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Enhanced the Physical Properties of Thin Films by Doping Zinc Oxide with Tin Prepared by the Pyrolysis Technique

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ABSTRACT

Spray pyrolysis was used in this work to create un-doped ZnO and Sn-doped films with varying mass fractions (2, 4, 6, and 8wt.%) of doping on a glass substrate. The effect of Sn doping on the optical and structural characteristics of the produced thin films was investigated. All of the films were polycrystalline and possessed a structure of hexagonal wurtzite with a preference for orientation along the (002) plane, according to XRD investigations. The peak intensity (002) for 6 wt% is higher than all of the chosen doping ratios. Except for the 8% that was (21) nm, the grain size (D) increased from (22-26) nm as the percentage of Sn doping increased. In order to evaluate the optical characteristics, the absorption and transmittance spectra were recorded in different wavelength ranges of 380-900 nm. This shows that, compared to the un-doped film, the absorbance decreases as the amount of doped tin increases. When the doping ratio ranged from (0 - 8) wt%, the optical energy gap was (3.23-3.59) eV. The transmittance increases with the percentage of Sn doping, reaching its maximum value (72%) at (8%) doping.

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تعزيز الخواص الفيزيائية للأغشية الرقيقة عن بواسطة تشويب أكسيد الزنك بالقصدير المحضر بتقنية التحلل الحراري

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الـــخُــلاصـــة

تم استخدام تقنية النحلل الحراري الكيميائي بالرش لإنشاء الأغشية الرقيقة *ZnO* غير المشوبة و المشوبة بالعنصر *Sn*، مع نسب وزنية مختلفة لـ *Sn* على القواعد الزجاجية. تم دراسة تأثير التشويب *Sn* على الخصائص التركيبية والبصرية للأغشية الرقيقة المحضرة مختبريا. وقد تم التحقيق في كيفية تأثير التشويب الأغشية الرقيقة مع *Sn* على خصائصها

الكلمات المفتاحية:

اوكسيد الخارصين
القصدير
الأغشية الرقيقة
التحلل الحراري بالرش
الاشعة السينية

التركيبية وفقًا لنتائج اختبارات انحراف الاشعة السينية حيث تبين انه كانت جميع الأغشية الرقيقة متعددة البلورات ولها بنية سداسية متراصة مع اتجاه السائد(٠٠٢) على طول المستوى. شدة الاتجاه (٠٠٢) لنسبة التشويب ٦٪ أعلى من جميع نسب التشويب المختارة. باستثناء النسبة ٨٪ التي كانت (٢١) نانومتر ، زاد حجم الحبيبي (D) من (٢٢-٢٦) نانومتر مع زيادة نسبة التشويب. من أجل تقييم الخصائص البصرية ، تم حصول على طيفي اختبارات الامتصاصية والنفاذية في مدى أطوال موجية مختلفة ولمدى الأطوال الموجية (٣٨٠-٩٠٠ nm). هذا يدل على أنه ، مقارنة بالأغشية غير المشوبة تقل الامتصاصية مع زيادة نسية القصدير المشوبة. عندما تراوحت نسبة التشويب (٠ - ٨)٪ كانت فجوة الطاقة الضوئية (٣.٢٣-٣.٥٩) الكترون فولت.اما قيمة النفاذية فأنها تزداد مع نسبة التشويب لتصل إلى أقصى حد لها (٧٢٪) عند (٨٪) من التشويب.

1. INTRODUCTION

Thin films were first created by several scientists in the 2nd half of the 17th century due to their significance in both theoretical and practical solid-state physics research [1]. Thin films can be manufactured using a variety of techniques, and each technique has unique characteristics that help it to achieve its intended function. In this study, we prepared thin un-doped ZnO films and doped ZnO films with various mass fractions of Sn (2, 4, 6, and 8wt%) using the spray pyrolysis deposit technique [2]. This method is summarized by the interaction between the hot substrate and the atoms of the materials deposited on the substrate. The materials in this way undergo pyrolysis deposition and then oxidize forming several layers on the substrate. Several factors, such as the period of spraying, the number of sprays, and the fraction of spray concentration in their solutions, can be modified to affect the thickness of the thin film. When compared to thin films produced utilizing other techniques, these films will have strong adhesion and be homogeneous to the substrate [3]. One of the compounds of zinc is un-doped ZnO, which is also a semi-conducting material. It belongs to the group of transparent conducting oxides (TCOs) that, in addition to possessing good electrical conductivity (22.6 S.cm^{-1}), exhibit increased transmittance in the visible range of the spectrum and reflection in the infrared regions [4]. Chemically, ZnO can be produced from zinc salts, by burning the element zinc in the air, or by thermally cracking its carbons or nitrates. It is a solid white compound that turns yellow when heated due to lattice distortions. On top of that, unlike cadmium compounds, it is non-toxic. In either alcohol or water, it does not dissolve. Alkali hydroxides, acetic acid, ammonium carbonate, ammonia, and mineral acids, including acetic acid, dissolve it. As a result, the compound is amphoteric oxide [5]. Sn is a white metal that is produced from the significant mineral cassiterite [6].

According to the research study by K. Salam et al. [7] by using the spray pyrolysis process, it was possible to successfully produce un-doped, Al-doped, and Sn-Al co-doped ZnO thin films. At 350 °C, thin films were deposited onto glass substrates. The Al-Sn doping had no effect on the structure of ZnO hexagonal Wurtzite, according to XRD. While the Sn-Al co-doped ZnO films became disoriented with a small loss of crystallinity, the resulting un-doped ZnO films were well oriented along the preferred (002) crystallographic plane. The band gap energy increased from 3.23 to 3.30 eV, and the average transmittance increased from 65% to 81%, according to the optical measurement.

A. Abdel-Galil et al. [8] utilized spray pyrolysis to develop nanostructured ZnO and

F:ZnO thin films at 400 °C on soda-lime glass substrates. Spray pyrolysis is a useful, cost-effective deposition approach. The XRD technique was used to investigate the crystalline surface and structural morphology of thin films as they formed. The deposited films' wurtzite hexagonal structure, with a mean grain size in the nanometer range, was revealed by XRD patterns. The F-doping content increases the average grain size of the ZnO film, according to XRD analysis. According to the transmission spectra of the deposited thin films, optical characteristics like the absorption coefficient and optical bandgap are determined. The F doping level somewhat reduced the ZnO film's direct optical band gap.

The researchers studied by K. Salim et al. [9] at 35 ± 10 ^{0}C, pyrolysis spray method was used to deposit ZnO thin films on glass substrates. For the objective of obtaining a bilayer-thin ZnO:SnO_2, a very thin sheet of SnO_2 was deposited beneath ZnO films. The bilayer underwent thermal annealing for a period of 1 hour at 350 0C. Thin films made of monolayer ZnO and ZnO:SnO_2 were examined for their structural, optical, and electrical characteristics. ZnO films' hexagonal wurtzite structure and ZnO:SnO_2 bilayer films' hexagonal tetragonal structure were both confirmed by XRD. The optical measurement revealed that for annealed ZnO:SnO_2 bilayer films, the average transmittance increased from 81% to 94%. For annealed ZnO:SnO_2 bilayer films, the optical band gap ranged from 3.22 to 3.31 eV.

The researchers Y. Bouznit et al. [10] used co-spray to create A:ZnO films that were Al-doped. The resulting films were evaluated using XRD. XRD analysis revealed that all films had a single-phase hexagonal Würtzite structure. With a straight optical band gap spanning from 3.24 to 3.28 eV, A:ZnO films demonstrated transparency in the visible range of greater than 80%. For all samples, a wide absorption band caused by the ZnO bond's stretching vibration at 410 cm^{-1} was observed.

The aim of the study is to create un-doped ZnO and ZnO:Sn-doped films with varying mass fractions using the spray pyrolysis method, deposit them on glass substrates at a limited temperature, and then investigate their structural characteristics using XRD measurements. Research also aims to investigate the characteristics of the prepared thin films, including their transmittance and absorbance, and to determine the optical energy gap and Urbach energy. Due to its practical uses in the production of solar cells, it is important to obtain a thin film with high specifications and to enhance its properties in the visible spectrum region.

2. MATERIALS AND METHODS

The Chemical Spray Pyrolysis System consists of a range of fundamental equipment for preparing thin films on various substrates such as: the spray nozzle, holder of sprayer nozzle, air pump, electrical heater and thermocouple. The substrate was made from typical glass with dimensions of 3 x 3 x 0.2 cm. An aqueous zinc acetate solution with a (0.2M) mixture was prepared by dissolving (2.2354 g) of it in (150 ml), adding a few drops of concentrated hydrochloric acid to enhance the clarity and homogeneity, and spraying the solution and depositing it on the hot glass substrate at (400 ^{o}C) to produce a ZnO film. Aqueous $SnCl_4$ (Stanic Chloride Hydrated) were applied to prepare ZnO doped with Sn films ($SnCl_4.5H_2O$) from (Limited Poole-England-General Purpose Reagent BDH) company, to prepare the solution, dissolved (3.4868 g) of $SnCl_4$ in (150 ml) of water, and then introduced to the zinc acetate solution in different volume proportions, and the solution was mixed using the same previous technique.

The glass substrate was positioned perpendicular to the heater in the centre below the sprayer. The ZnO layers were grown by spraying a solution above a heated glass substrate at 500 °C; the layers were stable due to the heat. The spray device's solution-dropping valve is opened, and the amount of flowing solution is controlled from which the spray rate is calculated. A heat-resistant beaker is placed at the bottom of the spray device to collect the solution drop and stop large drops from falling on the substrate, which could break the substrate or deform the thin film. The air pump is opened, the beaker is moved away, and then the deposition process begins, with the spraying time set. The substrate should be left on the electric heater for an hour to allow the prepared films to complete the oxidation and crystal growth processes and to avoid breaking the thin film due to the temperature difference.

Optical measurements were carried out by measuring the absorbance and transmittance spectroscopy, by using a spectrophotometer (Shimadzu UV-VIS 1800) for optical measurements in (1200–180 nm) of the wavelength ranges. In order to analyze the nature of the undoped ZnO thin film material and the effect of different doping ratios on the crystal structure of the prepared films, the XRD pattern of the films (Shimadzu XRD-7000) was studied.

3. RESULTS AND DISCUSSION

3.1. Structural Properties

The X-ray diffraction analysis of the produced thin films, which are undoped and doped with Sn at different doping ratios (2, 4, 6, and 8 wt%), indicated that they are polycrystalline structure and of the hexagonal wurtzite type [11]. All the prepared thin film XRD curves are shown in figure (1), and the sharp peaks that appear when XRD beams are scattered at various angles on the thin films were detected. These peaks penetrate into various levels, such as (100, 110, 002, 101 and 102) so that they are allowed to interfere constructively when the Wulff–Bragg condition is satisfied. We can observe that the dominant peak was (002). These results are consistent with JCPDS 36-1451 and are shown in tables 1. The results indicated that the intensity of the (002) peak decreases with the increase in the mass fractions of doped Sn compared to the un-doped ZnO films, and this demonstrates that the decrease in FWHM caused the crystallization rate to rise. The peak intensity (002) for 6 wt% is greater than all of the selected doping ratios because the rise in the height of some peaks (4 and 6 wt%) indicates an increase in crystallization of the thin films and a decrease in crystal imperfections by providing the potential energy for the materials' atoms to reposition themselves in the lattice and FWHM decreases. Regarding the doping with 8wt%, FWHM increases, and we observed an increase in the crystallization of the two planes (101) and (100) which may be attributed to the appearance of crystal defects.

The interfacial distance between the crystalline planes (d) was calculated using Bragg's law:

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

The Scherrer formula was used to determine the grain size (D):

$$D = 0.94\lambda/\beta \cos\theta \ldots\ldots\ldots.(2)$$

Where

n: diffraction order, λ=1.541Å of the X-ray wavelength, θ: Bragg diffraction angle, $\beta-$ Full Width at Half Maximum (FWHM). It was found that it increases with increasing doping with tin, because the curve width at the centre of the peak decreases and thus the particle size increases, the width of the curve at the peak's center is inversely proportional to the particle size, but the particle size decreases at the impurity percentage of 8% as shown in table (1):

Table (1): The JCPDS card and the results of the XRD of un-doped and ZnO:Sn thin films doped with different ratios

	2θ (degree)	d (Å)	hkl	FWHM (rad)	*D* (nm)		2θ (degree)	d (Å)	hkl	FWHM (rad)	D (nm)
ZnO (JCPDS)	31.7690	2.8143	100			*0 wt%. Sn*	31.8023	2.8389	100		
	34.4210	2.6033	002				34.2410	2.6131	002	0.0062	22
	36.2520	2.4759	101				36.2837	2.4860	101		
	47.5380	1.9111	102				47.2673	1.9169	102		
	56.6020	1.6247	110				56.2289	1.6319	110		
2 wt%. Sn	31.4258	2.8545	100			*4 wt%. Sn*	31.6203	2.8211	100		
	34.2553	2.6334	002	0.006	23		34.4722	2.6059	002	0.0053	26
	35.7332	2.5067	101				36.3542	2.4819	101		
	47.1735	1.9276	102				47.4254	1.9120	102		
	56.1257	1.6334	110				56.2756	1.6329	110		
6 wt%. Sn	31.1842	2.8543	100			*8 wt%. Sn*	31.5874	2.8221	100		
	33.8833	2.6360	002	0.0047	29		34.7637	2.6069	002	0.0065	21
	35.6908	2.5058	101				36.3507	2.4832	101		
	47.1508	1.9289	102				47.2343	1.9149	102		
	56.3374	1.6319	110				56.5706	1.6281	110		

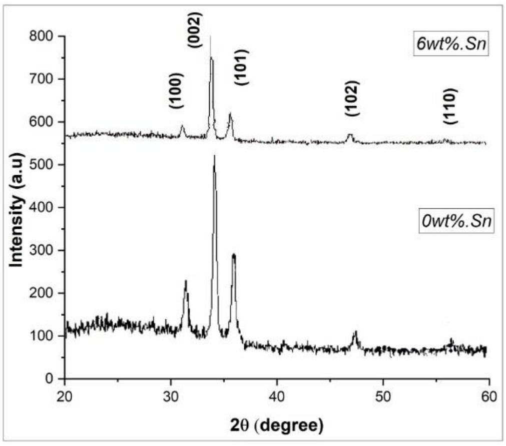

Figure (1-a): XRD comparison of ZnO:Sn thin films doped with 0 and 6wt%.

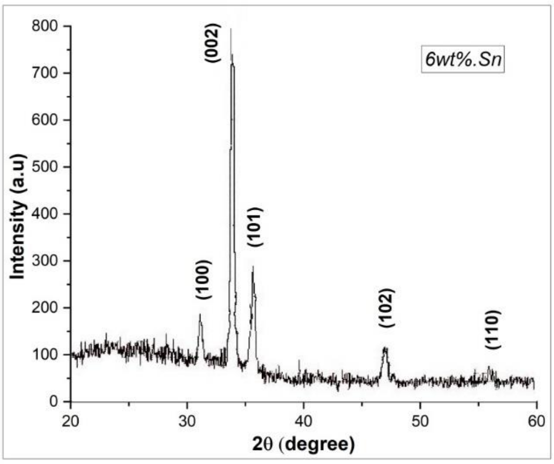

Figure (1-d): XRD of ZnO:Sn thin films doped with 6wt%.

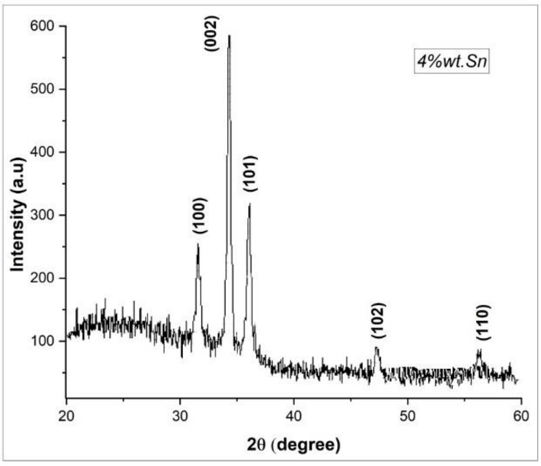

Figure (1-c): XRD of ZnO:Sn thin films doped with 4wt%.

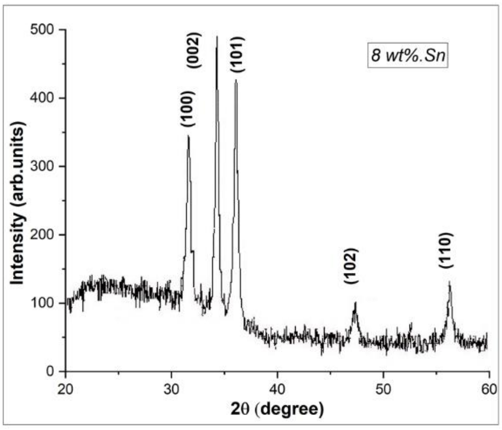

Figure (1-e): XRD of ZnO:Sn thin films doped with 8wt%.

3.2. Optical Properties

Figures (2) shows that all thin films absorption is greatest at the basic absorption edge (short wavelengths), indicating that the thin film exhibited high absorbance at short wavelengths. The absorption measurements were performed in the wavelength ranges of 380-900 nm. This indicates that the thin film exhibited high absorbance in short wavelengths, and it decreased with increasing wavelength, which indicates that the electron could not be excited by the incident photon to move it from the valence to the conduction band. Additionally, the absorbance falls as the amount of doped tin increases in comparison to un-doping films [12].

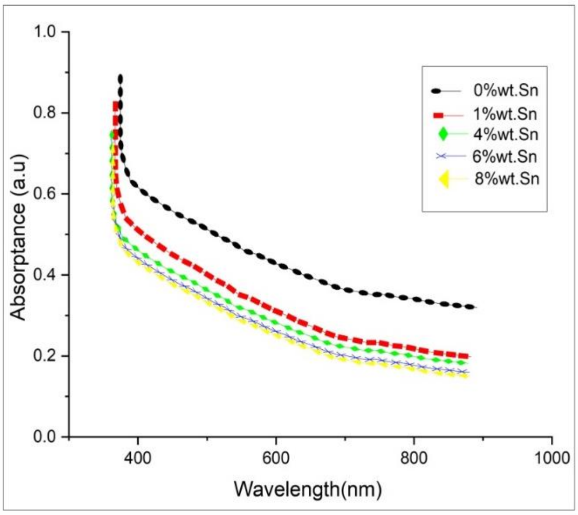

Figure (2): The absorbance as a function of the wavelength of un-doped and ZnO:Sn thin films doped with different ratios.

Concerning the transmittance spectrum as in figure (3), it demonstrated an opposite behaviour to the absorption, as the transmittance of un-doped and ZnO:Sn thin films doped is the least possible at the fundamental absorption edge (short wavelengths), and transmittance rises as wavelength increases and then shows a sharp increase until it stabilizes after the wavelength in the visible and near-infrared region but when doping, the transmittance rises as the doping rate increases, and the greatest transmittance at 8wt% doping.

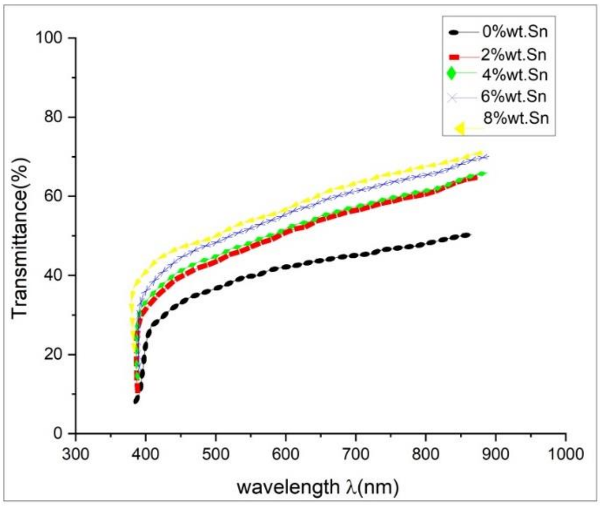

Figure (3): The transmittance as a function of the wavelength of un-doped and ZnO:Sn thin films doped with different ratios.

Figure (4) shows that, for all doping ratios, the doping of zinc oxide increased the optical energy gap, which meant that the absorption edge was displaced away from high energies as a result of the doping. The Bureshtain-Moss shift [13] can account for this rise, and since the levels close to the conduction band are filled with electrons, the electrons require more energy to jump, which gives the appearance that the energy gap is increasing.

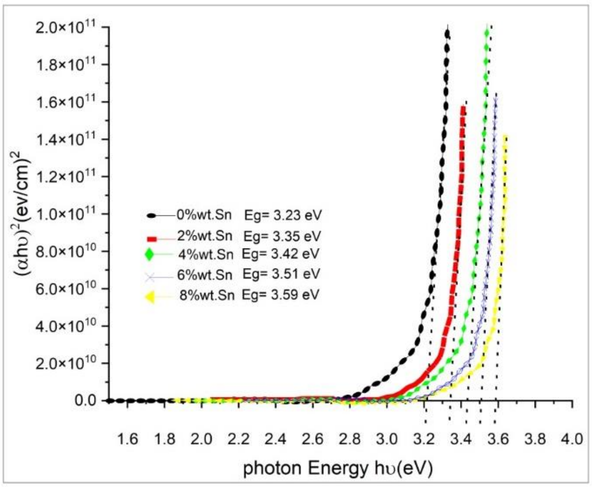

Figure (4): The optical energy gap as a function of the photon energy of un-doped and ZnO:Sn thin films doped with different ratios.

The energy of the Urbach tails for un-doped and ZnO:Sn thin films doped was shown in figure (5), where it can be seen that its value decreases as the percentage of doping with different ratios increases. This is because the number of local energy levels in the optical energy band gap decreases, and thus the number of Urbach tails decreases, and this leads to an increase in the optical energy band gap. This increase can be attributed to the Bureshtain-Moss effect [13].

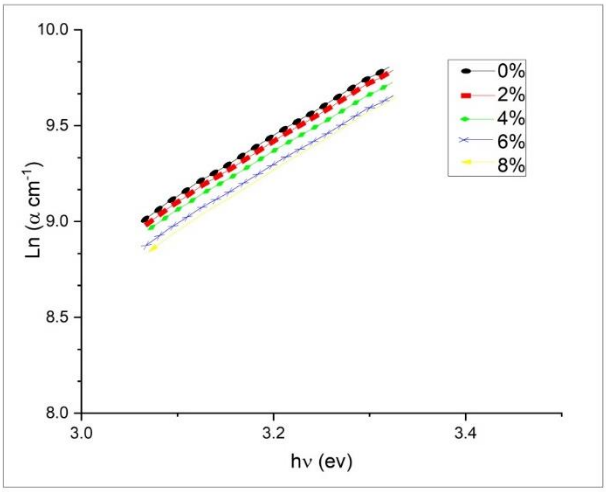

Figure (5): The energy of the Urbach as a function of the doped thin ZnO.

4. CONCLUSION

The polycrystalline and hexagonal zinc oxide films of the wurtzite type, with undoped and tin-doped structures, were deposited on glass substrates produced by the pyrolysis process, according to X-ray diffraction observations. The XRD results showed that the thin films of un-doped ZnO and Sn doped, increased doping led to an increase in crystallization by small mass fractions, with the doped films maintaining the hexagonal wurtzite structure for all doping ratios. According to the results of the optical tests, the electronic transitions had a direct electronic transitional character. Optical measurements result in increasing the optical energy band gap by increasing the percentage of doping with Sn.

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