure ZnO and Sn doped ZnO.

Sample	Energy gap (eV)
ZnO	3.4
ZnO: Sn 2%	3.3
ZnO: Sn 4%	3.2
ZnO: Sn 6%	3.2
ZnO: Sn 8%	3.1

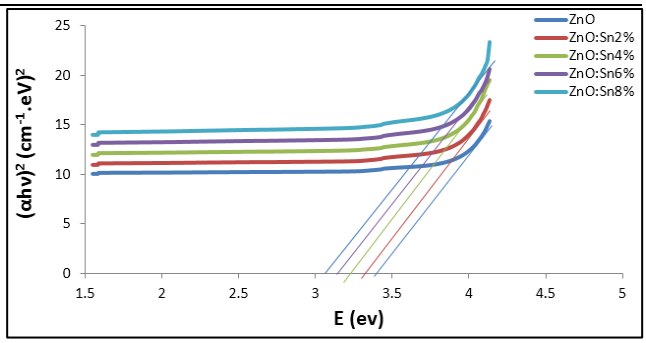

Figure 5. Band gap of pure and Sn doped ZnO with various concentrations.

The value of extinction coefficient k calculated using Eq. (5), and shown in Figure 6 relived that the extinction coefficient k decreases with the increase of wave length λ. The levels of spectra for doping are increased with increasing Sn concentration [15].

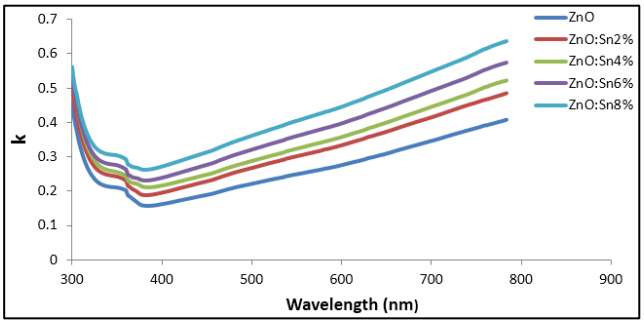

Figure 6. extinction coefficient of pure and Sn doped ZnO with various concentrations.

The value of the refractive index n calculated by using Eq. (4), and shown in Figure 7 that increase with the increase of wave length λ, and then decreases and retrain increase. The levels of spectra for doping are increased with increasing Sn concentration.

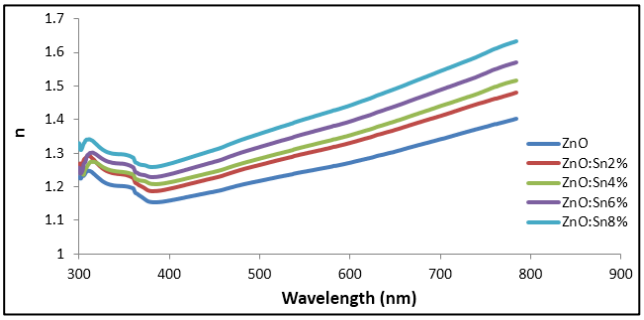

Figure 7. Refractive index of pure and Sn doped ZnO with various concentrations.

The real and imaginary dielectric were calculated by using Eq. (6). The real dielectric of pure and Sn doped ZnO shown in Figure 8 decreased with the increase of wave length λ. The levels of spectra for doping are increased with increasing Sn concentration. The ε_r is the same behavior of the refractive index n, and the imaginary dielectric ε_i shown

in Figure 9 were increase with the increase of wave length λ, and then decrease and retrain increase. The levels of spectra for doping are increased, with increasing Sn concentration. The ε_i is the same behavior of the extinction coefficient k.

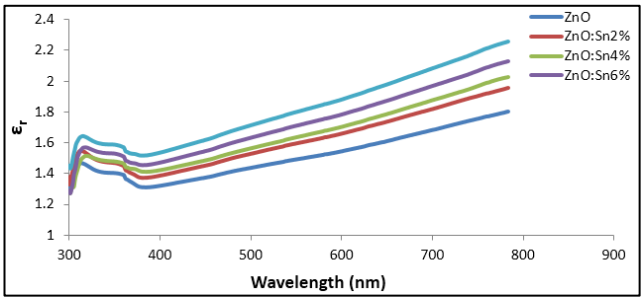

Figure 8. Real dielectric of pure and Sn doped ZnO with various concentrations.

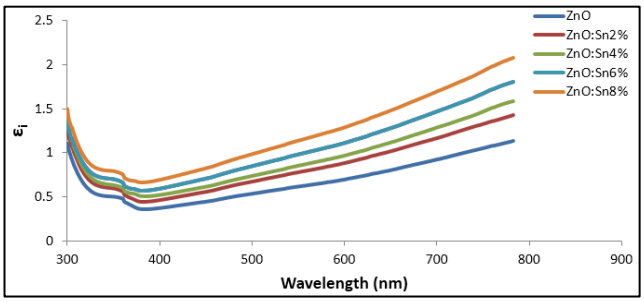

Figure 9. Imaginary dielectric of pure and Sn doped ZnO with various concentrations.

3.2 Optical limiting application

In order to test the effectiveness of the pure ZnO and Sn, Co-doped Zno with various concentrations of 2, 4, 6 and 8 V/V% to be an optical limiting, should be study the nonlinear properties of all samples. This section uses optical limiting as a function of concentration. The results obtained when the input power changed was a function of the output power for pure ZnO and Sn doped ZnO shows in Figure 10 the output power changes linearly with the input power when the power is low for all concentrations, but when the input power continues to increase, initially, when the input power is small, the output power increases with it linearly until the output power reaches its maximum value when the input power is 20 mW, and with an increase in the input power than this amount, the output power decreases slightly, and then its value is dispersed and its value decreases with increasing the concentration of Sn for all the concentrations of Sn added to ZnO. With the continuous increase in the input power, the output power reaches a constant value, it reaches a state of saturation and it is fixed at the point amplitude of the limiter that explains the property of the limiter. For doping, the figure shows the effectiveness of the optical limiting be reinforced and decreases with increasing concentration ratio, the properties of optical limiting become better, because of the sample with a higher concentration has more particles per unit volume to participate in the interaction during the nonlinear absorption processes [22].

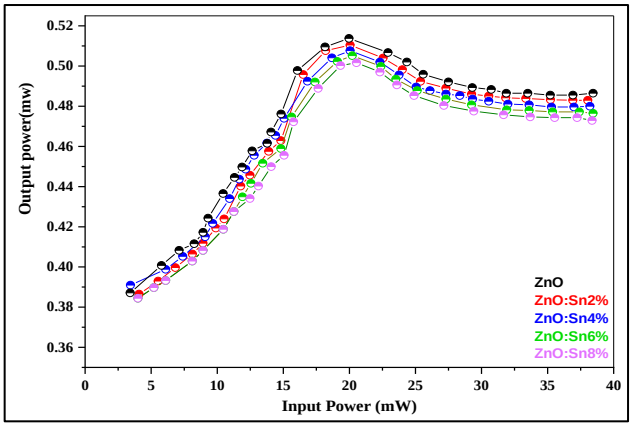

Figure 10. Optical limiting for pure ZnO and Sn doped ZnO with a various concentration.

Conclusion

In this work, Pure ZnO and Sn doped ZnO with various volume concentrations of 2, 4, 6, and 8 V/V% have been prepared by using the low cost and simple sol-gel method. The transmutation and absorption of pure and Sn doped ZnO were in the visible region. The band gap of ZnO value was 3.4 eV where it's value Sn doped ZnO for decreased with increasing concentration to 3.1eV and redshift. This material it's used as optical limiting that power output changes linearly with the input power when the power is low for all concentrations. However when the input power increased, the linear relationship change to be a curve between them starts with a slope from the linear relationship, in which case the power represents the limiting threshold.

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