STUDY OF AMMONIA GAS SENSOR BASED ON SNO_2 AND ZNO NANOCRYSTALLINE COMPOSITE MATERIAL

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Abstract

SnO_2 and ZnO are synthesized separately by microwave assisted technique.A stannous chloride and zinc chloride is used as a precursor with deionized water as a solvent. The nanocrystalline SnO_2-ZnO composites thick films are fabricated by screen printed technique. The morphology and nano structure have been characterized by field emission scanning electron microscopy (FE-SEM),chemical composition is investigated by energy dispersive analysis by x-ray (EDAX).Nanocrystalline spherical stannous oxide and ZnO rod were observed in FE-SEM.

Keywords: Sensor, Nanocrystalline, Scanning.

Introduction

Due to fast industrial growth and production development in every field like agriculture, fertilizers, appliances and many others the environmental pollution becomes hazardous problem as far as the health safety of human being and lives in the nature are concern. In order to escape from the disaster of pollution it is most imperative to develop highly sensitive and selective sensors for the detection of various hazardous gases in the atmosphere. Metal oxide base nanocrystaline chemical sensors are proved to be most promising among solid state gas detector due to their reliability and ease of manufacture and application. The sensitivity of such sensor can enhance by applying different available technique such as by using composite system of nano material and changing their composition,decreasing particle size, surface modification, , trying with different chemical etc.In case of sensor having comparatively smaller particle size, the available surface area will be more the result will be diffusion of more gas on the surface of sensor. This encourage reactivity of sensor with the gas leading of rise in sensitivity. The sensor characteristic such as sensitivity, response/recovery time and selectivity, are largely determined by the reactivity of active centers of the sensor and the diffusion of gas to these centers. Researchers in the beginning studied mostly on sensor base on single metal oxide. The disadvantage of such sensors is rather low sensitivity and selectivity to gases that have similar chemical characteristics or higher response /recovery time. Use of composite metal oxide base nanomaterial system could be promising approach for improving performance of sensor.

Enhance sensitivity and selectivity can be obtained by using mixture of metal oxide or composite system [1-4]. the electronic structure of the nanocrystal can be changed due to the interaction of different component in the composite sensor system leading to rise in reactivity of sensor with the target gas **.**By varying the composition,structure and work function of nanocomposite sensor the selectivity of sensor can be significantly improved**.** [5-6].The temperature corresponding to highest sensitivity may be shifted to higher or lower value by simply varying the chemical composition or their proportion in composite sensor system. Similarly opportunity for enhancing sensitivity may be generate by modifying chemical component or their quantity.(Eg. Selectivity of H_2 gas in presence

of CO shifted to higher temperature by adding small quantity of ZnO in CuO doped SnO_2[5]. Mixed metal oxide systems can be classified into three groups. The first category includes chemical compounds resulting from the chemical interaction between various oxides. Examples include $ZnSnO_3$ and Zn_2SnO_4 compounds formed in the ZnO-SnO_2 system [7] and/or chemical interaction of CdO with In_2O_3 borne to $CdIn_2O_4$ crystal.) [8] The interaction of SnO_2 with WO_3 in SnO_2-WO_3compositesystemborne to α-$SnWO_4$ phase which is sensitive to small amounts of CO and NO**[9]).**Solid solutions prepared by mixing two metal oxide is the second category of mixed oxide system. Mixture of $TiO_2$with $SnO_2$is the example of such second category, which form solid solutions over the entire range of compositions but only above a certain critical temperature [10-11]. Mixtures of metal oxide nanocrystals interacting with each other such as, In_2O_3-SnO_2, TiO_2-WO_3 and many others included in the third group. The characteristic of this group is that it gives neither individual compound nor solid solution [12-14].A variety of methods are used for producing mixed metal oxide nanocomposites. These methods include sol-gel technique using composition of mixed oxides from corresponding salt solution [15]. aerosol spraying of salt solutions with subsequent heat treatment[16]**,**the deposition by reactive metal sputtering from composite targets in the presence of oxygen[17-18] and the blending of individual metaloxide nanopowders[19]. It should be remember that the structure of the nanocrystalline components in the composite may change considerably from that of individual substances which form the base of the composite. Due to insertion of ions of one component in the lattice of other component for producing composite metal oxide system, probably high volume defects may be produce in nanoparticles. For example, in the synthesis of nanocomposite TiO_2-SnO_2 by RF-sputtering and by molecular beam, the nanocrystalline particles with high volume defects are produced.First the mixture of titanium and tin ions is prepared.This mixture is in amorphous form initially which transfer into crystalline composite form after annealing the amorphous mixture [10]. Reporter in this work studied on iso-type SnO_2- ZnO composite sensor especially the sensitivity and its response and recovery time.

Experimental-

AR grade stanous chloride from merk ltd.,AR grade zinc chloride (Merk ltd.) were used as a precursor. AR grade diluted ammonia solution is used as a base. The Stannous chloride was separately diluted with de-ionized water with simultaneous stirring. The PH of the solution was maintained by using liquid ammonia diluted with water. Similarly Zinc chloride solution was separately diluted with de ionized water with simultaneous stirring. The PH of the solution was also maintained by using liquid ammonia diluted with water. The resultant precipitate of stannous chloride and zinc chloride were separately washed with de-ionized water until chlorine ions are removed. The chlorine free precipitate was then irradiated with microwave energy using Samsung house hold microwave oven for optimum time. The radiation frequency was 2.45 Ghz. and its power up to 1 kwt. The resultant mixture of SnO and ZnO nanoparticles were then sintered at 400^0 C. For 5 an hour and their structure was analyzed by x-ray diffraction pattern (XRD) using Cukα wavelength of 1.54 AU. The morphology of the sample was studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).The elements and their percentage in the resultant nano crystalline sample was observed by energy dispersive analysis by x-ray (EDAX).The crystallinity of the composite sample was studied by selected area electron diffraction(SAED). FE-SEMmicrograph displayed crystalline size and the shape of grains. EDAX attributed expected chemical composition.

Preparation of thick film

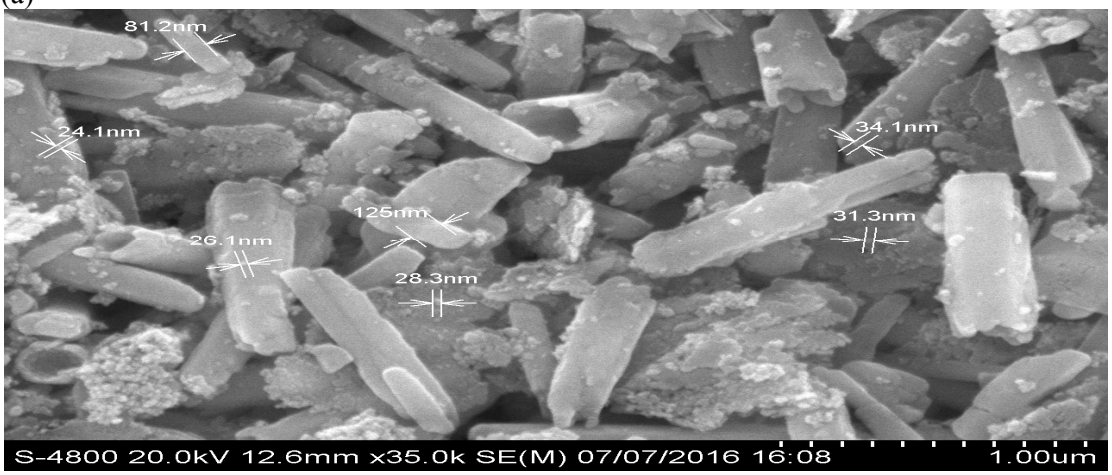
For preparation of SnO_2 – ZnO nano composite thick films the $SnO_2$and ZnO were synthesized independently by microwave assisted method. The quantities of SnO_2 and ZnO taken for fabricating SnO_2 – ZnO nano composite thick films were 90% - 10%, 80% - 20%, 50% - 50%, 20% - 80%, 10% - 90% (Percentage of SnO_2 is written first and second percentage is percentage of ZnO and same will be the trend here after). Thick films of synthesized nanostructure SnO_2 – ZnO nano composite were prepared by using screen printing technique. In

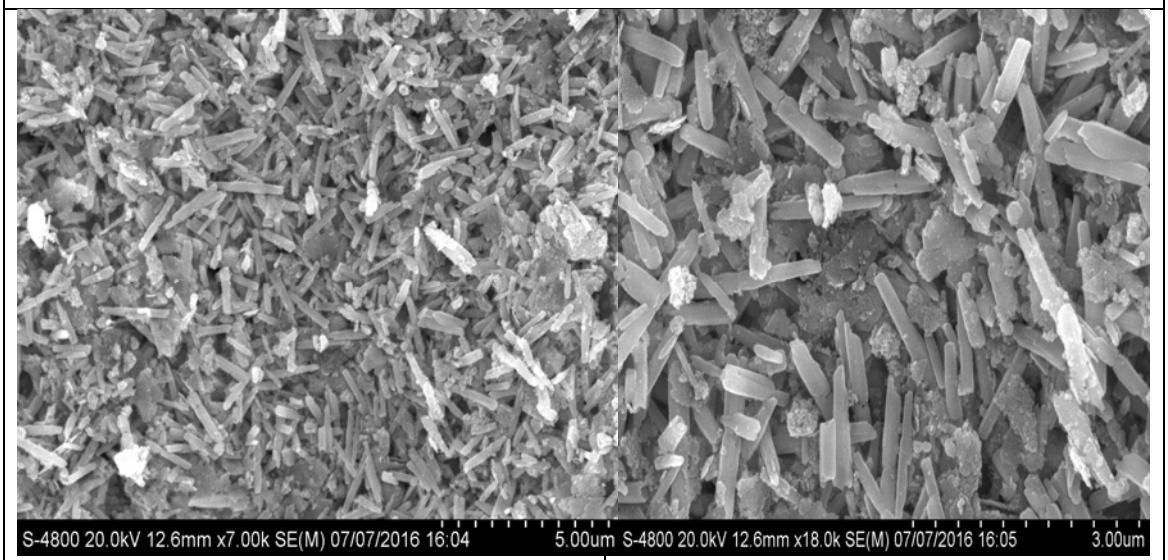
typical process, thixotropic paste was formulated by mixing the various quantity of synthesized SnO_2 and ZnO powder with ethyl cellulose (temporary binder) in mixture of organic solvents. The ratio of mixture of SnO_2 and ZnO to ethyl cellulose was 95: 05.The ratio of inorganic to organic part was kept as 75:25 in formulating the paste.The thixotropic pastes were screen printed on a glass substrate in desired pattern. The films prepared were fired at 500 ^{0}C for 5 hr. prepared thick films called as SnO_2 – ZnO nano composite thick film sensor. Different thick film sensors fabricated as in given table No.1.

Main system is SnO_2 – ZnO nano composite		
Sr No.	SnO_2–ZnO percentage	Meaning
1	90% - 10% or (90-10)	90% SnO_2 and 10% ZnO
2	80% - 20% or (80-20)	80% SnO_2 and 20% ZnO
3	50% - 50% or (50-50)	50% SnO_2 and 50% ZnO
4	20% - 80% or (20-80)	20% SnO_2 and 80% ZnO
5	10% - 90% or (10-90)	10% SnO_2 and 90% ZnO

Table – 1

(a)





(b) (c)

Fig 1(a-c)FE- SEM micrograph of 20%-80%= SnO_2 – ZnO composite nano material thick film

Scanning electron microscopy is convenient technique to study the microstructure of nano crystalline thick film sample. Field emission scanning electron microscopy FE-SEM was employed to characterize the surface morphology. FE-SEM micrograph of (20%-80%) SnO2-ZnO composite thick films are taken at north Maharashtra University Jalgaon. Fig4.2.1 (a-c) depicts the FE-SEM micrograph of 20% - 80% unmodified SnO_2 - ZnO composite sample at different magnification. As same SnO_2 and ZnO are used in all composite film,it is avoided to take the FE-SEM micrograph of (10%-90%) and (80%-20%) composite sample. As seen in fig Fig4.2.1(a**)** SnO_2 - ZnO composite film consist of randomly distributed ZnO rod and tube along with clumps of spherical particle of SnO_2.As in fig the ZnO rod having size 81.2 nm and 125 nm are distinctly seen in image. ZnO rod smaller than 81.2 nm are also present in micrograph. Smaller spherical particle (of size 24.1 nm,26.1 nm,31.3nm) could be attributed to SnO_2 particles. SnO_2 particles are rather agglomerated.

Elemental analysis : Energy dispersive spectroscopy analysis by X ray (EDS or EDAX

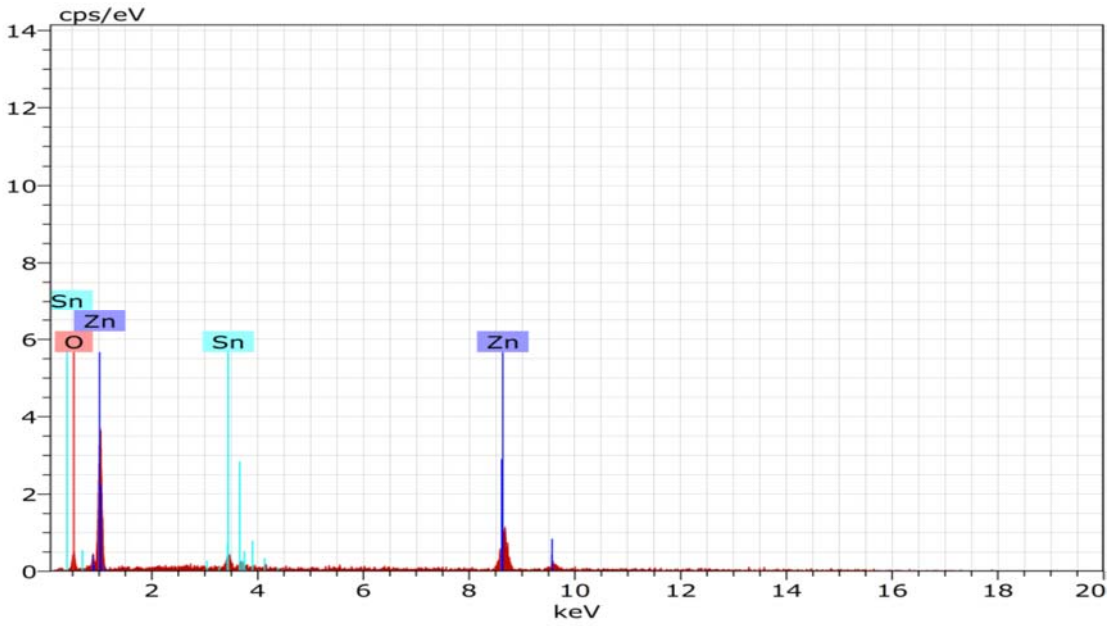


Fig: 2 EDS spectra of SnO_2 – ZnO (20 % - 80 %) composite thick film

Element	Atomic number	Mass %	At. Wt. %
O	**8**	**13.6**	**40.13**
Zn	**30**	**78.55**	**56.74**
Sn	**50**	**7.85**	**3.12**
Total		**100**	**100**

Table-2: Table showing elemental composition

Electrical characterization

A) I – V characteristics

Fig. No. 3 represents I –V characteristics of all SnO_2 – ZnO nano composite thick films at temperature 350^0C. the characteristics was studied with the help of Keithley 6487 picoammeter cum voltage source. Current was measured with forward bias voltage from 0 to 10 V with the step of 2V .The measurement is repeated with negative voltage.The nature of the I-V characteristics for particular samples shows that the contacts are ohmic in nature.

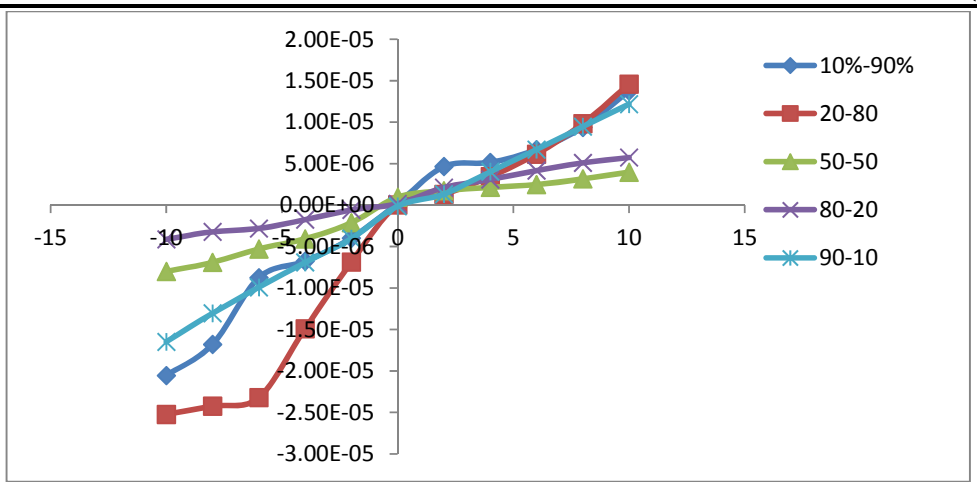


Fig 3 - V Characteristicof unmodified SnO_2 – ZnO nano composite

B)Electrical conductivity

The variation of log (σ) with reciprocal of temperature of all unmodified SnO_2 – ZnO nano composite thick films are shown in fig. the nature of conductivity shows the negative temperature coefficient of resistance ie. Semiconducting nature of all unmodified SnO_2 – ZnO nanocomposite thick films. All the samples have nearly equal conductivity .Conductivity of 50 - 50, 20 – 80 and 90 – 10 composite sample overlap on each other while the conductivity of sample 10 – 90 and 80 – 20 are negligibly smaller than first three. Log (σ) of different sample are -5.8, - 6.08, - 6.06, - 6.08, - 6 .7.from the mentioned value of log (σ) the sample (90 – 10) sensor exhibit highest value of log (σ) while sample (10 – 90) sensor has lowest value.Sensor and their corresponding highest electrical conductivity is depicted in table 3.

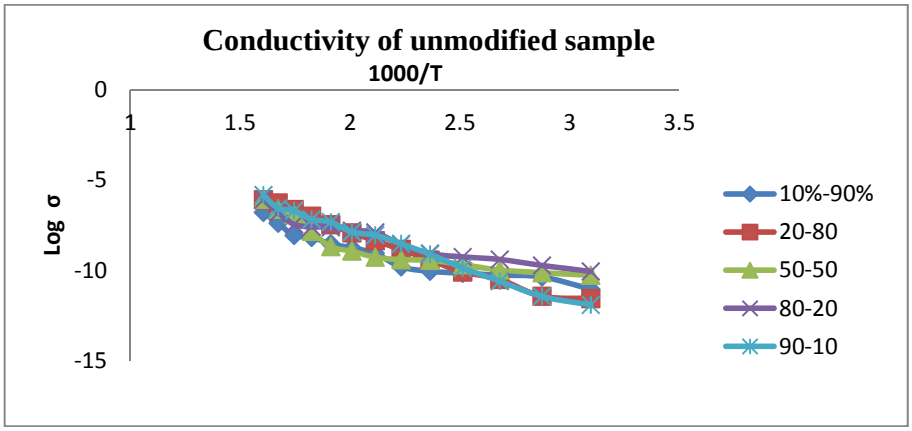


Fig : 4 Conductivity of unmodified sample

Table – 3: highest conductivity of sensors

Sensor	10%-90%	20-80	50-50	80-20	90-10
Highest conductivity	-6.78896	-6.08585	-6.06214	-6.08037	-5.82182

Fig. 4 shows the variation of sensitivity with operating temperature for pure SnO_2 and ZnO towards ammonia gas. The maximum sensitivity of pure SnO_2 for ammonia was 8 at100 ^{0}C.and that of ZnO was 3 at (50^{0}C) & (100^{0}C). Sensitivity of ZnO at 50 ^{0}C might be due to moisture and it is not that much considerable.

C) Sensitivity –Fig 5 and 6 depicts the variation of gas response with operating temperature for pure SnO_2 and ZnOand for all SnO_2-ZnO composite thick films sensors towards NH_3 gas, respectively. From each curve it is clear that for

SnO_2-ZnO based composite sensor gas sensitivity towards NH_3 gas increases with operating temperature reaches maximum corresponding value at optimum temperature and decreases further.The composite sensor (50-50) shows highest sensitivity towardsNH_3 gas among all sensors. The highest sensitivity exhibited by (50-50) sensor towards NH_3 is11 .It is slightly greater than the sensitivity of pure SnO_2(fig.4) and 3.6 times more than pure ZnO (fig.4).Sensitivity of (90-10),(80-20) and that of (20-80) is nearly equal with the sensitivity of pure SnO_2ie.(8)(fig4)but 2.6 times greater than that of pure ZnO. It is clear fromFig 5that the response of sensor towards NH_3 gas goes on increasing with operating temperature, reaches to maximum and decreases with the further increase of operating temperature. Response to a gas is related generally to the number of oxygen ions adsorbed on the surface of film. If film surface chemistry is favorable for adsorption, response and selectivity would be enhanced.Nature of sensitivity curve could attributed to all the factors and parameter which contribute in enhancement and depletion of sensitivity .Those factors are chemical composition, heterojunction effect, microstructure, effect of temperature. nonuniformity of grain of two component, intergrain boundaries. Highest conductivity of (90-10) sensor depicted the lowest adsorption capacity of oxygen molecule by the surface of respective sensor .this observation attributed the lowest sensitivity of (90-10) sensor. Further the optimum temperature for maximum sensitivity of (10-90) and (80-20) sensor shifted to 300 ^{0}C which is comparatively higher than for other sensor. It means more active region for (10-90) and (80-20) sensor might have got available at 300 ^{0}C.Adsorption of oxygen molecule on the surface of (10-90) and (80-20) sensor start at 300 ^{0}C.

NH3 Sensitivity		
sensor	SnO_2	ZnO
Max.sensitivity & corresponding temperature	8 (100 ^{0}C)	3(50 ^{0}C)& (100 ^{0}C)

Table :4 Highest sensitivity of pure SnO_2 and ZnO

NH3 Sensitivity					
Composite sensor	10% - 90%	20-80	50-50	80-20	90-10
Max.sensitivity & corresponding temperature	9.6 (300 ^{0}C)	8 (300 ^{0}C)	11 (200 ^{0}C)	8.1 (150 ^{0}C)	8.4 (150 ^{0}C)

Table :5 Highest sensitivity of different composite sensors

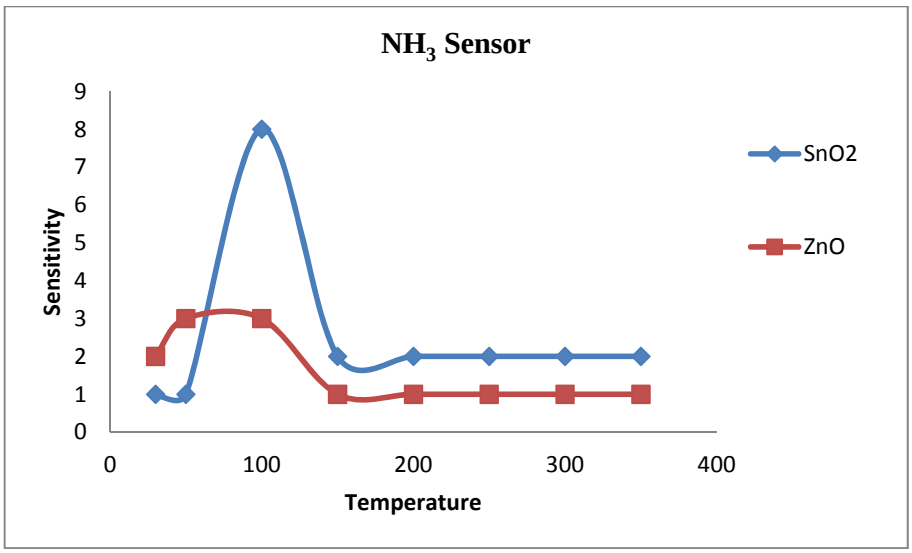


Fig 5: Sensitivity of SnO_2 and ZnO for ammonia

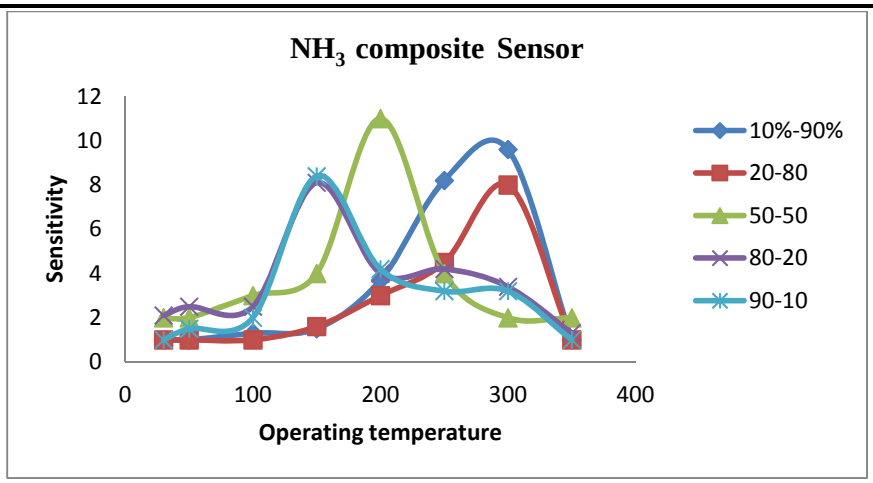


Fig 6 : Ammoniagas sensitivity of SnO_2- ZnO composite sensor

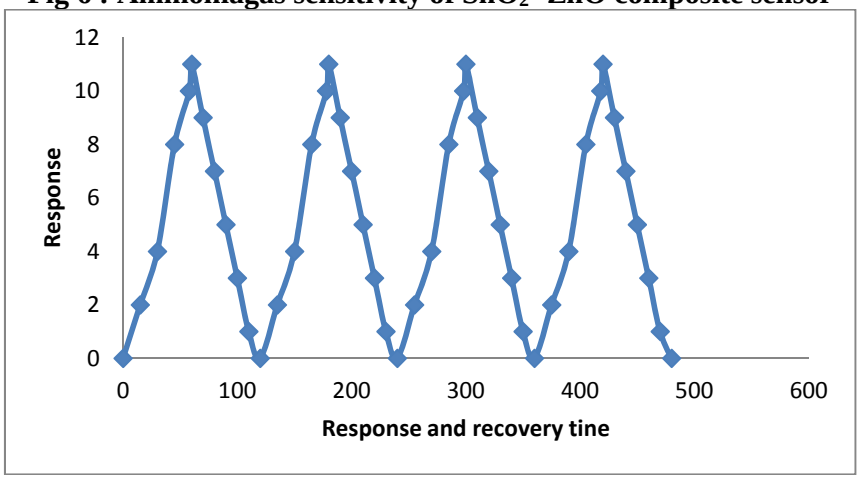


Fig 7: Response and recovery time of unmodified SnO_2- ZnO composite sensor

D) Response and recovery time

Response and recovery time of unmodified SnO_2-ZnO (50-50) composite sensor is depicted by fig.6,90% response level were attained in (58 sec).Recovery time of (50-50) sensor is about same (50 sec.).The response and recovery time of allunmodified composite sensor is tabulated in table.

Sensor	Response time	Recovery time
10-90	57	60
20-80	48	56
50-50	58	50
80-20	48	56
90-10	48	57

Table 5 – Response and recovery time of unmodified sensor –

6) Conclusions

Results and analysis from this study showed that the array of SnO_2–ZnO composite sensors is not that much effective for the detection of Ammonia. In particular, the composites materialswere seen to exhibit better response behaviours than the pure counterparts. The best performing composite towards ammonia was seen to be the (50 -50) SnO_2 - ZnO sensor device at 200 ^{0}C with a response of 11 towards 600 ppm. of the analyte. The response of (50 - 50) SnO_2 - ZnO sensor device slightly better than pure SnO_2 sensor but 3.6 times greater than pure ZnO. These results thus showed that a simple change in the concentration of the individual metal oxides within the composites could improved the gas response of the devices towards ammonia.

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