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The Effect of Doped and Undoped ZnO-V Thin Films on Nanostructural and Optical Properties

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ABSTRACT

The effect of doping with vanadium (V) at various weight fractions on the nanostructural and optical characteristics was evaluated. Thin films of zinc oxide (ZnO) were produced using the chemical spray pyrolysis (SP) process and deposited on a hot glass substrate at a temperature of 500°C and (500±40 nm) film thickness is an important feature in the applications and physical properties of thin films using the Gravimetric method.

Atomic force microscopy (AFM) images indicated that there was a difference in the nature of the produced thin film morphologies. All of the obtained films are polycrystalline with a single crystallization phase and have a structure of the wurtzite hexagonal type (002) plane, according to the X-ray diffraction (XRD) analyses except for doped films with a proportion of (4%) which was (101) plane .

By determining the optical energy gap data, the nature and characteristics of electronic transitions in the prepared films were investigated. V-doping of ZnO films modifies the values of all optical curves in the visible and infrared spectrums depending on the transmittance and absorbance spectra.

Keywords: Thin films, XRD, AFM, ZnO-V.

INTRODUCTION

Thin-film technology is one of the most significant techniques that contributed to the development of the study of semiconductors and gave a clear idea of many of their physical and chemical properties that cannot be studied while they are in their bulk state. Thin-film physics is one of the important branches of solid-state physics and has become a branch in its own right. This branch is concerned with micro-or even nano-devices with extremely thin walls (Polus, 2021).

The thin film preparation methods have developed and become highly accurate in determining the thickness and homogeneity of the thin film, and the use of these methods depends on several factors; the type of material used, the field of use of the prepared films, and the cost of preparation. The chemical spray pyrolysis (SP) technique was utilized in this research to produce films of ZnO that were both undoped and V-doped. The strong base adhesion of the thin films produced in this method gives them an advantage for studying a variety of physical properties and have good specifications (Nasir, 2012).

Due to their characteristics that make them suitable for electro-optical devices such as photovoltaic devices, organic light-emitting diodes, and as permeable layers in the contrast junction in solar cells, chromium-electric devices, and gas sensors, numerous ZnO films have attracted the interest of many researchers in the field of optoelectronics (Benhaliliba, 2021).

Vanadium is a part of the transition metal group. Its pentavalent character and chemical symbol (V) inform us that it has a broad range of oxidation states. It is a rare, soft and pliable element with a silvery-white color that is utilized to produce specific alloys by combining it with specific salts (Volkov *et al.*, 2020). Chemical spray pyrolysis is characterized by strong adhesion of the prepared materials to the base, and have good specifications so that be used in many physical properties, and used in solar cell and sensor applications (Workie *et al.*, 2023). The aim is to study the nature and type of electronic transitions of thin films prepared through the effect of vanadium doping on the structural properties of thin films and the benefiting from the new properties of the doped films in electro-optical applications and solar cell windows from the extent of the effect of vanadium doping on the optical properties of zinc oxide (ZnO) films.

MATERIALS AND METHODS

ZnO thin films were produced utilizing aqueous zinc acetate, which was produced at a concentration of 0.5 M and has a molecular weight of 183.48 g/mol. This zinc acetate is produced by Charlo Co. (Spain).

Preparation

Zinc acetate at a concentration of 0.5 M dissolved in 200 ml distilled water, continuously stirred for 20 min with a magnetic stirrer, and heated to function as a catalyst to produce a clear and homogeneous solution. A thin film ZnO was deposited after the solution was sprayed on the heated glass substrate using the SP technique.

A well-homogeneous solution of Vanadium dichloride (VCl_2), with a molecular weight of 121.847 g/mol, is dissolved in 200 ml of distilled water and continuously stirred for 25 min using a magnetic stirrer. This solution is then used to manufacture V-doped ZnO films at a concentration of 0.5 M.

Then a solution of VCl_2 is added to the zinc acetate solution in the required weight fraction 0, 1, 4, 6 and 8wt% and the solution is stirred well by the magnetic stirrer for 20 min to ensure good homogeneity. ZnO thin films doped with V were deposited as a result of the SP procedure after the homogenous solution was sprayed at 500 ^{o}C on the glass substrate. The electronic balance (Mettler AS-200) used to measure the film thickness by the Gravimetric method, with a sensitivity of (10^{-5}g), by weighing the glass bases before and after the deposition procedure.

The spray process continues at the same rate until the specified thickness is obtained. Thin films are deposited with a solution spray 10 s followed by a pause 2 min to allow the glass substrate to return to the specified decomposition temperature. To achieve the best film uniformity, the amount of solution spraying was calibrated, and the glass substrate was rotated during the spray process. To complete the oxidation and crystal growth processes of the produced films and prevent breaking of the glass substrate owing to temperature differences, the electric heater is shut off when the spray process is complete, and the glass substrate is left over it until it reaches room temperature.

Characteristics

Applying a two-beam spectrometer of the Shimadzu UV-1650PC UV-Visible spectrophotometer, the optical analyses included determining the absorbance and transmittance spectroscopy of the wavelength range (850–250 nm). As a function of wavelength, measure the values of both transmittance and absorbance.

To evaluate the form and character of crystallization of the produced thin film, the crystal structure of each film prepared using the XRD type PHILIPS-PW 1830/40 technology was determined.

The obtained samples were investigated using an SPM-AA3000 type atomic force microscope (AFM). The surface roughness and its rate (RMS), as well as the size and number of the grains, are all very determined using this technique.

RESULTS AND DISCUSSION

The doping process with V clearly effects the surface properties of the produced ZnO films, as shown by the images and AFM data, the surface structures of the doped films and for all doped ratios with dimensions 10x10 μm^2. In comparison to the surface morphology of undoped films, the surface grains of doped films are more homogenous with a decrease in their roughness values according to the root mean square (RMS) values, as indicated in the (Table 1) and Fig. (1). According to these results, the average grain size of the surface morphology of the produced ZnO films decreased with an increase in the percentage of V-doping, which is consistent with the results of the researchers' study (Li-Wei *et al.*, 2009). These results correspond with those obtained from X-ray diffraction calculations used to determine the rate of gran size with the results of RMS and observation of the images, we conclude the appearance of some nanostructures of the prepared films.

Table (1): Average surface roughness and root mean square measured by AFM roughness mean values for all prepared films

RMS (nm)	Surface roughness (nm)	Thin films
74.10	53.18	ZnO (0%)
32.10	25.42	ZnO-V (1%)
25.60	19.90	ZnO-V (4%)
16.10	11.98	ZnO-V (6%)
10.13	8.10	ZnO-V (8%)

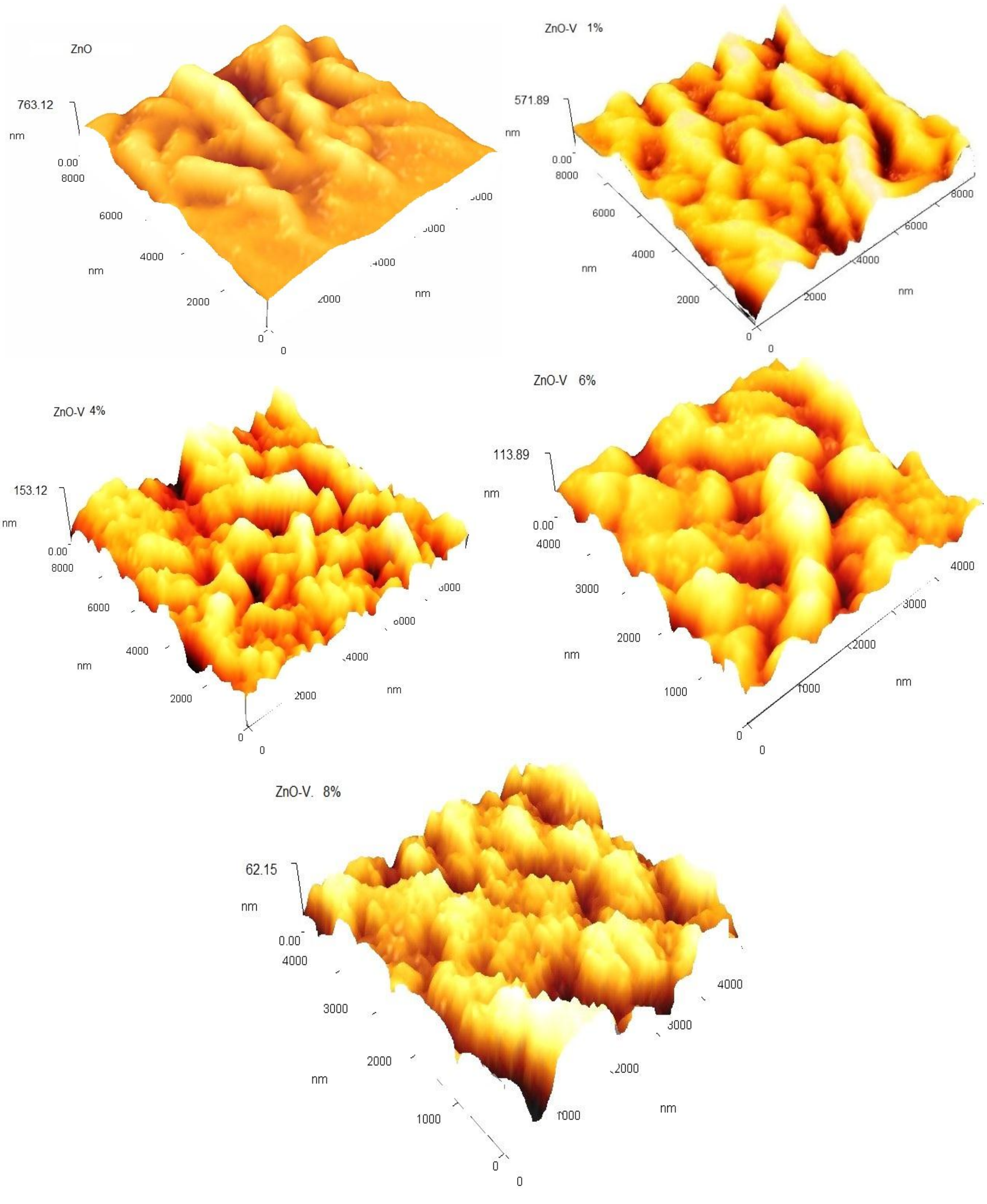

Fig. 1: AFM surface morphology of undoped and V-doped ZnO films with different doping ratios.

All of the prepared (undoped and V-doped) ZnO films have the polycrystalline structure of the wurtzite hexagonal type, according to the results of the XRD investigation, which were compared to the international label of ZnO (ICDD 36-1451). The most prevalent direction of film crystallization was (002) plane for all films with the exception of those with a doped rate of 4wt%, which was (101) plane. The XRD curve of the V-doped films shows that, in comparison to the diffraction form of the undoped ZnO films, the peak intensity decreases with an increase in FWHM at the middle of the maximum peak for all doping ratios. This indicates that when the percentage of V-doped films increases, the degree of ZnO films' crystallinity decreased (Kangarlou,2019). Diffraction pattern of doped and undoped zinc oxide films around 2θ values observed that there is a slight fluctuation in the peak positions. At all doping ratios, as all films have one crystal phase and no other crystal phase appears in the diffraction pattern.

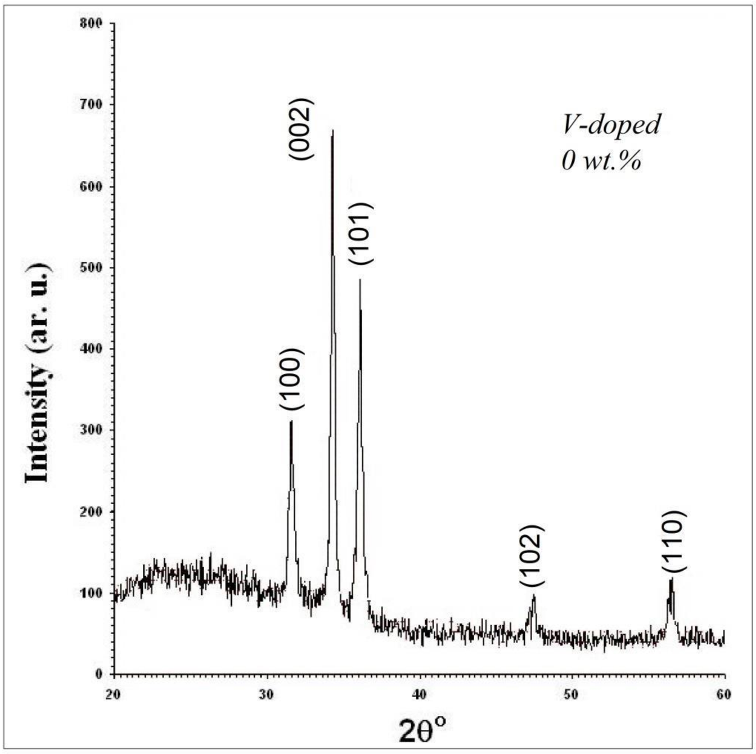

Fig. (2-a): XRD of undoped ZnO thin films.

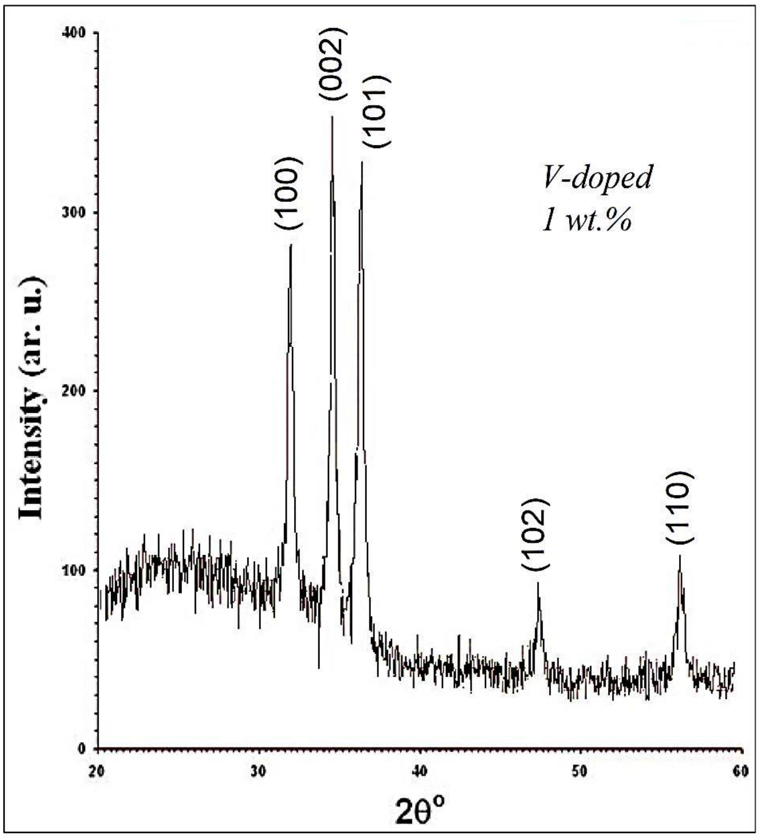

Fig. (2-b): XRD of ZnO thin films V- doped 1wt%.

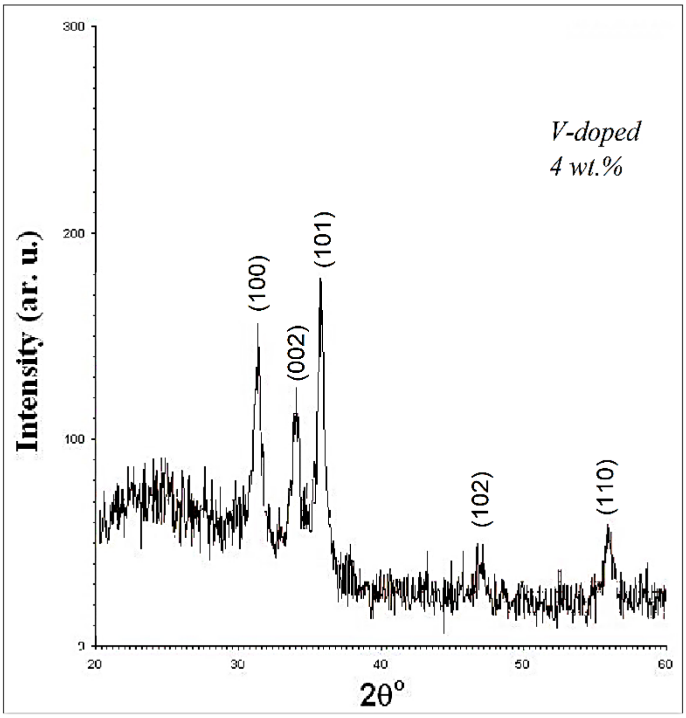

Fig. (2-c): XRD of ZnO thin films V-doped 4wt%.

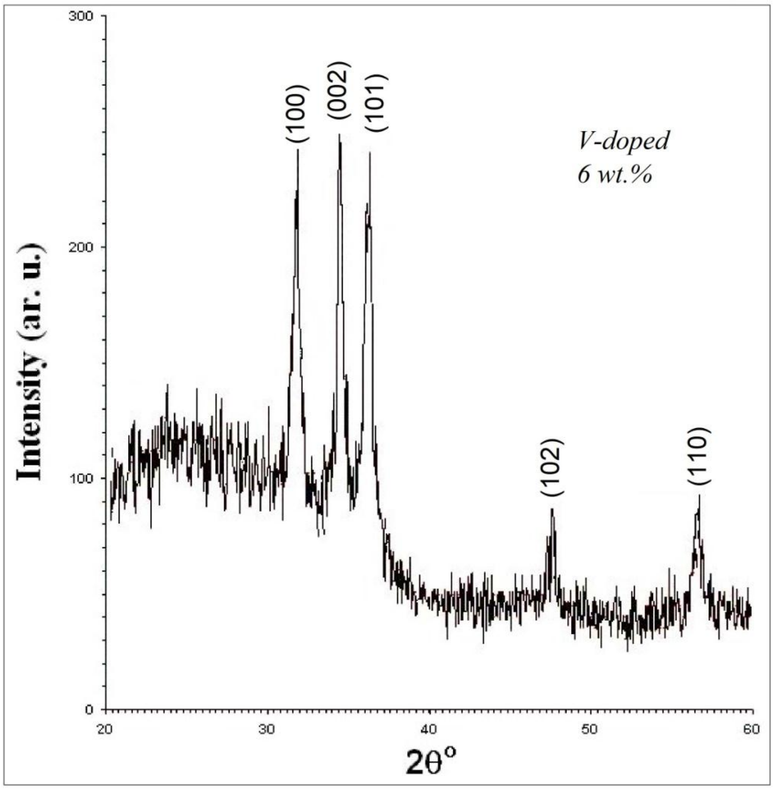

Fig. (2-d): XRD of ZnO thin films V-doped 6wt%.

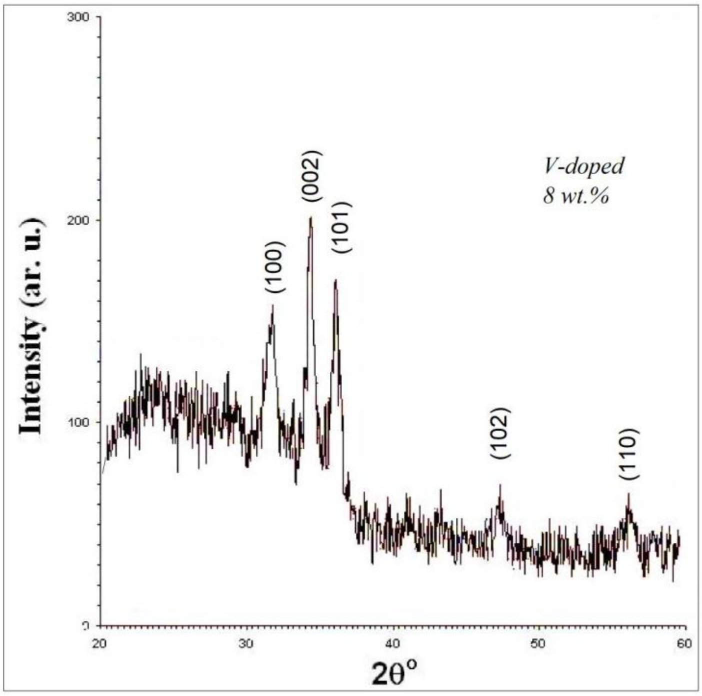

Fig. (2-e): XRD of ZnO thin films V-doped 8wt%.

The absorbance of the undoped ZnO films decreases with increasing wavelength, as shown by the absorbance spectrum curve in Fig. (3) because the incident photon's energy is less than the semiconductor's optical energy gap, it is physically impossible for it to excite the electron and jump it from the valence band to the conduction band. The rapid increase in absorbance values at high energies is attributable to the basic absorption processes carried on by the transfer of electrons from the valence band to the conduction band. The absorbance for all doping ratios in the visible and infrared ranges decreased as a result of V-doping. This is caused by the creation of donor levels as a result of V-doping within the energy gap near to the conduction band, which decrease the energy gap of the doping films and causes the absorption edge to shift towards long wavelengths, increasing the absorption of the composite material in the visible region (Tewari, 2011). For the doped state (8%), the absorption decreased in the infrared and visible spectrum regions, which caused the absorption edge to shift toward short wavelengths and increase the optical energy gap.

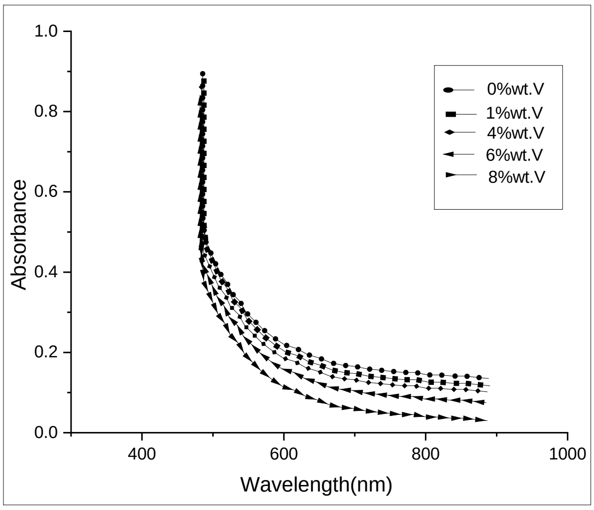

Fig. (3): The absorbance as a function of the wavelength of undoped and V-doped ZnO thin films with different doping ratios.

As shown in the Fig. (4), optical measurements revealed that all of the produced thin films have a high transmittance in the visible and near-infrared ranges. For all produced thin films, the transmittance value rises as the wavelength increases. When V-doping is used, the transmittance of the doped thin films rises in the visible and infrared areas compared to the transmittance of undoped thin films for all doping ratios. As compared to undoped films, the doped films' transmittance values in the visible region throughout the wavelength range are 1, 4, and 6wt% lower. The lattice deformation, scattering centers, and photon energy effects change if the thin film transmittance increases or decreases (Wang *et al.* 2009).

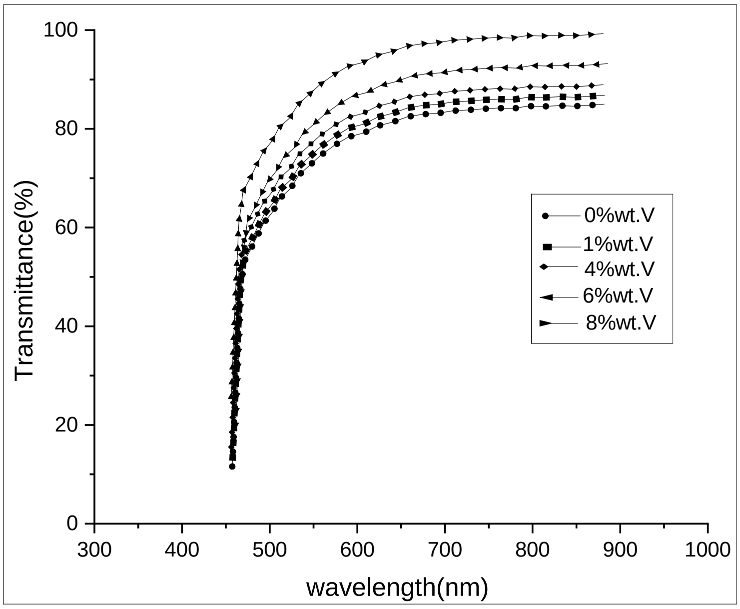

Fig. (4): The transmittance as a function of the wavelength of undoped and V-doped ZnO thin films with different doping ratios.

The relationship between $(\alpha h\nu)^2$ and the energy of the incident photon (hν) can be used to determine the energy gap. The optical energy gap for the allowed direct transition of the undoped zinc oxide films was 3.2 eV, and it decreased for all doping ratios excluding the doping 8wt% the energy gap increases in comparison to that of the undoped films due to the formation of donor levels below the conduction band as a result of the doping as shown in the Fig. (5). The optical energy gap values of the doping films have decreased led to levels are prepared to receive electrons inside the optical energy gap that absorb low-energy photons (shifting the absorption edge towards long wavelengths), which results in a decrease in the optical power gap (Soumahoro *et al.* 2010). The increase in the value of the optical energy gap of the doped films by (8%) leads to blocking the electronic transitions to these levels and thus to increasing the optical energy gap because the Fermi level is shifted towards the conduction band, which leads to occupying all the levels confined at the bottom of the conduction band with electrons.

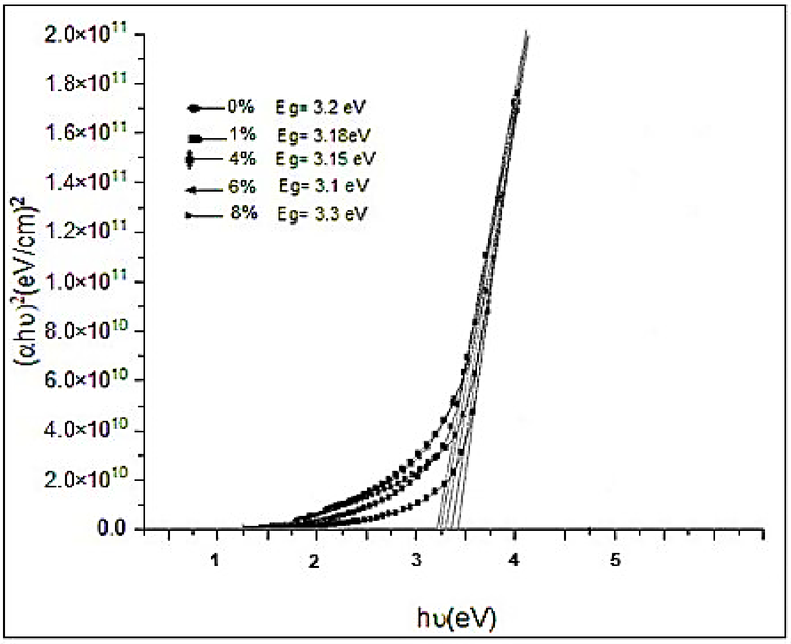

Fig. (5): The optical energy gap of undoped and V-doped ZnO films with different doping ratios.

CONCLUSIONS

The doping of ZnO with various ratios of V led to a reduction in the crystallization of the films, with all the doped films maintaining the wurtzite hexagonal structure and all the doping ratios. The absorption edge is sharp, which indicates that all the prepared films possess a polycrystalline structure. The optical properties of the energy gap of the V-doped films are in agreement with the optical properties of the energy gap of the ZnO films doped with transition elements and for low doping ratios (decreasing the value of the energy gap with the increase in the doping ratios). According to AFM measurements, 1% V-doping produced high-quality thin film morphologies. The absorption spectrum curve was decreased with increasing wavelength of the undoped ZnO films. V-doping led to a decrease in the absorbance values of the doped films and of all doping ratios in the visible and infrared regions. The prepared films are suitable for use in solar cells since the transmittance in the visible region is almost constant. The transmittance spectrum shows that the greatest stable transmittance of the prepared films was recorded in the infrared region, which confirms the importance of these films in optoelectronics applications.

REFERENCES

Benhaliliba, M. (2021). ZnO a multifunctional material: Physical properties, spectroscopic ellipsometry and surface examination. *Optik*, **241**(1-6). DOI: 10.1016/j.ijleo.2021.167197

Kangarlou, H. (2019). Production of zinc oxide thin films and crystals in different deposition times and investigation of their structural, optical and electronic properties. *Mater. Sci. Poland*, **37**(1), 90-99. DOI:10.2478/msp-2019-0007

Li-Wei, W.; Zheng, X.; Li-Jian, M. (2009). Influence of concentration of vanadium in zinc oxide on structural and optical properties with lower concentration. *Chinese Phys. Lett.*, **26**(7) 077801. DOI: 10.1088/0256-307X/26/7/077801

Nasir, B.; Manssor, M. (2012). Study the physical properties antimony doped zinc oxide thin films Prepared by chemical vapor deposition. **23**(6), 163-179. *Raf. J. Sci.*, DOI: 10.33899/rjs.2012.59641

Polus, T.; Zaker, T. (2021). Nonlinear optical properties of ZnO thin film at low laser intensity using Z-Scan technique. *Raf. J. Sci.*, **30**(4). DOI:10.33899/rjs.2021.69975

Soumahoro, I.; Moubaah, R.; Schmerber, G. (2010). Structural, optical, and magnetic properties of Fe-doped ZnO films prepared by spray pyrolysis method. *Thin Solid Films*, **518**(16), 4593-4596. DOI: 10.1016/j.tsf.2009.12.039

Tewari, S. (2011). Structural, electrical and optical studies on spray-deposited aluminium-doped ZnO thin films. *Pram. J. phys.*,**76**(1), 153-163. DOI:10.1007/s12043-011-0021-7

Volkov, A.; Kologrieva, U. (2020). Vanadium chemical compounds forms in wastes of vanadium pentoxide production. *Mat.*, **13**(21), 4889, DOI: 10.3390/ma13214889

Wang, L.; Meng, L.; Teixeira V. (2009). Structure and optical properties of ZnO:V thin films with different doping concentrations. *Thin Solid Films,* **517**(13) 3721-3725. DOI: 10.1016/j.tsf.2008.12.043

Workie, A.; Ningsih, H.; (2023). A comprehensive review on the spray pyrolysis technique: Historical context, operational factors, classifications, and product applications. *J. Analy. App. Pyr.*, **170**(105915). DOI: 10.1016/j.jaap.2023.105915

تأثير أغشية اوكسيد الخارصين غير المشوبة والمشوبة بالفاناديوم على الخواص البصرية والبنية النانوية

ماهر ناظر عبد الله

قسم الرياضيات/ كلية العلوم/ جامعة ديالى

الملخص

تم تقييم تأثير التشويب مع الفاناديوم بمختلف الكسور الوزنية على الخصائص البصرية والبنية النانوية. تم إنتاج أغشية رقيقة من أكسيد الخارصين باستخدام عملية التحلل الحراري بالرش الكيميائي وترسبت على قاعدة زجاجية ساخنة عند درجة حرارة 500^{+} درجة مئوية وبسمك حوالي (500±40) نانومتر هو سمة مهمة في تطبيقات وخصائص الأغشية الرقيقة باستخدام الطريقة الوزنية.

من خلال صور المجهر الذري للقوة (AFM) إلى وجود اختلاف في طبيعة مورفولوجيا الأغشية الرقيقة المنتجة جميع الاغشية الرقيقة التي تم الحصول عليها متعددة البلورات مع مرحلة تبلور واحدة ولها هيكل من النوع السداسي المرصوص بمستوى (002)، وفقًا لتحليلات حيود الأشعة السينية فيما عدا الاغشية المشوبة بنسبة (4٪) والتي كانت بمستوى (101). أشارت صور مجهر القوة الذرية إلى وجود اختلاف في طبيعة أشكال الاسطح للأغشية الرقيقة المحضرة.

من خلال تحديد بيانات فجوة الطاقة الضوئية، تم دراسة طبيعة وخصائص الانتقالات الإلكترونية في للأغشية الرقيقة المحضرة. يعدل التشويب بالفاناديوم لأغشية اوكسيد الخارصين قيم جميع المنحنيات البصرية في الطيف المرئي والأشعة تحت الحمراء اعتمادًا على أطياف النفاذية والامتصاص.

الكلمات الدالة: الأغشية الرقيقة، انحراف الاشعة السينية، مجهر القوة الذرية، اوكسيد خارصين– فاناديوم.