Jasim et al. *Iraqi Journal of Science, 2018, Vol. 59, No.1A, pp: 67-74*
DOI: 10.24996/ijs.2018.59.1A.9

ISSN: 0067-2904

In_2O_3-ZnO pyramids like structure prepared by Spray-pyrolysis Technique for gas Sensing Applications

Ismaail K. Jasim[1], Isam M. Ibrahim*[2], Marwan K. Alyas[1]
[1]Department of Physics, College of Education for Pure Science, University of Tikrit, Tikrit, Iraq.
[2]Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq.

Abstract

Polycrystalline Indium oxide (In_2O_3) and Indium oxide-zinc oxide (IZO) thin films mixed with 10% ZnO content were prepared by spray-pyrolysis technique at relatively low substrate temperature (150 ˚C).Field emission scanning electron microscope (FE-SEM) shows that the nanostructure at 10% ZnO content has pyramid like structure. The hall effect measurements show that the prepared samples have n-type charge carriers .The films were examined as gas sensor against H_2S gas at different operating temperatures (200, 250 and 300) ^oC, and it was found that the IZO sample a good sensitivity to H_2S gas ~ 572 % at operating temperature 200 ^oC, with relatively fast response time of 19 s and recovery time of 17 s.

Keywords: nano-pyramids, In_2O_3-ZnO mixed oxide, gas sensor.

المركب In_2O_3–ZnO الشبيه بالاهرامات والمحضر بتقنية الرش الكيميائي لتطبيقات المتحسسات الغازية

اسماعيل خليل جاسم[1]، عصام محمد ابراهيم[2*]، مروان خزعل الياس[1]
[1] قسم الفيزياء ، كلية التربية للعلوم الصرفة ، جامعة تكريت، تكريت، العراق.
[2] قسم الفيزياء، كلية العلوم ، جامعة بغداد، بغداد، العراق.

الخلاصة

حضرت اغشية رقيقة بتركيب متعدد التبلور من اوكسيد الانديومIn_2O_3 واوكسيد الانديوم–اوكسيد الزنك IZOبنسبة 10% ZnO بطريقة الرش الكيميائي الحراري على قواعد من الزجاج وعند درجة حرارة قاعدة (150^oC) . اظهرت صور المجهر الالكتروني الماسح FE–SEMان التركيب النانوي عند اضافة 10% ZnO يكون ذو تركيب شبيه بالاهرام.اظهرت قياسات هول ان العينات المحضرة لها نوع حاملات شحنة من نوع n–type . تم اجراء فحوصات للاغشية كمتحسس للغازات السامة ومنها كبريتيد الهيدروجين عند درجات حرارة تشغيل تتراوح بين (^oC 250,200 و300) ووجد ان عينه ال IZO لها تحسسية عالية لغاز كبريتيد الهيدروجين تتراوح 572% عند درجة حرارة 200^oC ، وبزمن سرعة استجابة 19 ثانية وزمن اعادة 17 ثانية.

Introduction

Nanotechnology, has the potential of developing devices smaller and more efficient [1]. It can created with different shapes such as spherical, tubes, pyramids, platelets and nanorods [2]. Spray pyrolysis is one of easiest chemical techniques used to fabricated thin films used in many fields [3]

*Email: Dr.issamiq@gmail.com

due its simplicity and low coast technique. It has been used in several industries such as in solar cell production [4]. Indium oxide In_2O_3 is n-type semiconductor with energy gap around 3 eV [5]. The most stable phase with cubic (bixbyite type) with lattice constant a = 10.12 Å [6]. Zinc oxide (ZnO) is an II-VI semiconductor with wide and direct band gap semiconductor with 3.3 eV band gap which crystallizes in the hexagonal wurtzite structure [7]. It has a very large exciton binding energy of 60 meV at room temperature [8], including excellent chemical and thermal stability. ZnO is useful in various technological domains such as transparent electrodes, solar cell, gas sensors, light emitting diodes, the active channel in thin films transistor and optoelectronic devices . Composite materials are made from two or more constituent materials with significantly different physical or chemical properties which remain separate and distinct at the macroscopic or microscopic scale within the finished structure. The results in better properties than those of the individual components used alone [9]. The film based gas sensors depending on the detection of variation in some electrical parameter, resistance or capacitance, of the film utilize n-type semiconducting metal oxides such as ZnO. Also, metal oxides are stable at increased temperatures in air [10]. There many researches based on composite with material for use in many applications such as gas sensing [11-13]. In this paper, structural, electrical and morphological properties of In_2O_3-ZnO thin film prepared by chemical spray pyrolysis techniques along with H_2S gas sensing has been presented.

Experimental

$InCl_3$ and $ZnCl_2$ with purity of 99.9% provided from Flukea company, was used to from aqueous solutions of 0.2 M of pure $InCl_3$ and with 10 % $ZnCl_2$.

Pure In_2O_3 and IZO thin films were deposited by spray pyrolysis technique. A glass substrate located on heat substrate, the temperature controlled by thermocouple at 150 ^{o}C. The solution flow rate was optimized to 1ml/min. The distance between the substrate and spray nozzle is adjusted at 30 cm. After the deposition operation was completed, the prepared samples leave on the heater until the temperature arrives the room temperature. The prepared films annealed at 400 ^{o}C under vacuum for one hour to enhance the film crystallinity. The deposited films were examined by x–ray diffraction system (type Shimadzu XRD 6000), Field effect scanning electron microscopy (type JSM-7600F produced by JEOL Ltd. Japan), UV-visible (SP-8001 spectrophotometer) and Hall effect measurements. Aluminum electrodes by using suitable mask, was deposited on the surface of the In_2O_3-ZnO mixed by thermal evaporation using Edward coating unit. The connections between the aluminum and very thin copper wires were done by high conductive silver as shown in Figure-1.

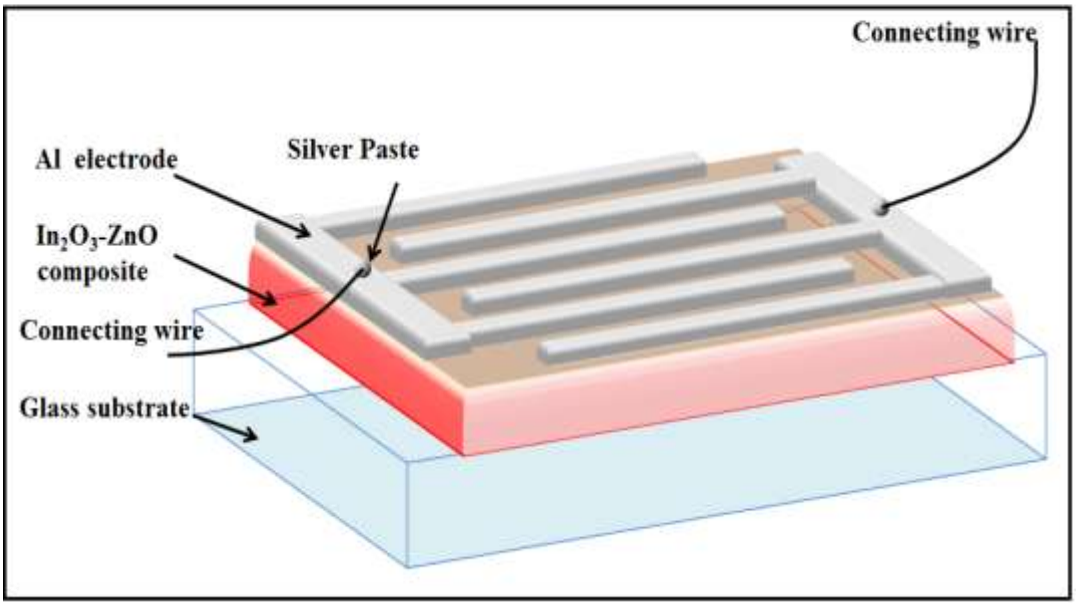

Figure 1- schematic for single layer gas sensing devices arrangement.

A vacuumed closed chamber, by rotary at approximately 1×10^{-2} mbar was made of stainless steel with controlled hot plate. A multi pin feed through at the base of the chamber allows the electrical connections to be established to the heater, thermocouple and sensor electrodes. The sample was put on the heater and the electrical resistance of the sensor was measured by the multi-meter, and transfer the data to computer in two cases of target gas (on and off).

Results and discussions

Figure-1 shows the x-ray diffraction pattern for pure In_2O_3 and In_2O_3-ZnO mixed thin films prepared at 10% ZnO content. The two patterns show poly crystalline structure. The pattern for pure sample show low crystallinity with peaks appear at $2\theta = 30.5910^0$ and 35.4012^0 belong to (222) and (400) planes for cubic In_2O_3 structure, which identical with standard card number (96-101-0589).

The second pattern, with 10% ZnO content, illustrates increasing in x-ray diffraction peaks intensities which indicate on enhanced the films crystallinity and with more number of peaks appeared at 2θ= 30.6165^0, 35.4499^0, 37.6664^0, 39.7193^0, 41.7553^0, 43.6569^0, 45.6369^0 and 50.9694^0 belong to (222), (400), (330), (402), (323), (422), (341) and (440) planes for cubic In_2O_3 structure with additional small peaks corresponding to hexagonal ZnO structure located at 31.8067^0, 34.4000^0 and 36.1440^0 for (100), (002) and (101) planes. The Indium oxide peaks appear to be with less width at half maxima, demonstrating increasing in the crystalline size of the indium oxide at this ratio. Increasing the crystalline size at this ratio may be due to that ZnO additive act as a catalysis which enhances the growth of crystals.

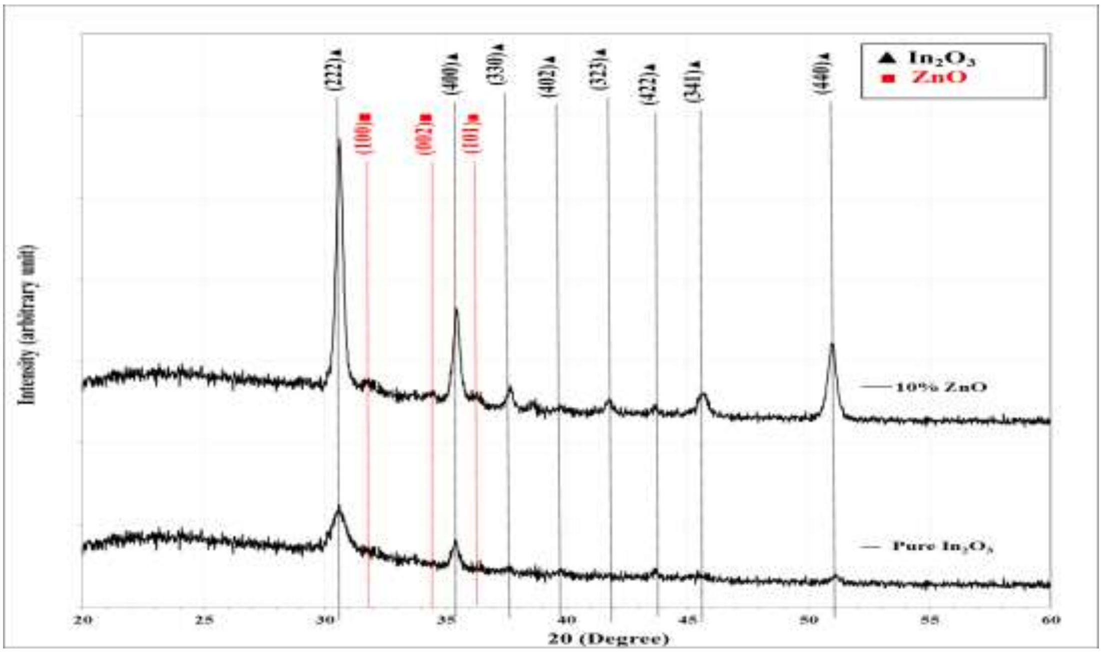

Figure 1- X-ray diffraction patterns for In_2O_3 and In_2O_3-ZnO composite thin films.

Table-1 shows the structural parameters for pure In_2O_3 and IZO mixed thin films prepared at 10% ZnO content, which encompass Bragg angle (2θ), full width at half maximum (*FWHM*), experimental and standard Inter-planar spacing d_{hkl} (calculated by Bragg's low), crystalline size (C.S) (calculated by Sherrer's formula) and their corresponding planes.

Table 1- structural parameters for In_2O_3 and In_2O_3-ZnO composite thin films

Sample	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	C.S (nm)	Hkl	d_{hkl} Std.(Å)	Phase	Card No.
Pure In_2O_3	30.5910	0.7040	2.9200	11.7	(222)	2.9214	Cub. In_2O_3	96-101-0589
	35.4012	0.3231	2.5335	25.8	(400)	2.5300	Cub. In_2O_3	96-101-0589
10% ZnO	30.6165	0.3232	2.9177	25.5	(222)	2.9214	Cub. In_2O_3	96-101-0589
	31.8067	0.5518	2.8112	15.0	(100)	2.8137	Hex. ZnO	96-901-1663
	34.4000	0.5000	2.6049	16.6	(002)	2.6035	Hex. ZnO	96-901-1663
	35.4499	0.3231	2.5302	25.8	(400)	2.5300	Cub. In_2O_3	96-101-0589
	36.1440	0.3660	2.4831	22.8	(101)	2.4754	Hex. ZnO	96-901-1663
	37.6664	0.2853	2.3862	29.4	(330)	2.3853	Cub. In_2O_3	96-101-0589
	39.7193	0.2664	2.2675	31.7	(402)	2.2629	Cub. In_2O_3	96-101-0589
	41.7553	0.3613	2.1615	23.5	(323)	2.1576	Cub. In_2O_3	96-101-0590
	43.6569	0.2094	2.0717	40.9	(422)	2.0657	Cub. In_2O_3	96-101-0590
	45.6369	0.4183	1.9863	20.6	(341)	1.9847	Cub. In_2O_3	96-101-0589
	50.9694	0.3995	1.7903	22.0	(440)	1.7890	Cub. In_2O_3	96-101-0589

Figure-2 shows the FESEM for the pure In_2O_3 and IZO mixed with two magnification powers ×6k and ×30k.

The FESEM image of pure In_2O_3 sample shows large blocks, with large meanders, extended to large areas. With more magnification, a spherical particles appear with size range from 50 nm to 100 nm, stick on these big mass. While IZO sample contains a large number of small pyramids crystals with 800 nm base sides length, these forms belong to the indium oxide pyramids with triangular plane sides in the direction of (222) for cubic structure for In_2O_3. This result is agree with Jia *et al.*, [14] in addition to small particles with octahedrons shapes, with about 100 nm diameter which agree with Zhang *et al.*, [15] aggregates to each other with a high density of contacts between the aggregates. Such morphology has high specific surface, which favors high gas sensor response [16].

In this range of aggregate composition the relationship between the particles of the catalytically active component-ZnO and In_2O_3 particles with a high concentration of conduction electrons is close to optimal for the maximum sensory effect in the detection of gases [17].

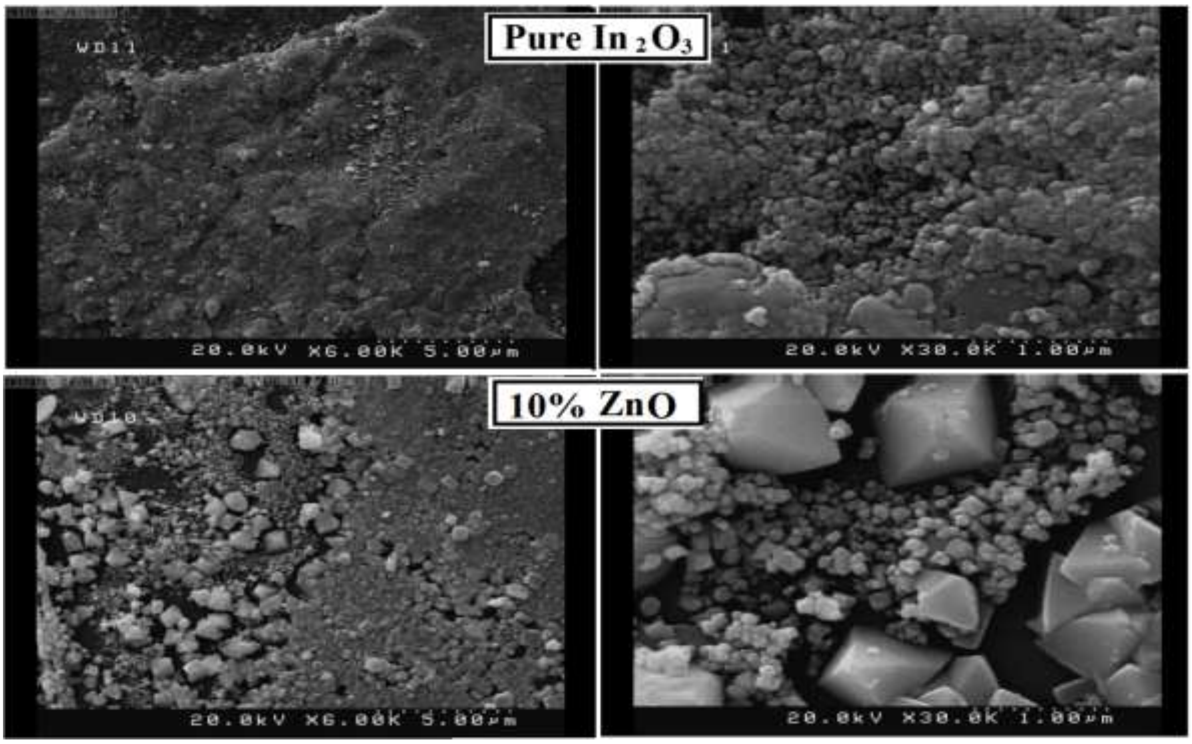

Figure 2- FESEM images with two Mag. powers for pure In_2O_3 and In_2O_3:ZnO thin films at 10% ZnO content

Hall Effect measurement was used to determine the electrical mobility, carrier concentration and majority of electrical carrier's type for pure In_2O_3 thin films and it's composite with ZnO. The results showed that the two films were n-type. The charge carrier (n_H) and mobility (μ_H) have been calculated using the Hall coefficient and film conductivity.

The values of n_H and μ_H with ZnO content were shown in Table-2. The carrier concentration increases at 10% ZnO content from 0.104×10^{13} cm^{-3} to 98.503×10^{13} cm^{-3} .

Table 2- Hall measurements of for In_2O_3-ZnO composite thin films with different ratio

Sample	$n\times10^{13}$ (cm^{-3})	type	μ_H (cm^2/v.sec)
In_2O_3	0.104	n	1020.17
IZO	98.503	n	1201.11

H_2S gas was used as a target gas for examination the pure In_2O_3 thin films and its mixed with ZnO. The two samples were tested at room temperature but did not show any sensitivity (or very low sensitivity) to hydrogen sulfide gas, so the test was repeated at higher temperatures (200, 250 and 300)˚C. Figures-(3, 4) show the variation of sensitivity with time for In_2O_3 and IZO mixed in two cases (gas-on and gas-off) respectively, with different operating temperatures. It can be noted that the sensitivity increase for IZO samples because of the difference in the nature of the surface and granular size of the samples surface, as demonstrated by measurements of the scanning electron microscopy, and also due to the difference in the charge carriers density, their mobility and the values of electrical conductivity of the tested samples. In addition the good sensitivity of IZO sample against H_2S gas due to the nanostructures was observed in this ratio, with the large surface area of the sample as shown in Figure-2, in addition to the degree of aggregation between particles that gave relatively high electrical conductivity and high mobility of charge carriers. The gas sensor parameters for the pure In_2O_3 and IZO mixed samples, against H_2S gas at different operating temperature were shown in Table-3.

The mechanism of sensitivity to the hydrogen sulfide gas depends on the reaction of the gas with the oxygen gas atoms, that is already absorbed on the surface of the material which comes from the atmosphere. This reaction will cause increase the number of existing charge carriers near the surface by injection electrons into the material to complete the reaction. This activity and speed his chemical reaction are depend on the temperature. This result is agreed with Zheng *et.al* [17] and Basyooni *et. al* [18].

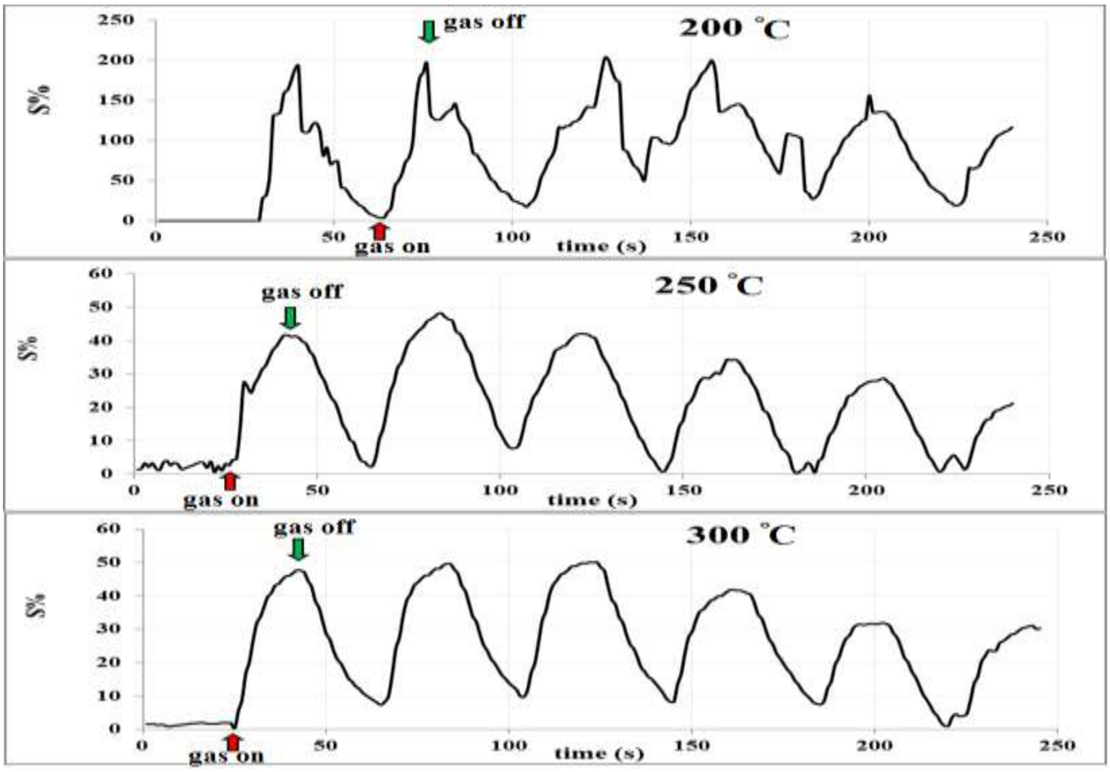

Figure 3- Sensitivity with time for In_2O_3 thin films, in cases gas-on and gas-off, at different operating temperatures (200, 250 and 300) ^{o}C.

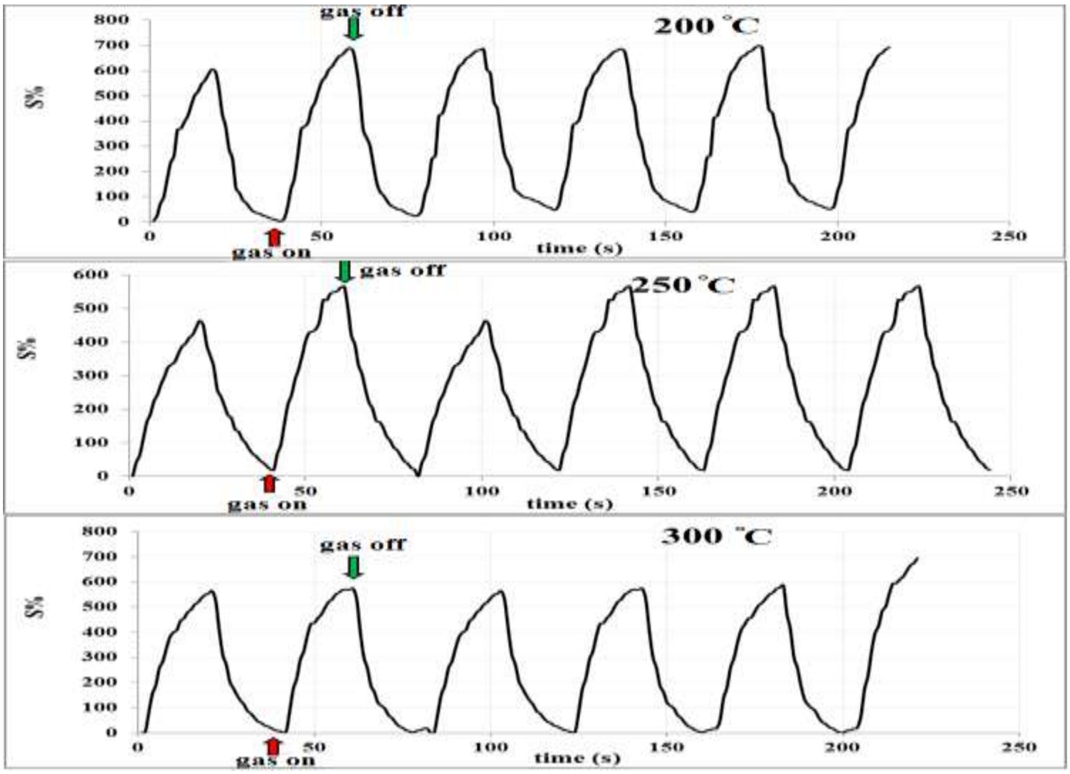

Figure 4- Sensitivity with time for the IZO thin films, in cases gas-on and gas-off, at different operating temperature (200, 250 and 300) ^{o}C.

Table 3 -Gas sensor parameters for Pure In_2O_3 and IZO mixed, against H_2S gas, at different operating temperature (200, 250 and 300) ^oC.

Sample	Operating Temp.(^0C)	Sensitivity (%)	response time (s)	recovery time (s)
Pure In_2O_3	200	190.0	16.0	26.0
	250	40.2	15.0	20.0
	300	47.0	19.0	21.0
10% $ZnO:In_2O_3$	200	572.0	19.0	17.0
	250	520.0	19.0	24.0
	300	550.0	17.0	16.0

Conclusions

Pure In_2O_3 thin films and IZO mixture at 10% ratio, deposited on glass by spray pyrolysis technique at 150 ^oC show polycrystalline structure identical with In_2O_3 standard peaks and with additional small peaks corresponding to hexagonal ZnO structure for composites samples with enhancement in films crystallinity for IZO sample.

The SEM measurement indicate the formation of nano-pyramids crystals shape, for sample with 10% ZnO ratio, with 800 nm base dimension length with sides in the direction of (222) for cubic structure for In_2O_3, and addition of small particles with octahedrons shapes, with about 100 nm diameter, aggregates to each other. The IZO sample has a good H_2S gas sensing due to their nano structures, in addition to the degree of aggregation between particles.

References

1. Group, F. **2006**. *Nanotechnology in Biology and Medicine*. Boca Raton: CRC Press.
2. Rashid, R., Murtaza, G. and Zahra, A. **2014**. Gold Nanoparticles : Synthesis and Applications in Drug. *Trop. J. Pharm. Res.*, **13**: 1169–1177,.
3. Nádherný, L., Sofer, Z. and Sedmidubský, D. **2012**. ZnO thin films prepared by spray-pyrolysis technique from organo-metallic precursor. *Ceramics*, **56**(2): 117–121,.
4. Rajput, J.K. and Purohit, L.P. **2016**. Nanoscience & Technology : Open Access Comparative Study of Synthesis of CdO-ZnO Nanocomposite Thin Films by Different Methods : A Review. *Nanosci. Technol. Open Access*, **3**: 1–5.
5. Walsh, A., Juarez, L. and Wei, S. **2008**. Nature of the Band Gap of In_2O_3 Revealed by First-Principles Calculations and X-Ray Spectroscopy. *Phys. Rev. Lett.*, **167402**: 2–5.
6. Zachariasen, W. **1927**. The crystal structure of the modification C of the sesquioxides of the rare earth metals, and of indium and thallium. *Norsk Geologisk Tidsskrift* , **9**: 310-316, 1927.
7. Christoulakis, S., Suchea, M., Koudoumas, E., Katharakis, M., Katsarakis, N., and et al. **2006**. Thickness Influence on Surface Morphology and Ozone Sensing Properties of Nanostructured ZnO Transparent Thin Films Grown by PLD. *Applied Surface Science*, **252**:. 5351–5354.
8. Mukherjee, B. **2009**. Synthesis, Structural, Optical and Electrical Properties of Zinc Oxide nanoparticles. MSc. Thesis, Indian Institute of Technology Madras.
9. Bardeen, J. **2003**. Solid State Physics. *Technology*, **108**: 1175–1204,.
10. Dixit, S., Srivastava, A., Srivastava, A. and Shukla, R.K. **2007**. Effect of Toxic Gases on Humidity Sensing Property of Nanocrystalline ZnO Film. *Journal of Applied Physics*, **102**(11):
11. Ibrahim, I.M. and Odhaib, H.M. **2017**. Enhancement of vanadium oxide doped Eu^{+3} for gas sensor application. *Iraqi J. Phys.*, **15**(33): 17–27.

12. Ibrahim, I.M., Sharhan, S.I. and Ibrahim, F.T. **2015**. Sensing behavior of CuO-doped ZnO / PS nanoparticles. *Mater. Lett*. **157**: 57–62.

13. Jassim, I.K., Rzaij, J.M., Ali, I.M. and IIbrahim, I.M. **2016.** Influence of Nd and Ce doping on the structural , optical and electrical properties of $V_2 O_5$ thin films. *Iraqi J. Phys.*, **14(**30): 73–82.

14. Jia, H., Zhang, Y., Chen, X., Shu, J., Luo, X., and Zhang,Z. **2003.** Efficient field emission from single crystalline indium oxide pyramids. *Appl. Phys. Lett.*, **82**:. 4146–4148.

15. Zhang, L., Fang, X., and Ye, C. **2007.** *Controlled Growth of Nanomaterials*. British Library: World Scientific NEW.

16. Stadler, A. **2012**. Transparent Conducting Oxides—An Up-To-Date Overview. *Materials (Basel).*, **5**: 661–683.

17. Zheng, Z., Zhu, L. and Wang, B. **2015.** In_2O_3 Nanotower Hydrogen Gas Sensors Based on Both Schottky Junction and Thermoelectronic Emission. *Nanoscale Res. Lett.*, **10**: 1–14.

18. Basyooni, M., Shaban, M. and El Sayed, A. **2017.** Enhanced Gas Sensing Properties of Spin-coated Na-doped ZnO Nanostructured Films. *Nat. Publ. Gr.*: 1–12.

19. Trakhtenberg, L.I., Khatami, S.M.N., Gerasimov, G.N. and Ilegbusi, O.J. **2015**. Effect of Composition and Morphology on Sensor Properties of Aerosol Deposited Nanostructured ZnO + In_2O_3 Films. *Mater. Sci. Appl.*, **6**: 220–227.