

Synthesis of ZnO-SnO₂ Nano-Thin Films on Porous Silicon as NH₃ Gas Sensing Performance

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Abstract: ZnO-SnO₂ nano thin films were fabricated by chemical spray pyrolysis technique on glass and porous silicon slides at 400°C. The structural properties of the prepared mixed films were studied by XRD and AFM techniques. It was found that the structure is a polycrystalline with nano grain size for the preferential orientation along (002) of ZnO. The prepared gas sensor of mixed ZnO-SnO₂ nano composite give a highest sensing response for 63 ppm NH₃ gas with (35%) on glass substrate at 200°C. High response and recovery times of 156 and 210 sec, respectively were found. The sensitivity of the prepared films on the glass is better than on porous silicon. The sensitivity, response time and recovery time were discussed in this study.

Key words: Nano thin films, gas sensor, porous silicon, NH₃ gas, polycrystalline, porous silicon

INTRODUCTION

Gas sensors are converted the gas interaction with metal oxide into an electrical signal change. Tin oxide was used as good sensor with high sensitivity for low gas concentration (Al-Jenaby and Al-Jumaili, 2016; Kolhe *et al.*, 2018; Patil *et al.*, 2011; Fahad *et al.*, 2016; Al-Jumaili *et al.*, 2016). Yet, it has poor selectivity in order to improve this characteristic SnO₂ mixed with another oxides such as In₂O₃, CdO and ZnO (Mondal *et al.*, 2014; Liangyuan *et al.*, 2008). Among these mixed oxides ZnO-SnO₂ nanocomposite has received a high attention due to its response toward the gases (Verma and Gupta, 2012; Sonker *et al.*, 2013; Karthik *et al.*, 2018). The sensitivity and selectivity improve with surface porosity, due to the increasing of gases adsorption on the surface, so, porous silicon gives a high surface area and an active surface for interaction with gases (Li *et al.*, 2014). Ammonia is a toxic gas which presents in atmosphere in low concentration in petro-chemical industries and in another factories and laboratories, so, the sensitivity measurement of this gas has a high importance. There are many researches were done to improve the response of NH₃ by different oxides (Zhang *et al.*, 2015). In the present study a pure and mixed ZnO-SnO₂ thin films were investigated as a gas sensor on glass and porous silicon slides with different operating temperatures.

MATERIALS AND METHODS

Pure and mixed thin films of ZnO-SnO₂ were prepared by chemical spray pyrolysis on glass and porous silicon

slides at 400°C. Porous silicon of p-type (111) with the resistivity 5-10 Ω/cm is prepared by electrochemical technique with 40 mA at 20 min. Pure and mixed films were prepared from aqueous solutions of 0.1 mol/L SnCl₂.2H₂O and ZnO.2H₂O with purity 99%. The ratio of mixed (10 mL SnCl₂+90 mL of ZnCl₂) and (40 mL SnCl₂+60 mL ZnCl₂) of the mixed films were denoted as ZS2 and ZS4, respectively. The time of spraying was 5 and 20 sec wait interval. The structure of the films was analyzed by XRD-SHIMADZU 6000 (Cu Kα radiation, λ = 0.154 nm) in 2θ range from 20°-70 and the morphology identified by AFM (AA3000 Scanning Probe Microscope SPM) technique. NH₃ sensing properties were evaluated from resistance change at different substrate temperature for the prepared nano mixed thin films.

RESULTS AND DISCUSSION

Characterization results: XRD of pure and mixed ZnO-SnO₂ prepared thin films were shown in Fig. 1. From curve (a) it can be seen that the diffraction peaks indexed to the ZnO hexagonal structure (CPDS 35-1414) with preferred (002) peak. The curve (b) shows corresponds peaks to tetragonal SnO₂ structure (JCPDS 21-1250). Figure 1c-f denote an XRD peaks of ZS2 and ZS4 mixed films deposited on glass and porous silicon. The XRD results are obtained two nanocomposite crystalline phases, one of ZnO with preferred (002) peak and the other of SnO₂ with many compounds of SnO₂, Sn₂O₃ and Sn₃O₄. The intensity of the preferred ZnO (002) peak in the mixed films were decreased with increasing of SnO₂ ratio.

The crystal size of the ZnO (002) peak was ranged between 17.68 and 41.73 nm. Thus, XRD studies prove that the mixed ZnO-SnO₂ thin films are nanocrystalline in nature (Table 1).

AFM images of ZnO-SnO₂ mixed thin films on glass and on porous silicon are shown in Fig. 2. Figure 2a illustrates the morphology of the ZS2 on glass, the average grain size was 53.4 nm, Fig. 2b illustrates the ZS4 on glass, the average grain size was increased to 84.02 nm. Figure 2c illustrates ZS2 on porous silicon, the average

grain size was 61.02 nm. Figure 2d illustrates ZS4 on porous silicon, the average grain size was 73.53 nm. The results obtain that the mixed films are nano grain size

Table 1: XRD parameters of (002) ZnO peak for ZnO-SnO₂ thin films

Samples	2θ (Exp.)	d _{hkl} Exp. (Å)	d _{hkl} Std. (Å)	FWHM	GS (nm)
ZnO(002)	34.4	2.6070	2.6032	0.190	44.38
ZS2/glass	34.1	2.6255	2.6032	0.270	30.82
ZS4/glass	34.2	2.6181	0.8788	0.903	9.21
ZS2/PS	34.5	2.5960	2.6032	0.450	18.51
ZS4/PS	34.6	2.5893	2.6032	0.290	28.73

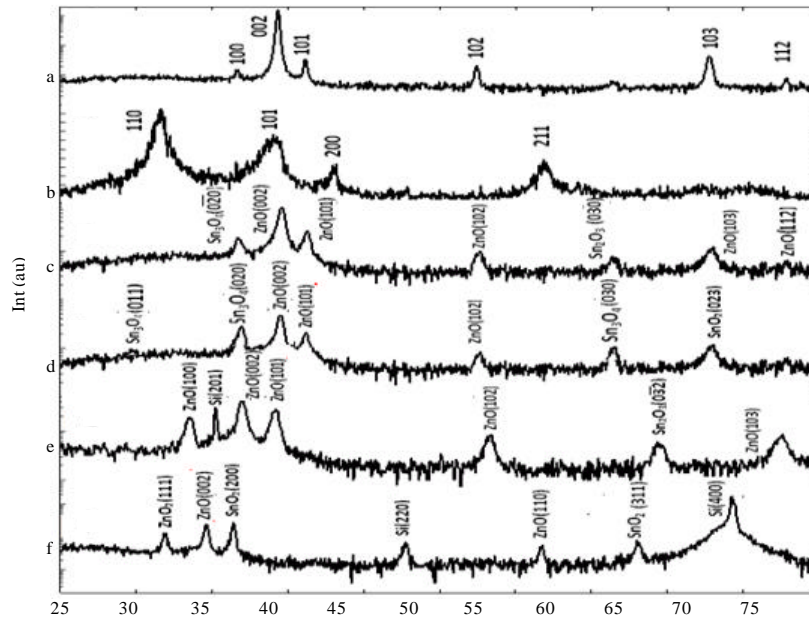


Fig. 1: XRD patterns for prepared ZnO-SnO₂ Mixed: a) ZnO; b) SnO₂; c) ZS2/glass; d) ZS4/glass; e) ZS2/PS and f) ZS4/PS

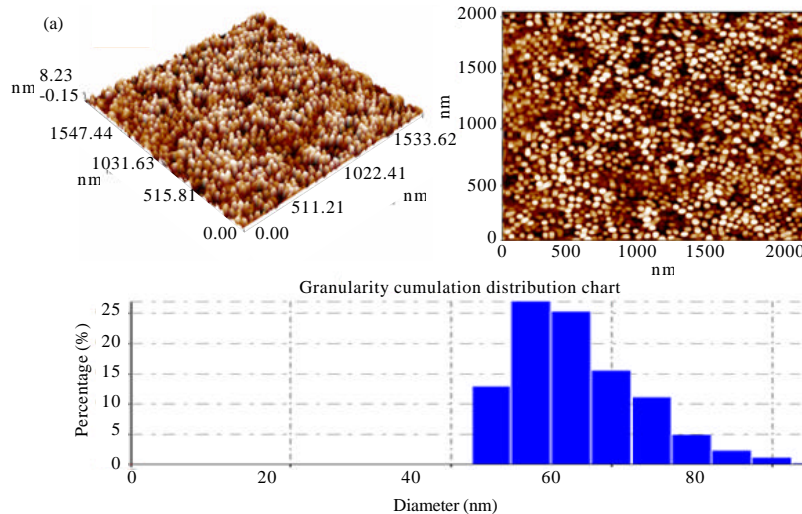


Fig. 2: Continue

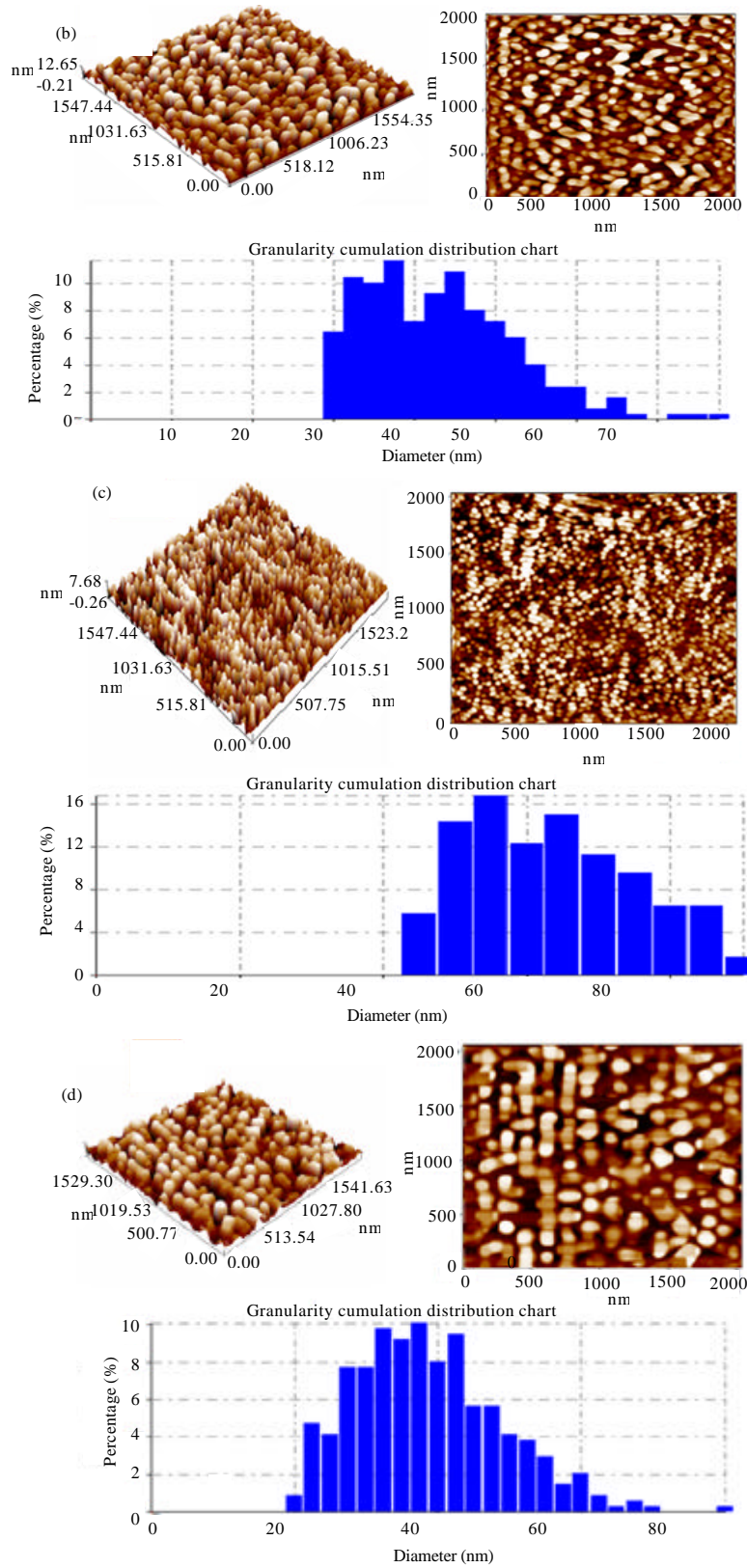


Fig. 2: AFM images of prepared ZnO-SnO₂ mixed thin films: a) ZS2/glass; b) ZS4/glass c) ZS2/PS and d) ZS4/PS

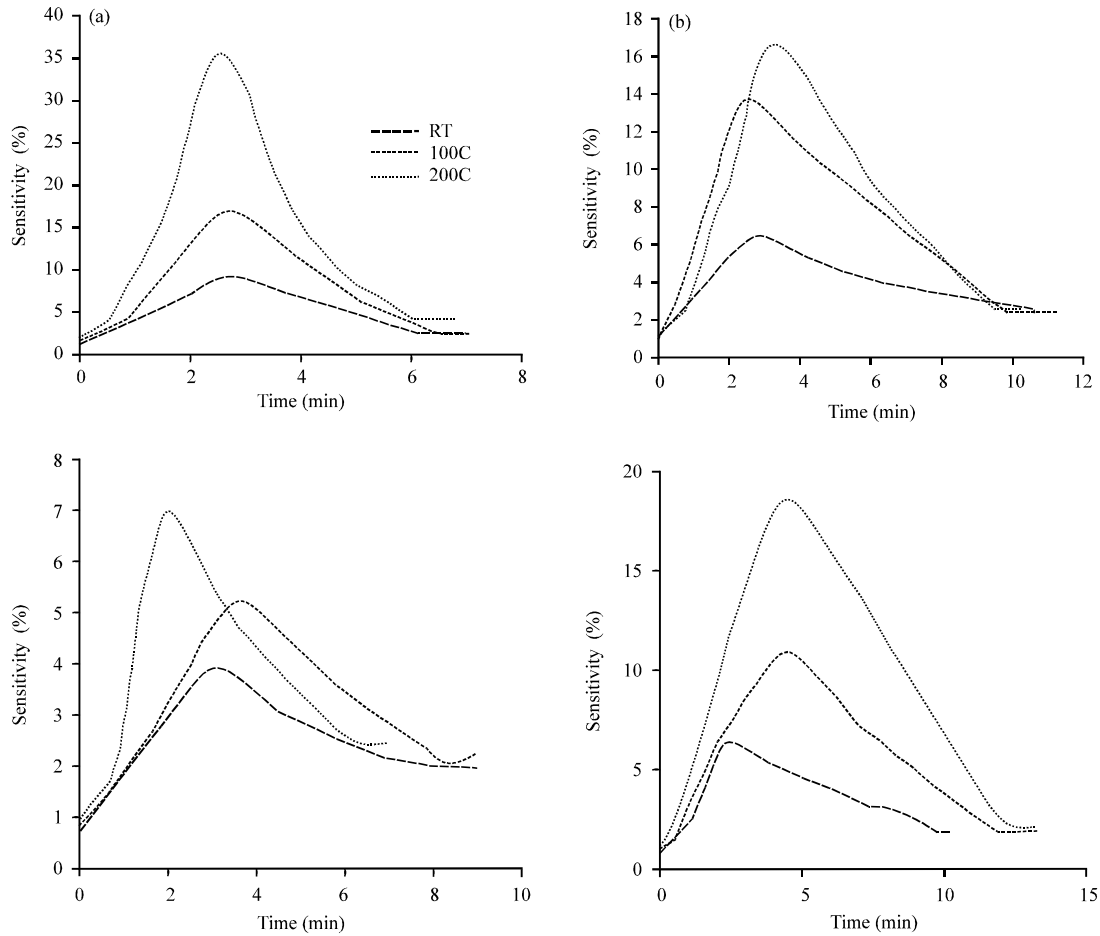


Fig. 3: The change in sensitivity with time for ZnO-SnO₂ toward NH₃; a) ZS/glass; b) ZS2/PS; c) ZS4/glass and d) ZS4/PS

ranged between 53.4 and 84.02 nm depend on the mixed ratio and on the substrate type. The grain size increased with the increasing of the SnO₂ ratio as shown in Table 2.

Gas sensing studies: The nanocomposite ZnO-SnO₂ thin films were as a gas sensing detector toward 63 ppm NH₃ gas in different operating temperature. NH₃ is a reducing gas when it react with n-type surface the resistivity will decrease according to the relation (Vinoth and Gopalakrishnan, 2017):

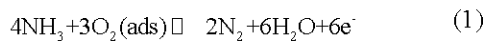


Figure 3 shows the change of sensor response with time at different operating temperatures for the mixed ZnO-SnO₂ nanocomposite. The sensitivity evaluated according to the following relation:

$$S = \frac{R_a - R_g}{R_a} * 100\% \quad (2)$$

Table 2: AFM analysis of ZnO-SnO₂ mixed thin films

Sample of ZnO-SnO ₂	Average diameter (nm)	Average roughness (nm)	RMS roughness (nm)
ZS2/glass	53.40	2.090	2.420
ZS4/glass	84.02	3.220	3.710
ZS2/PS	61.02	2.060	2.420
ZS4/PS	73.53	0.482	0.557

where, R_a and R_g represent the resistance of the films in air and in gas, respectively. When NH₃ gas inserted in the sensing chamber, sensitivity increased to a constant value and when the gas go out the sensitivity decreased to the initial level. Also, from Fig. 3, the response time (t_{res}) and the recovery time (t_{rec}) are evaluated. Table 3 shows the sensitivity value, response time and recovery time with operating temperature for each sensor. From Table 3, all the sensors are operating at RT (25°C) and the best sensitivity at this temperature for ZS2 film on porous silicon is 23.3%. The ZS2 film on glass gives a good sensitivity of 35% at 200°C operating temperature. The response time and recovery time for all sensors were high as shown in Table 3 which may be related to the incorporation reaction of the gas with mixed oxide.

Table 3: The sensitivity value, response time and recovery time for the ZnO-SnO₂ on the glass and porous silicon towards NH₃ gas

Sample	T (°C)	Sensitivity (%)	Response time (sec)	Recovery time (sec)
ZS2/glass	RT	08.9	174	204
	100	16.6	168	228
	200	35.0	156	210
ZS4/glass	RT	04.0	186	318
	100	05.3	216	288
	200	07.1	120	258
ZS2/PS	RT	06.4	162	468
	100	13.7	144	426
	200	16.6	192	378
ZS4/PS	RT	23.3	280	469
	100	08.0	138	432
	200	13.8	264	433

The interaction of NH₃ with ZnO as reported in the literature gives low sensitivity, for example (Li *et al.*, 2014; Al-Jenaby and Al-Jumaili, 2016) found the value of sensitivity of ZnO toward 50 ppm NH₃ equal to 18% with response time of 660 sec and recovery time 600 sec. Zhang *et al.* (2015) and Kolhe *et al.* (2018) studied the sensitivity of ZnO nanostructure toward 10-50 ppm NH₃ equal 49.5% and Wagh *et al.* (2004) reported a sensing value of ZnO: Mg toward 50 ppm NH₃ ranged between 27.3-68.6% depending on doping concentration and substrate temperature. The effect of substrate temperature on the sensitivity may be explained as when the temperature increased the amount of oxygen adsorption decreases, so, the interaction of the gas with the oxygen decreased. This lead to decreasing in the sensor response as which found by Li *et al.* (2014) Al-Jenaby and Al-Jumaili (2016). But in this study the sensor response increased with the increasing of temperature. This may be related to the interaction between NH₃ and the mixed ZnO-SnO₂ film structure and the n-n effect of MO-MO junction.

The sensitivity value of films deposited on porous silicon is lower than its value on the glass slides. This may be an explanation of the interaction of reduced NH₃ gas with n-type metal oxide. The porous silicon enhances the porosity of the thin films. That gives high surface area and then it increase the oxygen adsorption which cause to decrease the sensitivity as explained by Li *et al.* (2014) Al-Jenaby and Al-Jumaili (2016). Also, this behavior may be related to the p-n junction between PS-MO.

CONCLUSION

A nano mixed polycrystalline thin films of ZnO-SnO₂ are prepared by simple chemical spray pyrolysis method. The structure morphology and gas sensing

toward 63 ppm NH₃ were investigated. The mixed films of ZnO-SnO₂ gives a sensing response at RT, then it increased with increasing of the operating temperature due to the n-n heterojunction between oxides and p-n heterojunction between ps and metal oxide. The films deposited on glass slides have higher sensitivity (35%) than that deposited on porous silicon of 13.8% at 200°C. While the response time and recovery time were >200°C which is relatively high value.

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