INVESTIGATION OF STRUCTURAL AND AMMONIA GAS SENSING PERFORMANCE OF SnO_2–ZnO NANOCOMPOSITE SENSORS

Unhale S.B.

Department of Physics, Dr. Manorama and Prof Haribhau Shankarrao Pundkar Arts, Commerce and Science College, Balapur, Dist. Akola, M.S. 444302

Abstract

This research investigates the synthesis, structural characterization, and ammonia gas sensing performance of **SnO_2, ZnO, and their nanocomposites**. X-ray diffraction analysis confirmed the crystalline nature of the materials, with ZnO exhibiting a hexagonal wurtzite structure and nanometer-scale crystallite sizes calculated using Scherrer's formula. The nanocomposites showed enhanced surface properties suitable for gas sensing applications. Ammonia sensing studies conducted at room temperature (100–800 ppm) revealed that sensor sensitivity increases with increasing gas concentration. Among the prepared sensors, the **B5 composition (SnO_2 : ZnO 25%wt.)** exhibited the highest sensitivity (1.554), maximum resistance change, and faster response–recovery behavior, indicating its suitability for efficient ammonia gas sensing applications.

Keywords: Nanocomposites, **SnO_2, ZnO,** Sensitivity, Static Response

1. Introduction

In recent years, there is an enormous increase in environmental pollution due to the combustion of fuels from vehicles, population growth and fast industrialization. Thus, the air quality has become dangerous due to human-made pollution, ultimately causing foremost alarm for the atmosphere, animals, and even for human being. To prevent environmental disaster, before it is too late, it is essential that such pollutant has to be detected and controlled. A large variety of toxic gases in the earth atmosphere, such as NO_2, SO_2, CO_2, CH_4, NH_3, H_2S and such others, require to be detected for environmental security purposes. Thereby creating substantial need to improve gas sensing material, that also comprise various applications such as food technology, industrial manufacturing, medicinal diagnosis, national defense as well as securities, to find unsafe gases in mines etc.[1,2].

Semiconductor gas sensors utilizing SnO_2 and ZnO have been studied extensively since they were first proposed by Seiyama [3]. These metal oxide semiconductor based gas sensors can detect various gases by using the surface conductivity change due to the adsorption and desorption of gases. These sensors are worked on the principle of adsorption-desorption mechanism and hetero-contact type sensing mechanism. The electrical property of the surface of the sensor is changed due to the adsorption of foreign species on the surface of the semiconducting material.

Many metal oxides are suitable for detecting combustible, reducing, or oxidizing gases by conductive measurements. The following oxides show a gas response in their conductivity: Cr_2O_3, Mn_2O_3, Co_3O_4, NiO, CuO, SrO, In_2O_3, WO_3, TiO_2, V_2O_3, Fe_2O_3, GeO_2, Nb_2O_5, MoO_3, Ta_2O_5, La_2O_3,CeO_2, Nd_2O_3 [4]. Metal oxides selected for gas sensors can be determined from their electronic structure. The range of electronic structures of oxides is so wide that metal oxides were divided into two the following categories [1]; (1) Transition-

metal oxides (Fe_2O_3, NiO, Cr_2O_3, *etc.*), (2) Non-transition-metal oxides, which include, (a) pre-transition-metal oxides (Al_2O_3, *etc.*) and (b) post-transition-metal oxides (ZnO, SnO_2, *etc.*).

Pre-transition-metal oxides (MgO, *etc.*) are expected to be quite inert, because they have large band gaps. Neither electrons nor holes can easily be formed. They are seldom selected as gas sensor materials due to their difficulties in electrical conductivity measurements. Transition-metal oxides behave differently because the energy difference between a cation d^n configuration and either a d^{n+1} or d^{n-1} configurations is often rather small [5]. They can change forms in several different kinds of oxides. So, they are more sensitive than pre-transition-metal oxides to environment. However, structure instability and non-optimality of other parameters important for conductometric gas sensors limit their field of application. Only transition-metal oxides with d^0 and d^{10} electronic configurations find their real gas sensor application. The d^0 configuration is found in binary transition-metal oxides such as TiO_2, V_2O_5, WO_3. d^{10} configuration is found in post-transition-metal oxides, such as ZnO, SnO_2.

The composite ZnO-SnO_2 sensors exhibited significantly higher sensitivity than sensors constructed solely from tin dioxide or zinc oxide when tested under identical experimental conditions [6]. Sensors based on the two components mixed together are more sensitive than the individual components alone suggesting a synergistic effect between the two components. Taking SnO_2-ZnO binary oxides responding to butanol as an example, they hypothesize that butanol is more effectively dehydrogenated to butanal by tin dioxide, but that tin dioxide is relatively ineffective in the catalytic breakdown of butanal. On the other hand, zinc oxide catalyses the breakdown of butanal extremely effectively. A combination of the two materials would effectively dehydrogenate butanol and then subsequently catalyse the breakdown of

butanal. The catalysis results obtained when using the composite support this idea. This explanation suggests that not all composite gas sensors will have better performances than those of individual components alone [7-13].

The principal aim of the present research is development of gas sensors based on thick film with two metal semi-conducting oxides viz. SnO_2, ZnO, and Al_2O_3 as functional materials. This has particular emphasis on the problem of sensitivity; range and remarkable selectivity towards the reducing gas mainly NH_3 gas.

2. Experimental

2.1 Synthesis of Nano-crystalline Materials

The methods of synthesis of nano-particles can be broadly classifiedin the three categories namely, liquid phase synthesis, gas-phase synthesis and vapour-phase synthesis . In the present work of thesis, we have used sol-gel method (which is under liquid phase synthesis) for the synthesis of pristine nano-particles of SnO_2, ZnO, TiO_2,and PPy [14].

2.2 Synthesis of Tin Oxide (SnO_2)

All the chemicals used in this study were of GR grade purchase from Sd-fine, India (purity 99.99%). The chemicals are used without any further purification. Stannous chloride dehydrates ($SnCl_2.2H_2O$), Ammonia solution and deionized water were used during reaction. The conducting silver paint (Sigma Aldrich Chemical, USA) is used to form electrodes.

In preparation of SnO_2, 2 g (0.1 M) of stannous chloride dehydrate ($SnCl_2.2H_2O$) is dissolved in 100 ml water. After complete dissolution, about 4 ml ammonia solution is added to above aqueous solution with magnetic stirring. Stirring is continued for 20 minutes. White gel precipitate is immediately formed. It is allowed to settle for 12 hrs. Then it is filtered and washed with water 2-3 times by using deionized water. The obtain precipitate were mixed with 0.27 g

carbon black powder (charcoal activated). The obtained mixer is kept in vacuum oven at 70 ºC for 24 hours so that the mixer gets completely in to dried powder. Then this dry product was crushed into a find powder by grinder.Now obtained product of fine nanopowder of SnO_2 was calcinated at 700ºC up to 6 hours in the auto controlled muffle furnace *(GAYATRI Scientific, Mumbai, India.)* so that the impurities from product will be completely removed [15].

2.3 Synthesis of Zinc Oxide (ZnO)

All the chemicals used in this study were of GR gradepurchase from Sd-Fine, India (purity 99.99%). The chemicals are used without any further purification. Zinc acetate dehydrate $Zn(O_2CCH_3)_2(H_2O)_2$, sodium hydroxide, Methanol and deionised water was used during reaction. In preparation Zinc Oxide (ZnO) 0.2M Zinc Acetate dehydrates was dissolved in 100 ml deionised water was ground for 15 min and then mixed with 0.02 M solution of NaOH with the help of glass rod. After the mixing the solution was kept under constant magneticstirring for 15 min. and then again it was ground for 30 min. The white precipitate product was formed at the bottom. Then abundant liquid was discarded and the product was washed many times with the deionized water and methanol to remove by products. The final products was then filtered by using wattman filter paper and obtain precipitate in the form of white paste, now this paste was kept in a vacuum oven at 80 ºC for 4 hrs. so the moisture will removed from the final product and we will get dry product. Then this dry product was crushed into a find powder by using grinding machine and finally this fine nano-powder of ZnO was calcinated at temperature 800 ºC for 6 hrs. in the auto controlled muffle furnace *(Gayatri Scientific, Mumbai, India.)* so that the impurities from product will be completely removed and get a final product of ZnO nanoparticles [16].

2.4 Sample Codes

The prepared samples are coded as below, listed in the table 1

Table 1: Sample Codes and their compositions

Sr. No.	Sample and composites	Sample Codes
1.	SnO_2	B1
2.	SnO_2- ZnO 05% wt.	B2
3.	SnO_2- ZnO 10% wt.	B3
4.	SnO_2- ZnO 15% wt.	B4
5.	SnO_2- ZnO 20% wt.	B5
6.	ZnO	B6

3. Results and Discussion

3.1 X-ray Diffraction of SnO_2, ZnO and their compositions

Fig. 1 shows the X-ray diffraction patterns of pure and composites of SnO_2 - ZnO , calcinated at 150^{o}C for about 5 h. It is recorded in terms of 2θ in the range 10 to 100^o. It is observed that as the mole % of ZnO in SnO_2 increases, the intensity of corresponding peak increases. ZnO (hexagonal) crystallizes in the wurtzite structure. The lattice parameter values obtained for ZnO are a = b = 3.249 Å and c = 5.201 Å with c/a ratio of 1.6. The main peak of maximum intensity was found to be at 34.43^o and corresponding to (0 0 2) plane. Others planes of ZnO are (1 0 0), (1 0 1), (1 0 2), (1 1 0). The crystallite size (D) was calculated from Scherer's formula using FWHM and it is listed in the table 2.

Table 2. Average crystallite size of SnO_2, ZnO and their compositions

Chemical Composition	Maximum Intensity Peak	FWHM (2θ) degree	Average Crystallite Size

	Position (2θ) degree		(D) in nm
SnO_2	53.22	0.1865	162.22
SnO_2- ZnO 05%	34.67	0.2322	166.32
SnO_2- ZnO 10%	35.82	0.2532	168.32
SnO_2- ZnO 15%	35.43	0.2611	169.09
SnO_2- ZnO 20%	33.17	0.1687	98.65
ZnO	34.43	0.2367	166.93

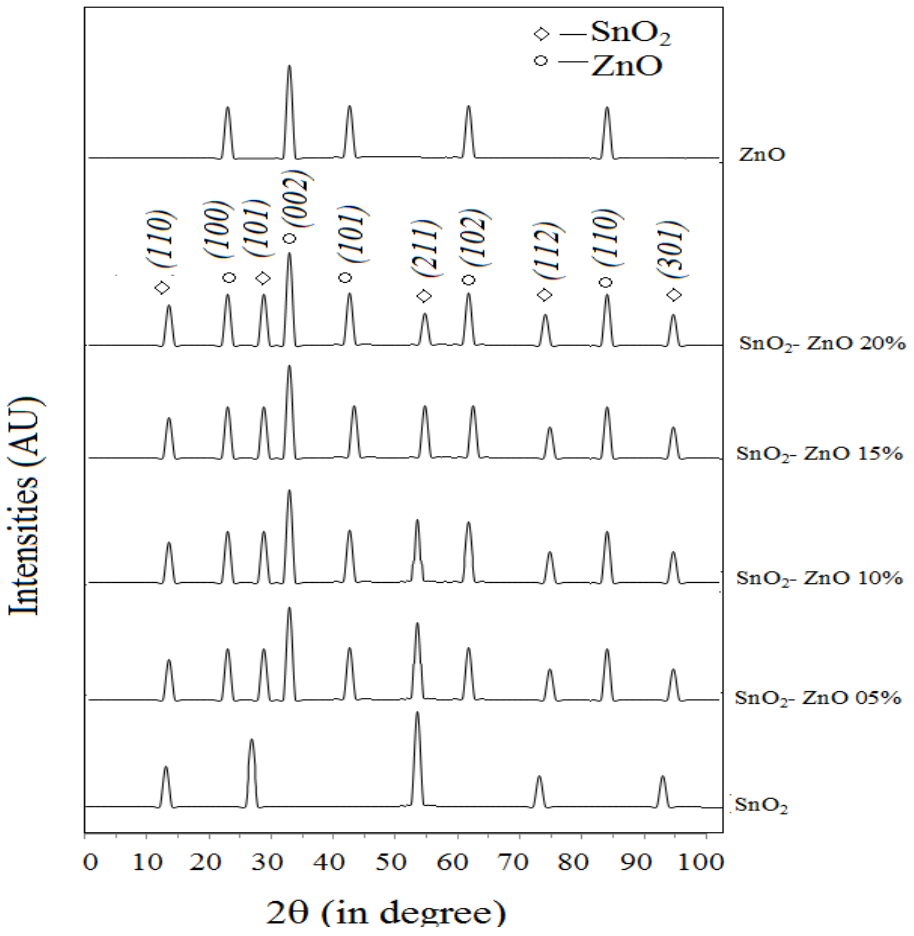

Fig.1. XRD spectra of composites of SnO_2 & ZnO

3.2 Ammonia Gas Detection (Sensing) Properties

Since, ammonia gas is a reducing gas because it donates loan pair of electrons and hence its resistance increases with increase of ammonia gas concentration [16-19]. The sensitivity of the sensor is given by,

$$S = \left(\frac{R_{gas} - R_{air}}{R_{air}} \right) = \left(\frac{\Delta R}{R_{air}} \right)$$

Where, R_{gas} = resistance of the sensor in presence of gas and

R_{air} = resistance of the sensor in air

The variations of sensitivities of different series and sensors with concentration of ammonia gas at room temperature are shown below.

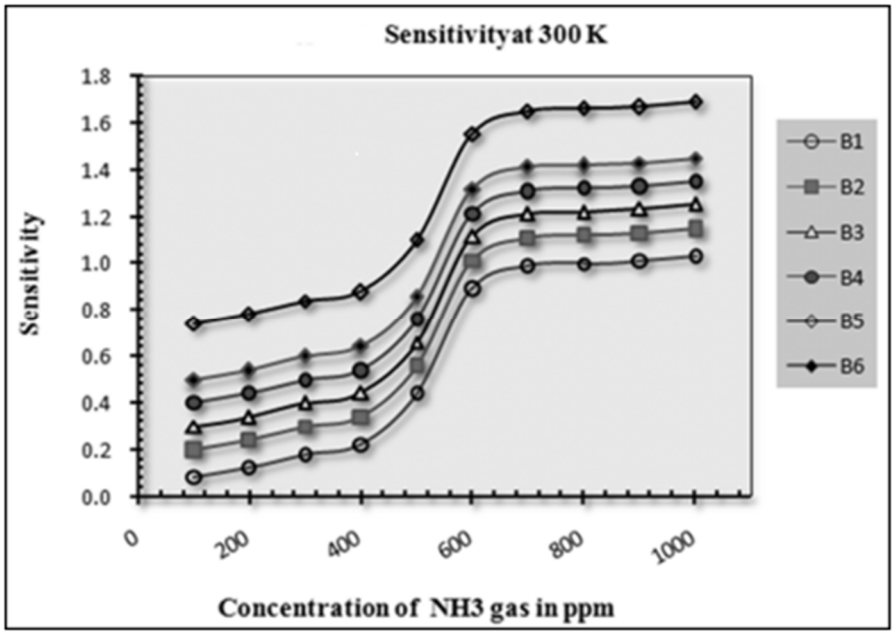

Fig. 2: Variations of sensitivity with NH_3 gas concentration

From Ammonia gas detection graphs (Fig. 2) it is manifested that: as ammonia gas concentration increases from 100 ppm to 400 ppm, there is little increase of sensitivity, from 400 ppm to 600

ppm, sensitivity increases linearly and becomes maximum at 600 ppm. With further increase in ammonia gas concentration, sensitivity increases by little amount. Fig. 2 shows the variation of sensitivity for B1 to B6 sensors with increase of ammonia gas concentration. This series also showed linear variation of sensitivity in the 400 ppm to 600 ppm ammonia gas concentration. From Fig. 2, maximum sensitivity was found to be 1.554 for B5 sensor[20-22].

3.3 Static Responses of Sensors

Static response of samples at 200, 400 and 600 ppm is shown Fig. 3

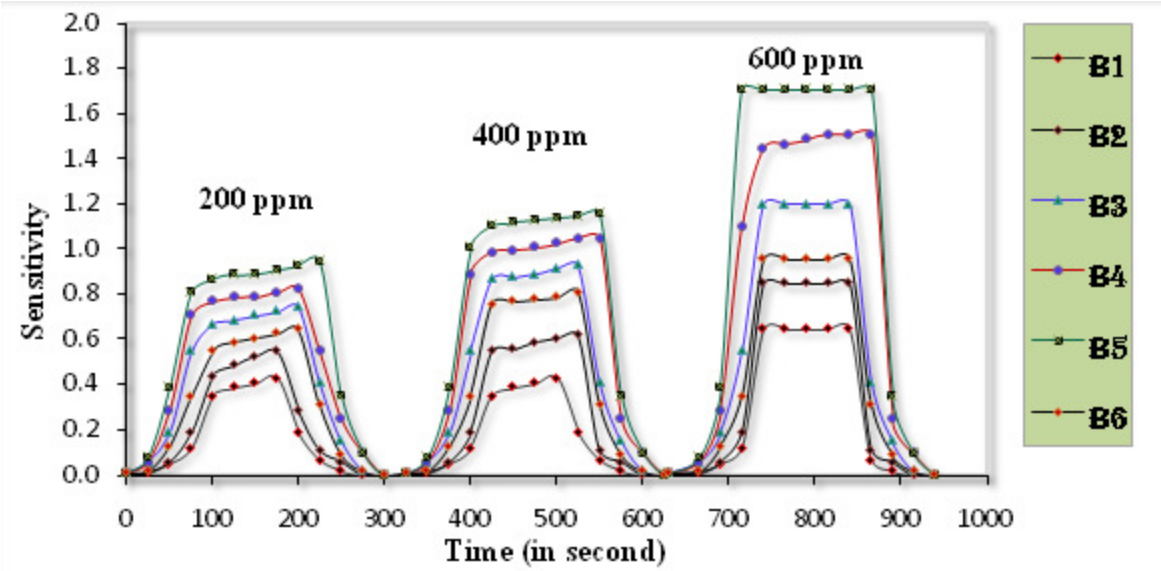

Fig. 3: Static response (response and recovery times)

It is obsevred that B5 (SnO_2- ZnO 20%) sensor is fast in response and recovery times. Response time was found tobe 62 s and that recovery time was 99 s. Thus B5 sensor is fast that other sensors.

Conclusions:

The present study investigated the structural and ammonia gas sensing properties of SnO_2, ZnO, and their nanocomposites. X-ray diffraction analysis confirmed the crystalline nature of the materials, with ZnO exhibiting a hexagonal wurtzite structure and nanometer-scale crystallite size. The gas sensing results showed that sensor sensitivity increases with increasing ammonia concentration. Among the prepared sensors, the B5 composition (SnO_2- ZnO 20%) demonstrated the highest sensitivity and maximum resistance change at 600 ppm NH_3 concentration. It also exhibited faster response and recovery times compared to other sensors. These results indicate that SnO_2–ZnO nanocomposite materials are promising candidates for efficient room-temperature ammonia gas sensing applications.

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