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Research Article

Effect of doping with In_2O_3 on some properties of ZnO: SnO_2 thin film prepared by thermochemical hydrolysis method and its use in gas sensing applications

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Abstract. The current study aims to prepare thin films from (ZnO: SnO_2) mixture. Undoped membranes (ZnO: SnO_2) dotted with (In_2O_3) and with a percentage of doping (3.5, 7%) based on chemical thermal dissolution (CSP) technology, by depositing them on glass floors at a temperature of 400 degrees Celsius and at a rate of one spray for four seconds in every one minute. To obtain thin films with high homogeneity and transparency, in order to impose a study of the structural properties of the prepared films and the possibility of these films responding as a gas sensor.

1. Introduction

Thin-film technology is one of the most important technologies that deal with systems with very little thickness ranging from tens of nanometers to a few micrometers, which contributed to the development of the study of semiconductors and gave a clear idea about many of the physical properties and crystalline structure of the fabricated membrane material, as well as knowledge of the nature of electronic transitions, and the capacity of their efficiency in The field of scientific and practical application, which led to the development of a technique for producing thin films with good specifications and low cost [1].

Thin films have industrial and technological importance, as they are included in many electronic applications, where many parts of electronic circuits have been replaced, such as rectifiers, capacitors, transistors and digital computers, as well as membranes have been used. In optical applications and in the interference process used in photocopying devices and in coating lenses, mirrors and filters for some wavelengths with special specifications to be used in solar cells, photo cells and detectors in general [2,3] .

Transparent Conducting Oxides (TCOS) are considered one of the most important semiconductors, and they are compound semiconductors consisting of metal combined with oxygen, like ZnO and SnO2, and it is characterized by its high conductivity and optical transmittance [4,5], which made it take a prominent place in theoretical and applied research in physics The solid state has been used in window coatings, thermal mirrors, audio-wave devices, and others [6,7].

2. The method of work

In this research, glass bases of Chinese origin were used with dimensions (2.5 * 2.5) cm

Before starting the process of preparing these membranes, the glass slides were cleaned as follows

1- Wash the glass bases with distilled water for five minutes
2- Put it in ethanol (96%) for five minutes and then wash it with distilled water.
3- The slides were immersed in acetone for five minutes to remove the plankton from the slides after being immersed in distilled water for five minutes.
4- The samples were dried with special paper to get rid of the plankton and impurities that might affect the membrane structure

Thin films (ZnO) were prepared by thermochemical method using zinc chloride hydroxide salt solution (Zinc Chloride Hydrated) and its chemical symbol ($ZnCl_2.2H_2O$). From (Limited Poole-England-General Purpose Reagent BDH) company, the solution was prepared by dissolving (1.7228 g) of it in (100 ml) distilled water (0.1 M) and the solution was mixed well in a flask (150 ml) with the addition of some drops of acid Concentrated Hydrochloric to obtain a clear, plankton-free solution, this solution is placed in the tank of the sprayer. Zinc oxide (ZnO) films can be obtained by spraying the solution onto heated glass bases at a temperature (400 ° C), if the prepared films have a yellow color. The series of thermochemical reactions that lead to obtaining zinc oxide is represented by the following chemical equation:

$$ZnCl_2 + O_2 \xrightarrow[400\,^\circ C]{\Delta} ZnO \downarrow + 2CL_2 \uparrow + O_2 \uparrow$$

Due to the heat a zinc oxide film remains on the base, and it is necessary to place the glass bases on the electric heater for 20-30 minutes to reach the desired temperature before starting the spraying process. As well as placing the glass bases on the electric heater for a period of no less than an hour after completing the spraying process, in order to allow the membranes to complete the oxidation process [8].

It is possible to obtain tin dioxide (SnO_2) films by spraying the solution on hot bases of glass at a temperature of (400 ° C). :-

$$SnCl_4 + 2H_2O \longrightarrow SnO_2 + 4HCl$$

Due to the heat, the tin dioxide film remains on the base, and it is necessary to place the glass bases on the electric heater for at least half an hour to reach the required temperature before starting the spraying process.

It is also necessary to leave the glass bases on the electric heater for an hour after completing the spraying process in order to allow the prepared films to complete the oxidation and crystal growth process .

Table 1 The table shows the volumetric ratios of the films prepared and used in this research

percentage	**ZnO**	**SnO2**	**In2O3**
1- Pure	100	0	0
2- Pure	0	100	0
3- Pure	0	0	100
4- tainted ingot	35%	35%	30%
5- tainted ingot	25%	25%	50%
6- tainted ingot	15%	15%	70%

3. Results and discussion

Structural properties

X-ray diffraction (XRD) to know the nature of the crystal structure, the main crystal phases and the orientation of the films prepared under certain conditions, as well as to determine some structural parameters such as crystal size, curve width of the mid-maximum peak and the distance between levels. The results of the structural examinations showed no membranes(ZnO pure)

Prepared at a temperature of 400 Celsius, these films are polycrystalline, hexagonal compact structure with a number of distinct peaks, namely (100), (002), (101), (102), (110), and (103), and the prevailing trend was the level (002) As in Figure (1), this tendency in the crystallization of ZnO films is attributed to the (Drift) model [9].

Which is called the fastest survival model, and according to this hypothesis, the process of nuclei formation takes several directions in the early stages of membrane growth, and then these start to compete during their growth, so the faster nuclei continue to grow while the growth of the others is successful. The results of (XRD) for (SnO_2 pure) films prepared at (400) Celsius showed that these films are of polycrystalline nature with a quaternary structure, and we note the presence of a number of peaks related to SnO_2 films, which are (110), (200), (220), (301), with a prevailing trend which is the level (110) and this is in agreement with most of the published research for Sno2 membranes prepared by different methods[10,11]

The results of (XRD) also showed that (In_2O_3) pure (In_2O_3) films prepared at a temperature of (400) are polycrystalline with a cubic structure for the levels (222), (411), and (332), with a prevailing trend, which is the level (222), and when comparing these results for the (In_2O_3) with (JCPDS) card (44-1087) the results were in agreement to some extent, and this agrees with what was stated by researcher Sariya and his group [12].

As for the films saturated with In_2O_3 in proportions (3,5 and 7) prepared at a temperature of 400 °C, we find that there are no new peaks for a new formation, and this means that the unit of crystallization peaks has not changed. Significantly, meaning that the activation or mixing did not lead to a significant increase in the peaks formed as a result of crystallization, and that the slight rise in some peaks is an indication of the crystallization visit to the material and the reduction of its crystal defects, which gives it the potential energy of the atoms for covalent rearrangement. crystallization better and better

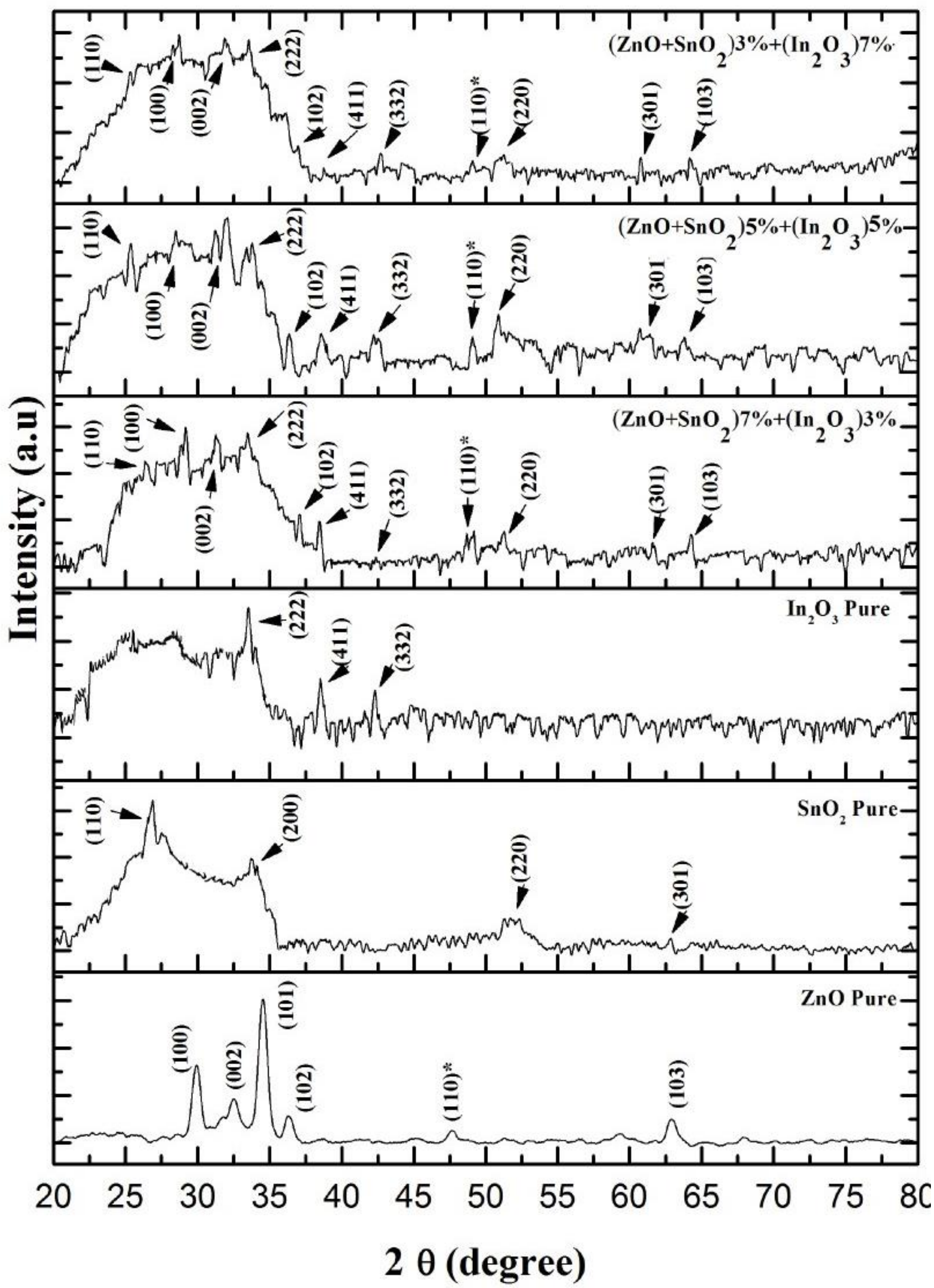


Figure (1) shows the (XRD) results of films prepared at 400°C

Table (2): X-ray diffraction results for pure and spotted films (In_2O_3) with different ratios

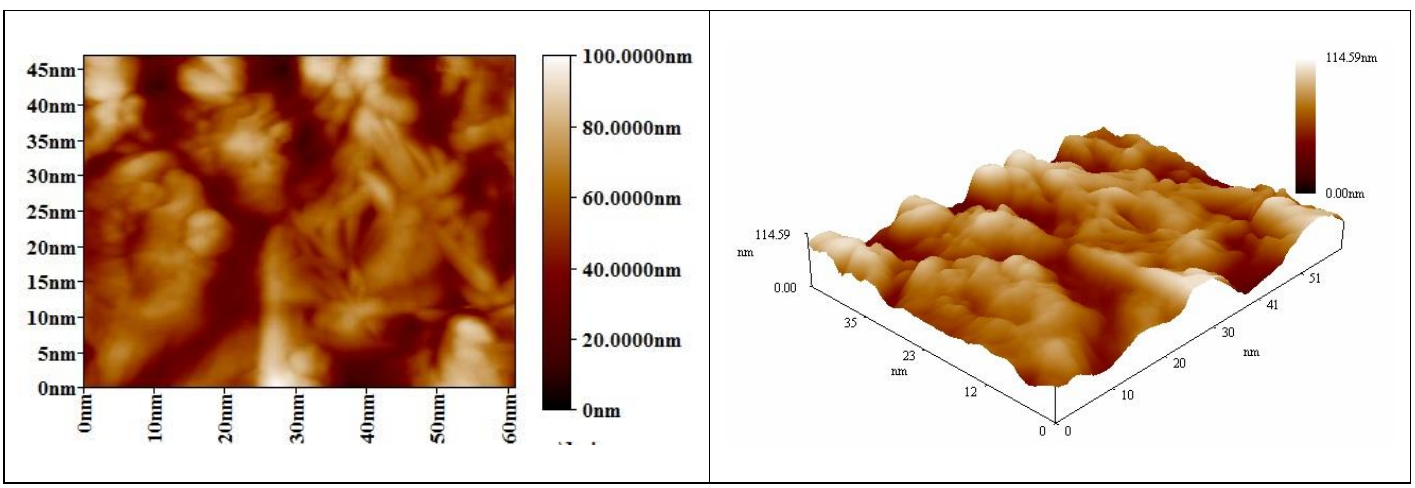
Sample	**hkl**	**2 θ (deg)**	**θ (deg)**	**D(Nm)**	**FwHu**	**D(Nm)**
1. ZnO pure	002	33.358	16.679	0.268281	0.0139	10.8718
2. SnO_2 pure	110	26.6	13.3	0.33471	0.0118	12.6059
3. In_2O_3 pure	222	33.64	16.82	0.266099	0.00837	18.06808
4. 3% In_2O_3	002 110 222	32.15 26.3 34.24	16.075 13.15 17.12	0.27808 0.33846 0.261572	0.01047 0.0069 0.0174	14.38877 21.54466 8.705268
5. 5% In_2O_3	002 110 222	32.17 26 35.24	16.085 13 17.62	0.277915 0.33422 0.25437	0.0097 0.00698 0.0174	15.53175 21.2847 8.729064
6. 7% In_2O_3	002 110 222	32.15 26.34 35.14	16.075 13.17 17.57	0.27808 0.33795 0.25507	0.0071 0.0063 0.0052	21.21837 23.5984 29.20071

Atomic force microscopy (AFM) assay results.

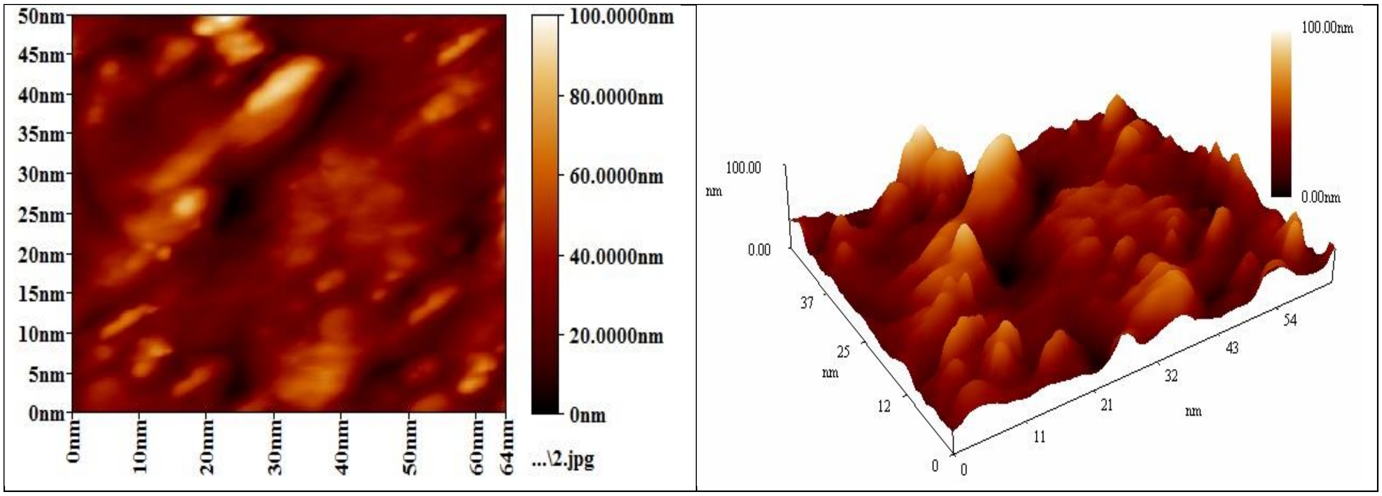
The study of desktop topography (AFM) which is the ability to visualize and analyze these surfaces and is important to learn about the homogeneity properties or properties related to each feature, the graphology of the graph and the knowledge and study of parameters such as temperature, thickness, etc. from page (3)

The surface roughness and the mean square root of the roughness as well as the average grain size (Dav) are shown for all films prepared at (400C). We notice from Table No. (3) that the increase in the average square values (Rms) of the prepared films is accompanied by an increase in the values of ground roughness. We note that there is a difference in the average particle size (Dav)

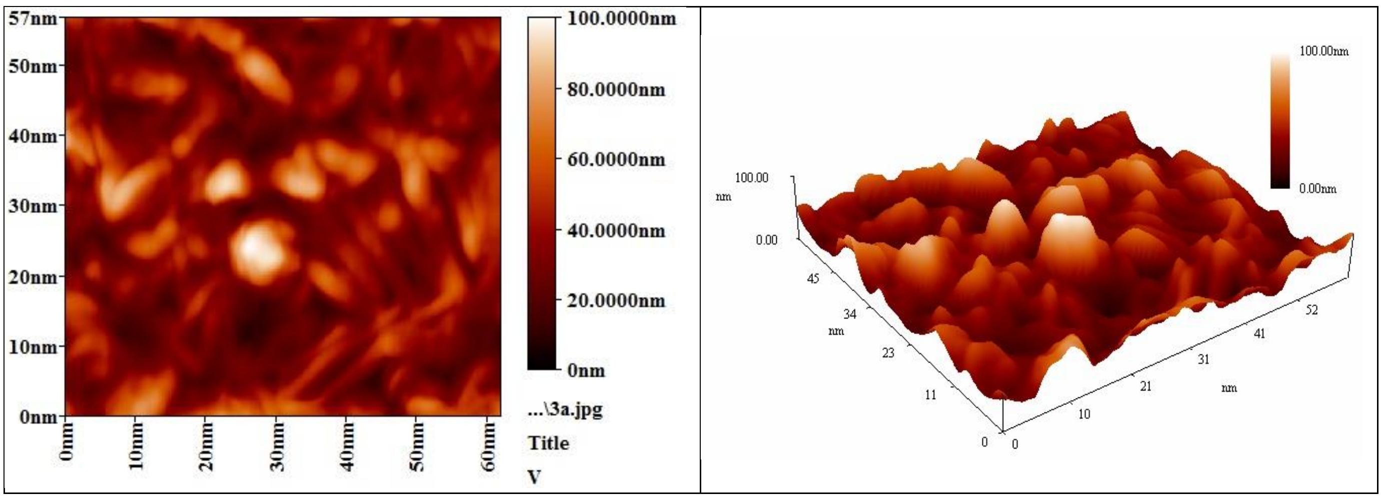
For AFM and between the particle size values obtained by the spark equation XRD, we solve for the sparks on the crystal size of a single crystal, but in the AFM measurement we get the particle size ratio, that is, the group of atoms [13].



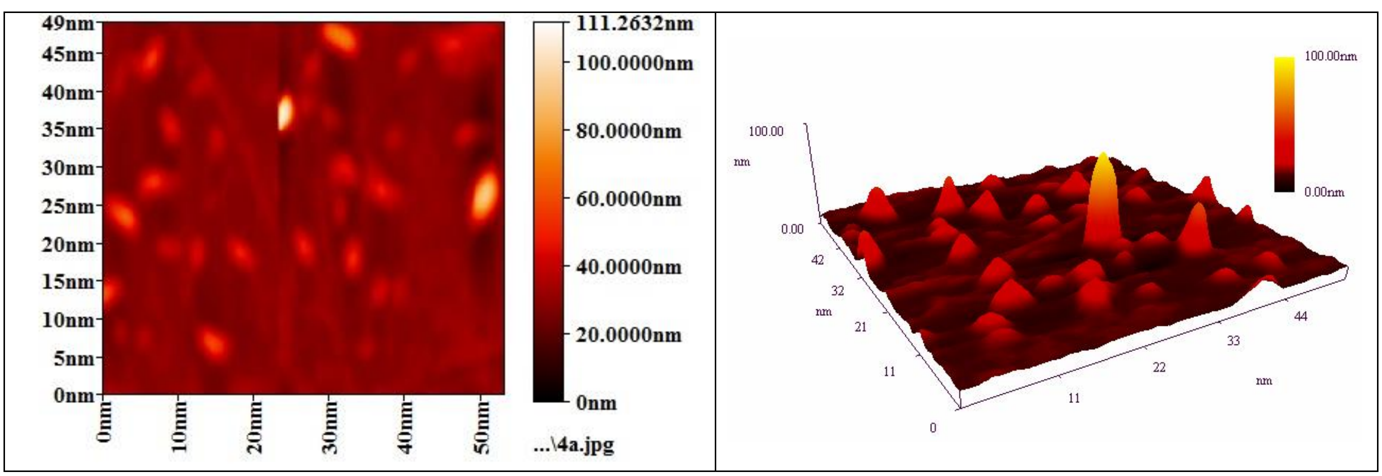
sample (1) ZnO



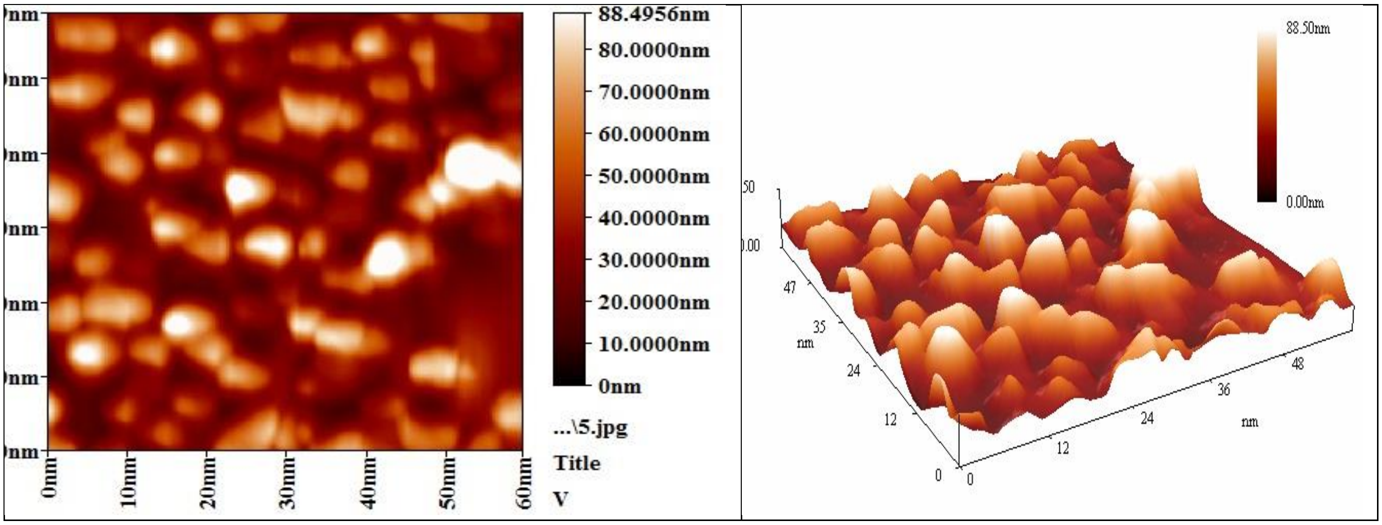
sample (2) SnO2



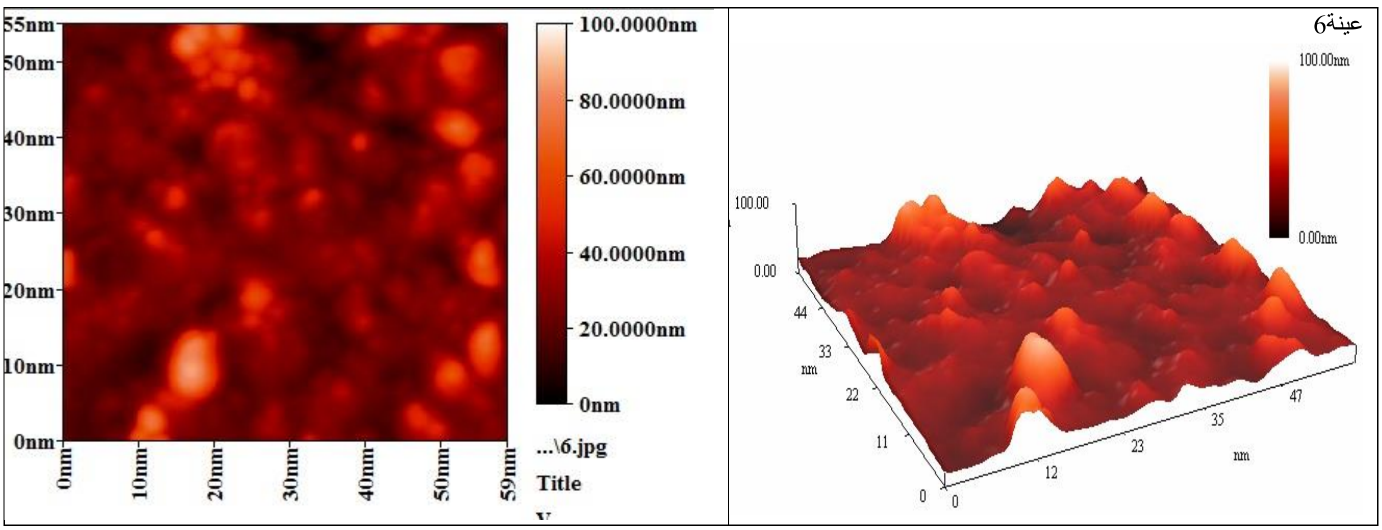
sample (3) In_2O_3



sample (4)3% In_2O_3



sample (5)5% In_2O_3



sample (6)7% In_2O_3

Figure (2)

Table (3) Shows the measurement results (AFM) for the prepared pure films doped with (In_2O_3).

Sample	RMS	Roughess	Dav (nm)
1. ZnO pure	16.1	13	19.81
2. SnO_2 pure	13.8	10.8	22.03
3. In_2O_3 pure	15.3	12	40.25
4. 3% In_2O_3	7.11	6.03	42.03
5. 5% In_2O_3	11.4	7.95	51.08
6. 7% In_2O_3	17.6	15.2	53.71

Allergic properties

The sensitivity was calculated from Equation $s = \frac{Ra\_Rg}{Rg} * 100\% \ldots \ldots 1$

Where (Ra) and (Rg) are the electrical resistance of the sensor in the air and in the presence of gas, respectively. The allergic properties of the prepared films were studied, pure and dotted in different proportions, with gas concentration (100ppm) and thickness (200nm), as the gas used is (NO_2), which is an oxidizing gas. When the gas is oxidized by evaporation of the surface of the (n-type) semiconductor membrane, the concentration of The charge carriers (electrons) on the surface of the membrane will decrease, causing an increase in the resistance of the membrane. Using equation (1), the sensitivity was calculated with the doping ratios. We note that the sensitivity increases with the doping rate and temperature, as in Figure (3) and it is clear from Table (4) the sensitivity values. At the optimum temperature (100C), we notice from the table an increase in sensitivity by increasing the percentage of doping with (In_2O_3) and the reason is due to the homogeneity of the membrane surfaces and the lack of crystal defects, including the grain boundaries on the surface of the membranes, which increased the adsorption of the gas and its interaction with the membrane surfaces

Table (4) sensitivity values (5) for pure films doped with (In_2O_3) at (100) °C

Sample	Sensitivity % at the optimal temperature(100) °C
7. ZnO pure	10.62030075
8. SnO_2 pure	20.62937063
9. In_2O_3 pure	22.7953411
10. 3% In_2O_3	30
11. 5% In_2O_3	23
12. 7% In_2O_3	54.61538462

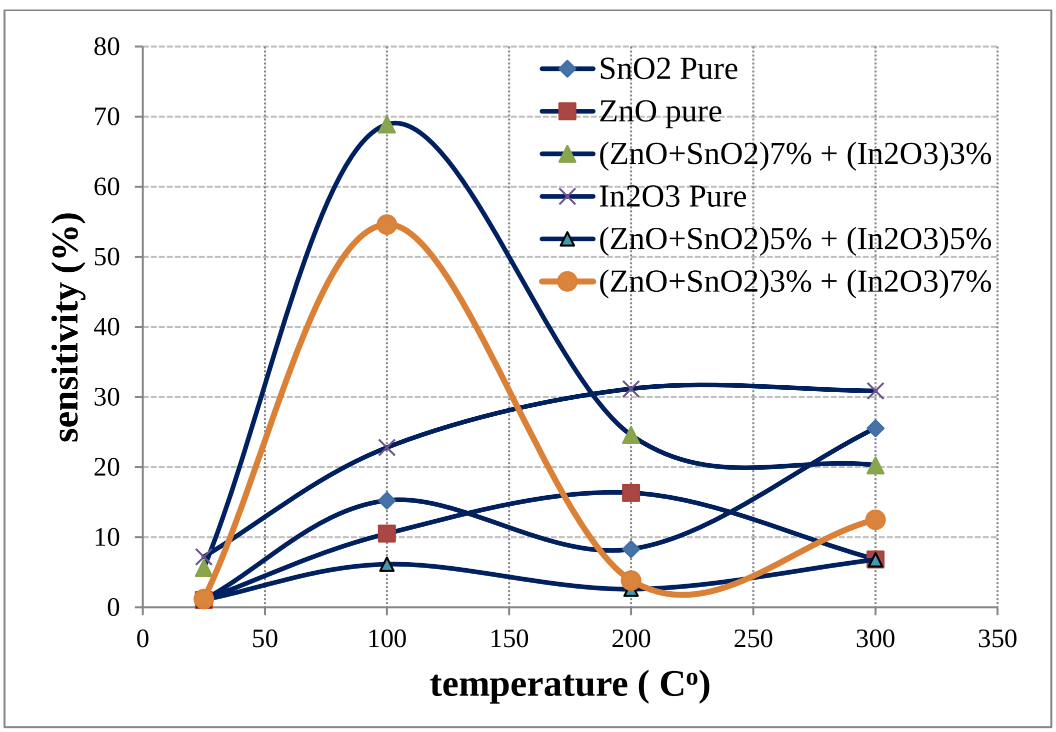


Figure (3)

Conclusion

1- Pure (ZnO) (SnO_2) films dotted with (In_2O_3) in different proportions and deposited on glass bases were prepared by pyrochemical method.

2- The results of the structural tests showed that the (ZnO) films are undoped and dotted with (In_2O_3) is a plug-in polycrystalline structure with a dominant (002) orientation, and the doping led to an increase in the grain size (D) and a decrease in the curve width of the half of the maximum peak.

3- The results of the structural tests showed that the (SnO_2) films, undoped and dotted with (In_2O_3) are polycrystalline with a tetrahedral structure with a dominant direction (110), and the doping led to an increase in the particle size (D).

4- It was also found that the sensitivity values and the return time of the prepared films increase with the increase in the percentage of doping, and thus we conclude that (ZnO) and (SnO_2) films are among the important films that can be used in an excellent way as sensing elements for the detection of toxic gases such as carbon dioxide and others.

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