Journal of Engineering and Applied Sciences 14 (Special Issue 5): 9056-9061, 2019
ISSN: 1816-949X

Synthesis of ZnO-SnO_2 Nano-Thin Films on Porous Silicon as NH_3 Gas Sensing Performance

Mohammed N. Jasim and Hamid S. Al-Jumaili
Department of Physics, College of Education for Pure Sciences, University of Anbar, Anbar, Iraq
mhamadnajeeb87@gmail.com, +9647807834988

Abstract: ZnO-SnO_2 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-SnO_2 nano composite give a highest sensing response for 63 ppm NH_3gas 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, NH_3 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 SnO_2 mixed with another oxides such as In_2O_3, CdO and ZnO (Mondal *et al*., 2014; Liangyuan *et al*., 2008). Among these mixed oxides ZnO-SnO_2 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 concertation 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 NH_3 by different oxides (Zhang *et al*., 2015). In the present study a pure and mixed ZnO-SnO_2 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-SnO_2 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 • /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 $SnCl_2.2H_2O$ and $ZnO.2H_2O$ with purity 99%. The ratio of mixed (10 mL $SnCl_2$+90 mL of $ZnCl_2$) and (40 mL $SnCl_2$+60 mL $ZnCl_2$) 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 K• radiation, • = 0.154 nm) in 2• range from 20°-70 and the morphology identified by AFM (AA3000 Scanning Probe Microscope SPM) technique. NH_3 sensing properties were evaluated from resistance change at different substrate temperature for the prepared nano mixed thin films.

RESULTS AND DISCUSSION

Charcteriztion results: XRD of pure and mixed ZnO-SnO_2 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 SnO_2 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 SnO_2 with many compounds of SnO_2 ,Sn_2O_3 and Sn_3O_4. The intensity of the preferred ZnO (002) peak in the mixed films were decreased with increasing of SnO_2 ratio.

Corresponding Author: Mohammed N. Jasim, Department of Physics, College of Education for Pure Sciences, University of Anbar, Anbar, Iraq, mhamadnajeeb87@gmail.com, +9647807834988

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-SnO_2 thin films are nanocrystalline in nature (Table 1).

AFM images of ZnO-SnO_2 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-SnO_2 thin films

Samples	2• (Exp.)	dhkl Exp. (Å)	dhkl 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

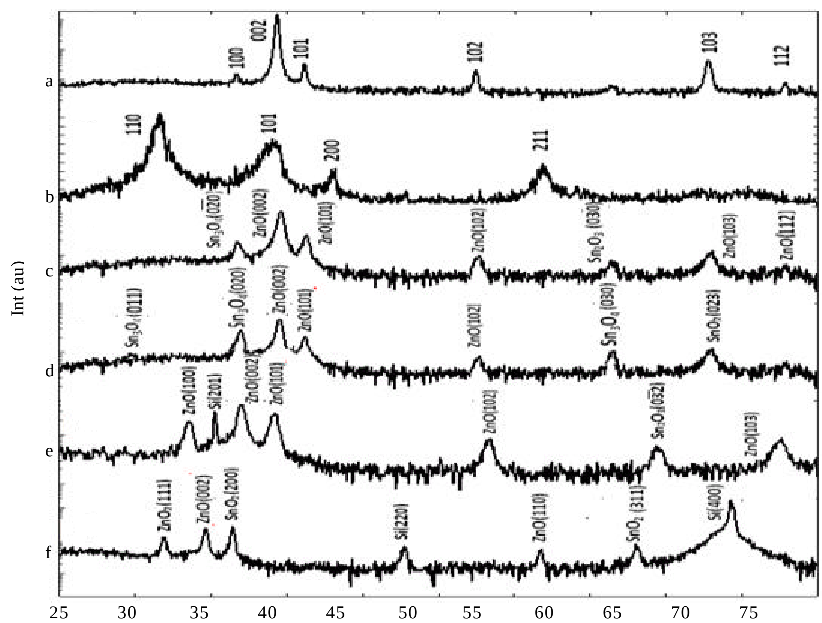

Fig. 1: XRD patterns for for prepared ZnO-SnO_2 Mixed: a) ZnO; b) SnO_2; c) ZS2/glass; d) ZS4/glass; e) ZS2/PS and f) ZS4/PS

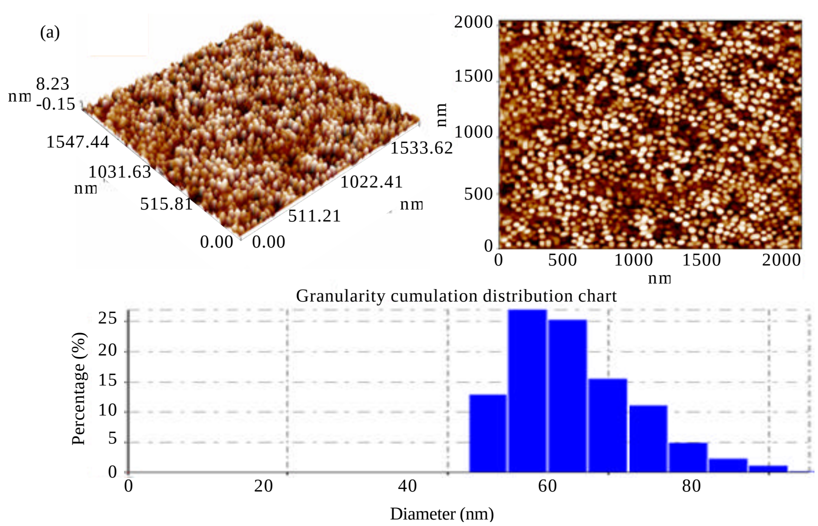

Fig. 2: Continue

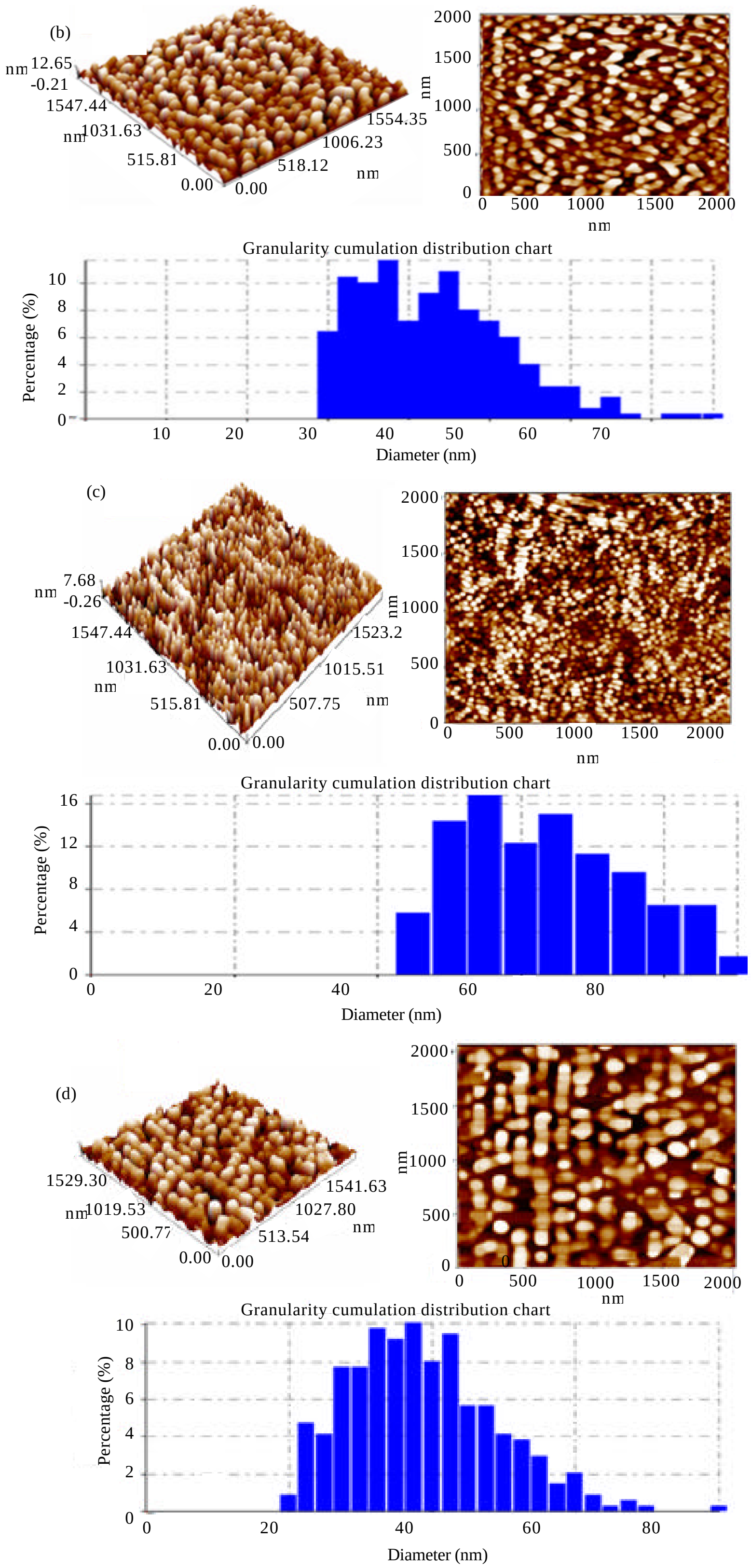

Fig. 2: AFM images of prepared $ZnO-SnO_2$ mixed thin films: a) ZS2/glass; b) ZS4/glass c) ZS2/PS and d) ZS4/PS

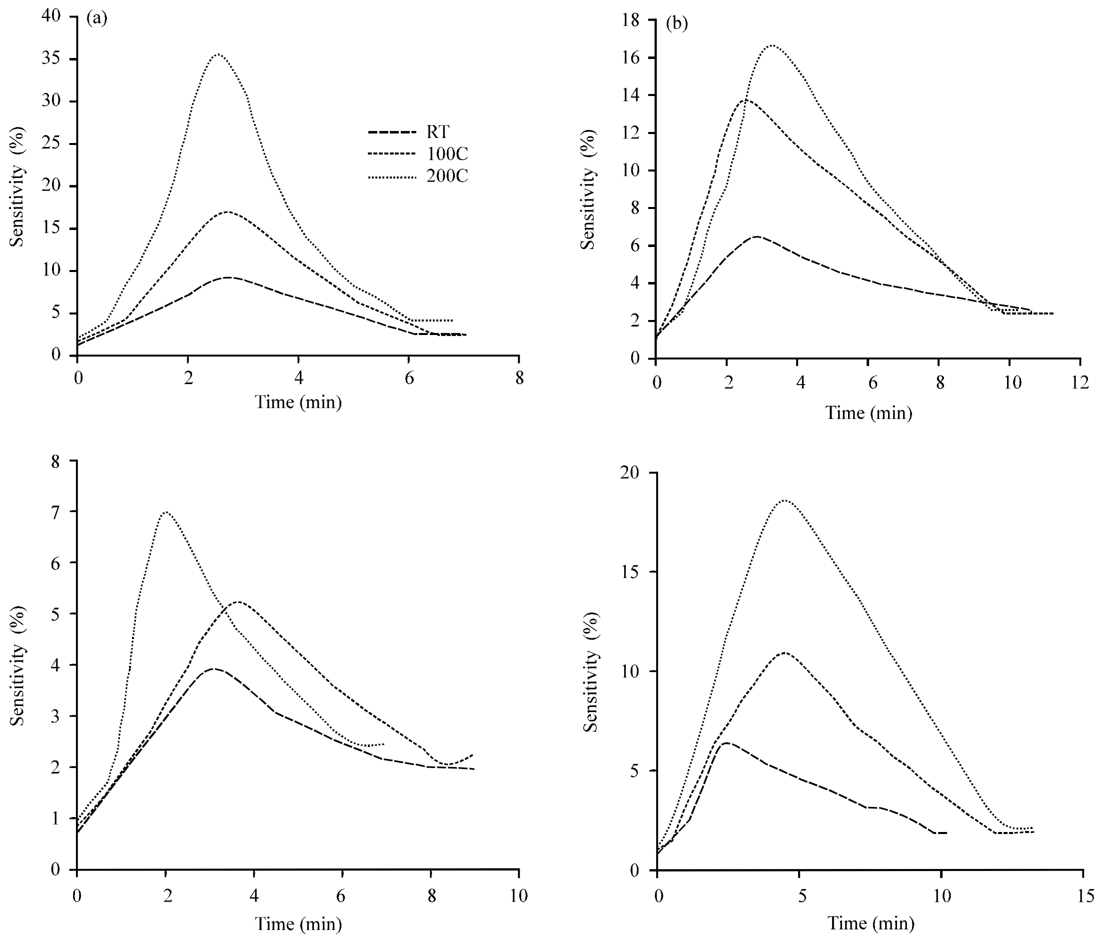

Fig. 3: The change in sensitivity with time for ZnO-SnO$_2$ toward NH$_3$: a) ZS/glass; b) ZS2/PS; c) ZS4/glass and d) ZS4/PS

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 SnO$_2$ ratio as shown in Table 2.

Table 2: AFM analysis of ZnO-SnO$_2$ 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

Gas sensing studies: The nanocomposite ZnO-SnO$_2$ thin films were as a gas sensing detector toward 63 ppm NH$_3$ gas in different operating temperature. NH$_3$ is a reducing gas when it react with n-type surface the resistivity will decrease according to the relation (Vinoth and Gopalakrishnan, 2017):

$$4NH_3+3O_2(ads) \rightarrow 2N_2+6H_2O+6e^- \quad (1)$$

Figure 3 shows the change of sensor response with time at different operating temperatures for the mixed ZnO-SnO$_2$ nanocomposite. The sensitivity evaluated according to the following relation:

$$S=\frac{Ra\text{-}Rg}{Ra}*100\% \quad (2)$$

where, R$_a$ and R$_g$ represent the resistance of the films in air and in gas, respectively. When NH$_3$ 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 $ZnO-SnO_2$ on the glass and porous silicon towards NH_3 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 NH_3 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 NH_3 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 NH_3 equal 49.5% and Wagh *et al*. (2004) reported asensing value of ZnO: Mg toward 50 ppm NH_3 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 NH_3 and the mixed $ZnO-SnO_2$ 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 NH_3 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 $ZnO-SnO_2$ are prepared by simple chemical spray pyrolysis method. The structure morphology and gas sensing toward 63 ppm NH_3 were investigated. The mixed films of $ZnO-SnO_2$ 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 timed recovery time were >200°C which is relativity high value.

ACKNOWLEDGEMENT

This research is supported and revised by the Scientific Committee in Physics Department, College of Education for Pure Science at the University of Anbar.

REFERENCES

Al-Jenaby, A.Z. and H.S. Al-Jumaili, 2016. Structure and optical properties of Ag-doped tin oxide thin films. Intl. Res. J. Eng. Technol., 3: 40-45.

Al-Jumaili, H.S., J. Najim and D.A. Al Qader, 2016. Structure and optical properties of ZnO: Al and ZnO: Cu nanoparticale thin films. Asain J. Appl. Sci., 4: 498-504.

Fahad, O.A., H.S. Al-Jumaili and M.H. Suhail, 2016. Studies on spray pyrolysis SnO_2: $In2O_3$ thin films for NO_2 gas sensing application. Adv. Environ. Biol., 10: 89-97.

Karthik, T.V.K., L. Martinez and V. Agarwal, 2018. Porous Silicon ZnO/SnO_2 structures for CO_2 detection. J. Alloys Compd., 731: 853-863.

Kolhe, P.S., A.B. Shinde, S.G. Kulkarni, N. Maiti and P.M. Koinkar *et al*., 2018. Gas sensing performance of Al doped ZnO thin film for H_2S detection. J. Alloys Compd, 748: 6-11.

Li, C.F., C.Y. Hsu and Y.Y. Li, 2014. NH_3 sensing properties of ZnO thin films prepared via. sol-gel method. J. Alloys Compd., 606: 27-31.

Liangyuan, C., B. Shouli, Z. Guojun, L. Dianqing and C. Aifan *et al*., 2008. Synthesis of $ZnO-SnO_2$ nanocomposites by microemulsion and sensing properties for NO_2. Sens. Actuators Chem., 134: 360-366.

Mondal, B., B. Basumatari, J. Das, C. Roychaudhury and H. Saha *et al*., 2014. $ZnO-SnO_2$ based composite type gas sensor for selective Hydrogen sensing. Sens. Actuators B. Chem., 194: 389-396.

Patil, G.E., D.D. Kajale, D.N. Chavan, N.K. Pawar and P.T. Ahire *et al*., 2011. Synthesis, characterization and gas sensing performance of SnO_2 thin films prepared by spray pyrolysis. Bull. Mater. Sci., 34: 1-9.

Sonker, R.K., A. Sharma, Shahabuddin, M. Tomar and V. Gupta, 2013. Low temperature sensing of NO_2 gas using SnO_2-ZnO nanocomposite sensor. Adv. Mater. Lett., 4: 196-201.

Verma, M.K. and V. Gupta, 2012. Highly sensitive ZnO-SnO_2 nanocomposite H_2 gas sensor. Proceedings of the 14th International Meeting on Chemical Sensors (IMCS 2012), May 20-23, 2012, Nuremberg, Germany, pp: 787-790.

Vinoth, E. and N. Gopalakrishnan, 2017. Effect of temperature on NH_3 sensing by ZnO: Mg thin film grown by radio frequency magnetron sputtering technique. Proceedings of the International Symposium on Dae Solid State Physics Vol. 1942, April 26, 2017, AIP Publishing, Melville, New York, USA., pp: 1-4.

Wagh, M.S., L.A. Patil, T. Seth and D.P. Amalnerkar, 2004. Surface cupricated SnO_2-ZnO thick films as a H_2S gas sensor. Mater. Chem. Phys., 84: 228-233.

Zhang, Y., T. Liu, J. Hao, L. Lin and W. Zeng *et al*., 2015. Enhancement of NH_3 sensing performance in flower-like ZnO nanostructures and their growth mechanism. Appl. Surf. Sci., 357: 31-36.