COMPARATIVE STUDY ON AMMONIA SENSING PROPERTIES OF SNO_2 NANOCOMPOSITES FABRICATED VIA ELECTROSPINNING AND SOL-GEL PROCESSES

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Abstract

In this paper, the performance of cerium doped SnO_2 nanofibers towards ammonia synthesized by electro spinning is compared to the undoped SnO_2 prepared by traditional Sol-Gel method. .The synthesis of nanofiber and normal SnO_2 were characterized by XRD, SEM and FTIR. The response of both Sensor towards ammonia gas at different concentration (50-500ppm) with different operating temperature (225^0C-400^0C) were studied. Maximum Sensing response was seen in Nanofiber than in Nanocones prepared by the Sol-Gel method. Moreover, Nanofiber achieve a good sensitivity, fast response, low ppm detection, smaller grain size and good stability towards the target gas. These results bespeak the potential application of cerium-doped Tin oxide Nanofibers for fabricating high performance Ammonia sensors.

Keywords: *Tin Oxide, Sol-Gel, Electrospinning Gas Sensing Chamber Ce-doped, Metal oxide semiconductor*

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1. INTRODUCTION

Tin oxide is n type semiconductors which are most commonly used for gas sensing. Last decades has witnessed the upcoming of one dimensional SnO_2 nonomaterials such as a nanowires [1,2], nanofibers, nanobelts[3] and nanoribons[4] because of the large surface areas and unique electrical properties compare from the normal nanocones. The Principle behind the sensing is the reactions between gas molecules and SnO_2 surfaces such that oxygen molecules will be adsorbed on to the surface thereby increasing the resistance and finally decreasing the conductance. When exposed to reducing or oxidizing gases, the trapped electron will return to the conduction band thereby increasing the conductance [9-11]. Tin oxide is considered as one of the strongest contenders to be used as active material for gas monitoring devices [5].Apart form that tin oxide has good physical and chemical properties such as wide band gap of 3.6 eV, dielectric constant and finally Easiness to synthesize.

Metal oxide are commonly and widely used as sensing material for the detection of the hazardous and toxic gases. Here the tin oxide proves to be one of the best in the nanoregime. Different techniques can be employed for the synthesizing the nonomaterials. The most commonly used techniques are vapour deposition[6] , Rf sputtering [7],hydrothermal method[8] , electrospinning [9-12],sol-gel[13-19],spray pyrolysis[18]etc . Among them Electrospinning and Sol-Gel are of our interest. One dimensional as well as quasi dimensional nanostructures can be fabricated successfully.

In preparation of the nanofibers, the electrospinning technique is considered as effective and versatile. The electrospinng technique consist of three major parts : high voltage power supply, Spinning nozzle and collection plate. During the working process the electric field is applied between collection plate and the spinning nozzle. The solution from the syringe could be collected at the collector plate due to the electric field force, surface tension and gravity[20-22] Moreover Electrospun fibers have high surface to volume ratio and enhance the gas sensing properties. The Electrospun method is capable of synthesizing 1D nanostructure which are uniform in diameter, large in surface area and long in length [23,24].

On other hand the sol-gel is simplest and easiest method for synthesizing nanoparticles[13-19,25].It is able to produce a very fine powder, homogenous in nature and uses low temperature. But the drawback of this method is its long processing time, residual hydroxyl, residual carbon and also cause large shrinkage [29]. Doping with different materials proved to be effective method to improve the gas sensing properties. among the different materials Ce ion was found to be effective for the improving the performance of the gas sensor[26-28].

In this paper we report a simple approach to fabricate Ce-doped nanofiber by electrospinning and normal SnO_2 by sol-gel method and later comparing both nanoparticles sensing properties towards ammonia. We found that the Ce doped nanofiber exhibit excellent sensing characteristics such as high sensitivity, fast response time, good stability and low ppm detection than that of the nanoparticles prepared by sol-gel

2 EXPERIMENTAL

2.1 Materials and Methods

All chemicals were of analytical grade and solutions were prepared with double distilled water. Peristaltic pump were used to achieve constant flow rate.

2.2 Synthesis of Ce-doped SnO_2 Nanoparticles

2.2.1 Electrospinning Method

The starting material for the preparation of the nanofiber is $SnCl_2.2H_20$ (stannous chloride)[39.32]. First the Stannous chloride is mixed equally with NMP(N,N-dimethylformamide) and Ethanol to obtain an equal weight ratio of 1:1.After mixing the solution is vigorously stirred for one hour . Then PVP(polyvinylpyrolidone) having mass 12% is mixed with 6 mol% of cerium nitrate to above solution and stirred for two hours to obtain the corresponding sol. The solution is stirred for two hours with mild heating. After stirring the solution is transferred to 2-ml disposable syringe having needle diameter of 0.5mm and electro spuned at 20 KV. The distance between the syringe and the spinning nozzle is of 18 cm. The nanofiber were completely annealed in air at temperature of 600^0C for six hours in order to remove the polymer component. The final product would be dark reddish powder . The fig.1 shows the schematic diagram of the electrospinning.

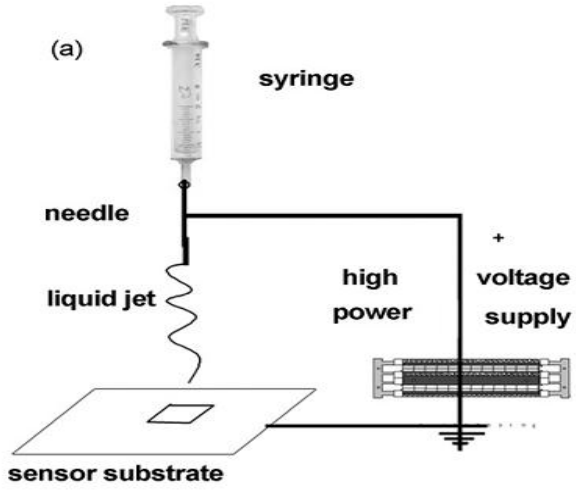

Fig.1 Schematic illustration of the basic setup for electrospinning

2.2.2 Synthesis of SnO_2 nanoparticles by sol-gel:

SnO_2 is prepared by traditional sol-gel technique [33,34].0.3 M Tin(IV) chloride pentahydrate were added to 0.5 M starch solution and stirred for half an hour. Stirring is done with the help of magnetic stirrer. To the above solution ammonia is added drop wise and stirred vigorously for 2 hours. The solution is allowed to settle down overnight and precipitate is washed and centrifuged for more than 10 minutes and filtered. The powder is washed with double distilled water and later kept in oven for drying at 80^oC for overnight. Calcination at 600^0C for 10 hours should be done in order to get fine power of tin oxide

2.3 Sensor Setup:

Overall setup of the gas sensing is shown below in Fig.2. The Gas sensing setup consist of gas chamber, heater, thermocouple and Agilent millimeter. The film is placed on the substrate holder inside the gas chamber and heated to desired temperature. The initial resistance of both nanoparticles are measured and recorded. After that ammonia gas is injected into the gas chamber and the substrate is heated to 350^0C to assist the reaction of the analyte gas with the thin film. The temperature inside the chamber is maintained constant with the help of the PID controller (closed loop system)

The resistance of the SnO_2 changes when it reacts with the ammonia gas. The resistance value is measured with the help of Agilent millimeter and it is recorded down until steady state is obtained. The experiment is repeated for different temperature and for different ppm concentration. Flow rate has been introduced with the help of peristaltic pump. Dor different flow rate the response towards ammonia is noted down.

Fig.2 Temperature controlled gas sensing chamber

3. RESULTS AND DISCUSSION

3.1 XRD Analysis

The XRD pattern for both nanoparticles are shown in the fig.3. All the peaks can be assigned to diffraction from rutile type SnO_2, and also weak traces of Ce is seen in the nanofiber sample. The incorporation of the Ce is marked as the blue dot in the XRD figure. Five diffraction peaks were seen at 26.88^0, 33.92^0, 37.99^0, 51.90, 54.78^0 and 65.80^0 having miller indices(110), (101), (200), (211), (220), (002), (321). Sample is correlated from JCPDS reference data(JCPDS 41-1445). Broadening of the peaks in Ce-doped SnO_2 nanofiber may be due to the incorporation of the Ce ions. The crystalline size is estimated using scherrer formulae[31.32].

$$D = 0.89\lambda/(\beta\cos\theta)$$

Where D represents the particle size, □ is the Bragg angle is the full width at half maxima, and lambda value 1.541876 A ˚. The particle size of the Nanosphere is found to be around 10.6nM. and that of Nanofiber of 27 nM.

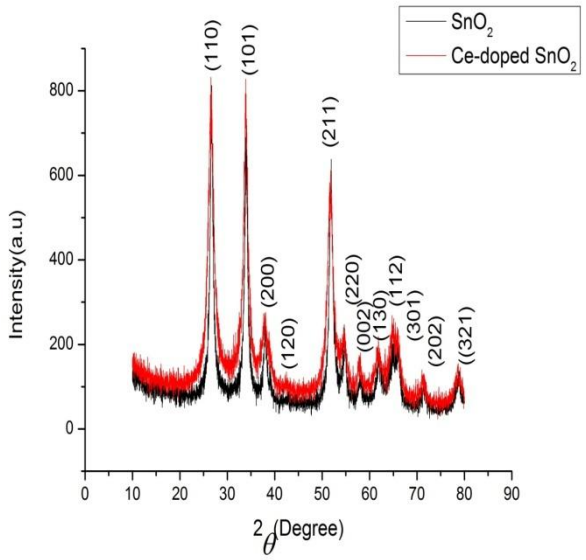

Fig.3 XRD pattern of Ce- Doped SnO_2 and Sno_2

3.2 Microstructure and Morphology

Scanning electron microscopy(SEM) image shows well coated surface of the Tin oxide prepared by electrospinning and sogel. Fig.4(a) & 4(b) clearly shows the formation of the nanofiber. Nanofibers were formed as expected . Addition of the dopants would increase the diameter rather than decreasing. The fiber diameter is much smaller than the undoped SnO_2 prepared by sol-gel method. The grain size of the nanofiber is also much smaller that the undoped one. But the specific surface area for doped one are much larger than that of undoped SnO_2. SEM images of normal SnO_2 were also shown below. It clearly shows the formation of the nanocones and are closely packed. In order to study the composition EDAX analysis was carried out for both nanoparticles. The Table.1 and Table.2 shows the EDAX composition of the nanofiber and nanocones. From the SEM image the particle size are almost clearly in agreement with the crystalline size calculated from the XRD. The EDAX analysis for both Nanofibers and nanospheres were carried out and Fig6 and fig. 7 Shows EDAX composition

Table 1 EDAX analysis of Nanofiber

Sl NO	Element	Weight%	Atomic %
1	N	-21.00	-75.17
2	O	38.09	120.01
3	Cl	20.75	29.50
4	Sn	56.98	24.20
5	Ce	5.19	1.87

Table 2 EDAX analysis of Nor,al SnO_2

Sl NO	Element	Weight%	Atomic %
1	Sn	60.54	17.17
2	O	40.08	84.32
3	N	-0.62	-1.49

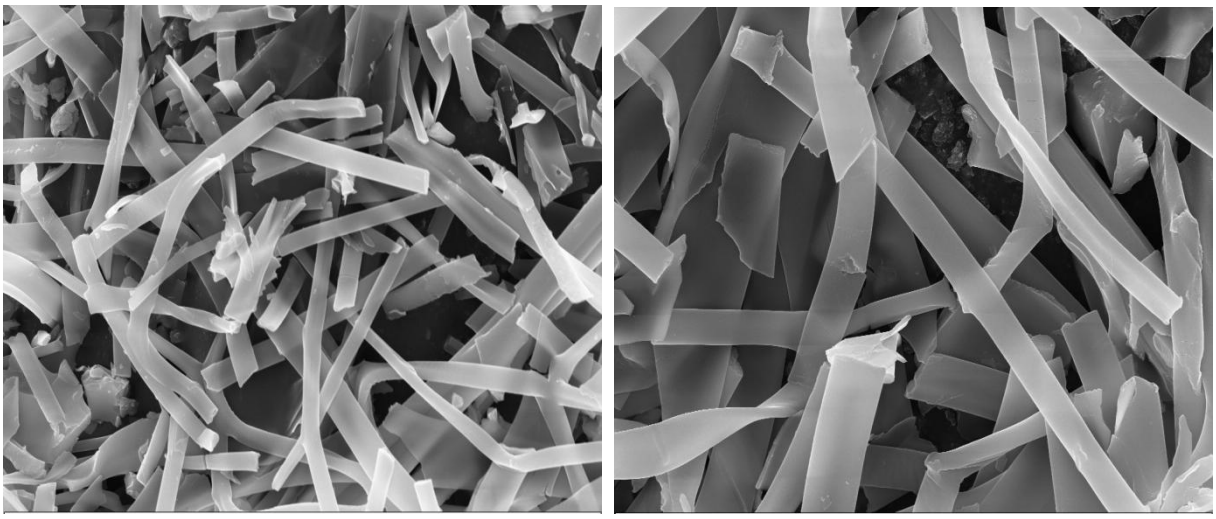

Fig.4 (a) (b) show high magnification and low magnification of nanofibers

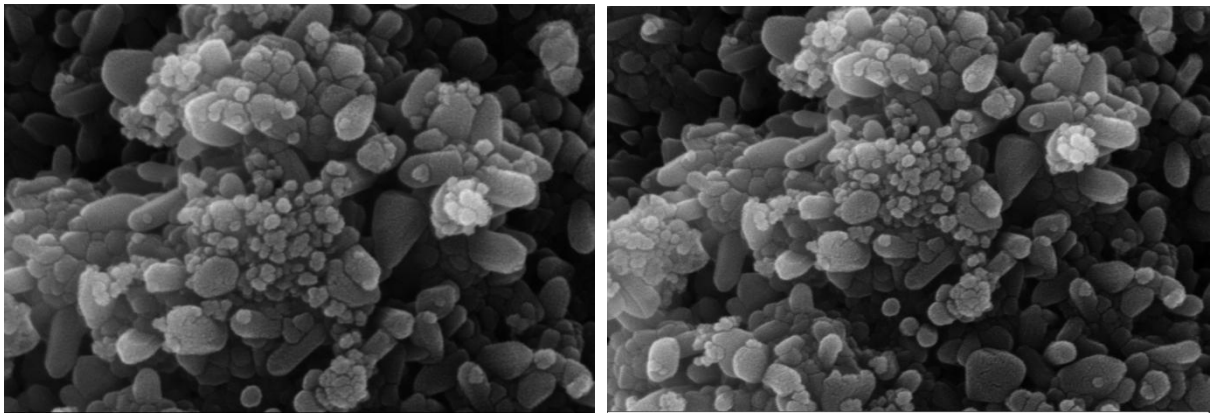

Fig 5 (a) &(b)show high magnification and low magnification of the normal SnO_2

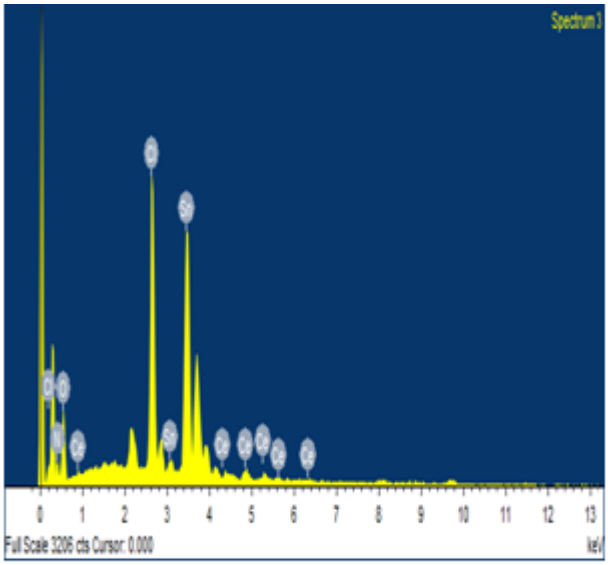

Fig6. EDAX analysis of Nanofibers

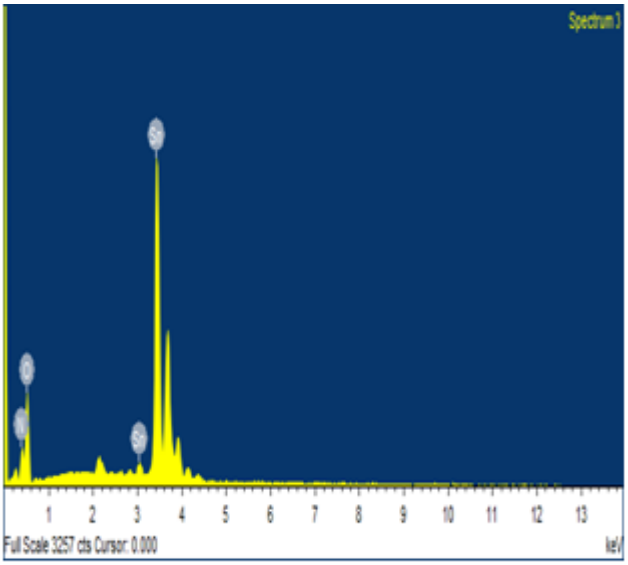

Fig.7 EDAX analysis of Nanocones

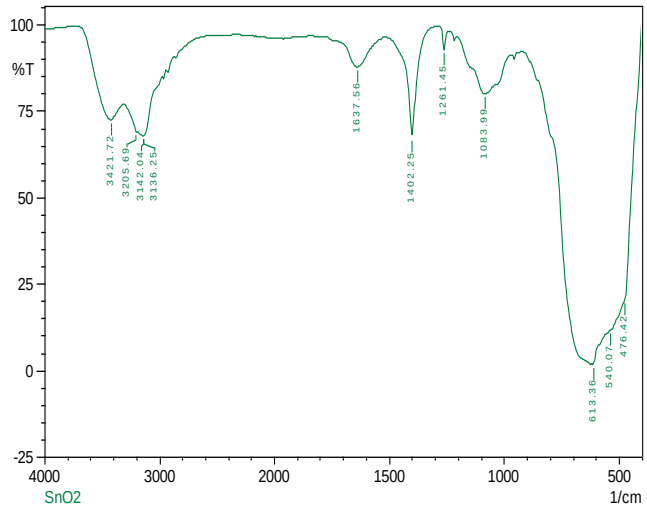

Fig.8.FTIR analysis of Ce-doped SnO_2

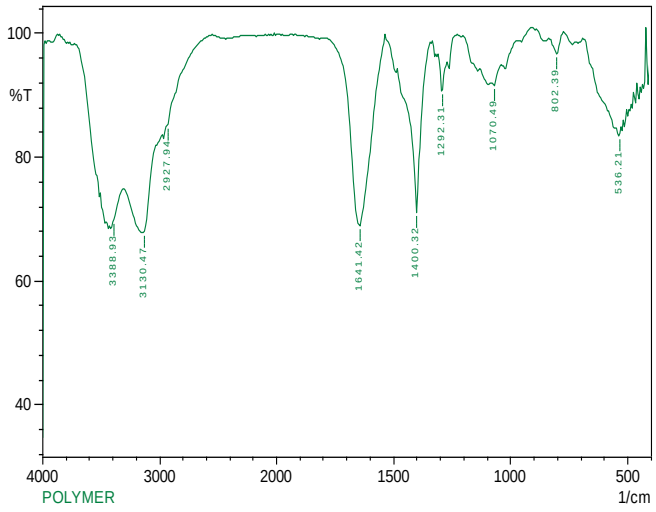

Fig.9.FTIR analysis of Ce-doped SnO_2

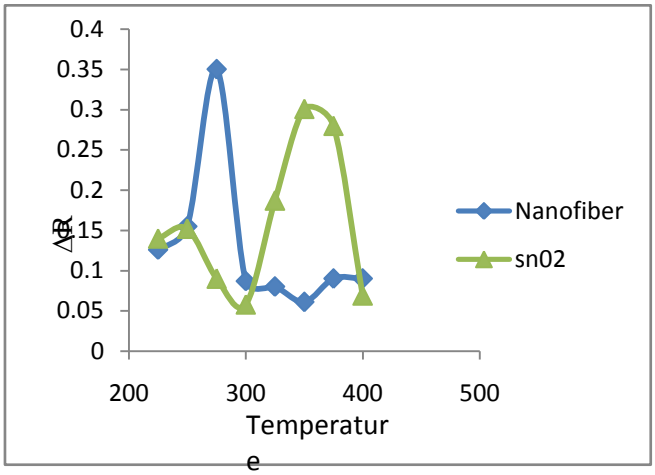

Fig.10 Relationship btw resistance change and working temperature

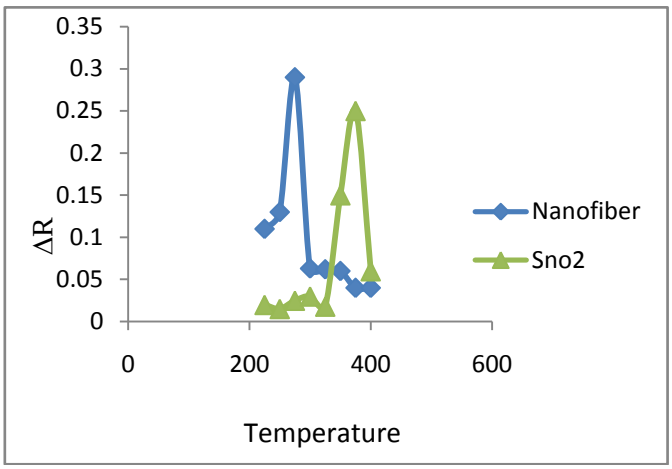

Fig.11 Relationship btw resistance change and working temperature for fixed ppm

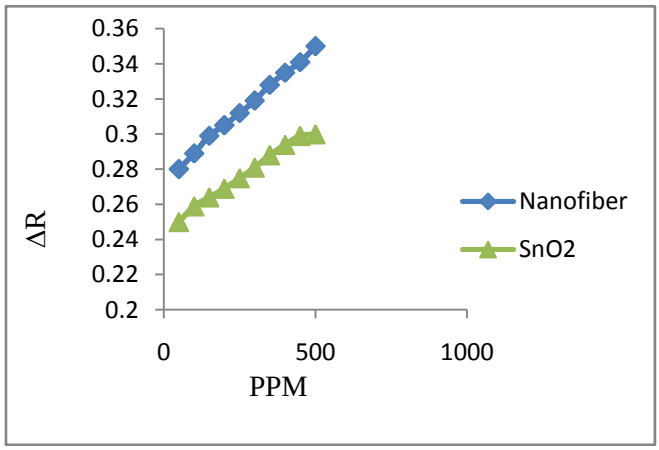

Fig. 12 Response of nanoparticles towards different ppm concentration

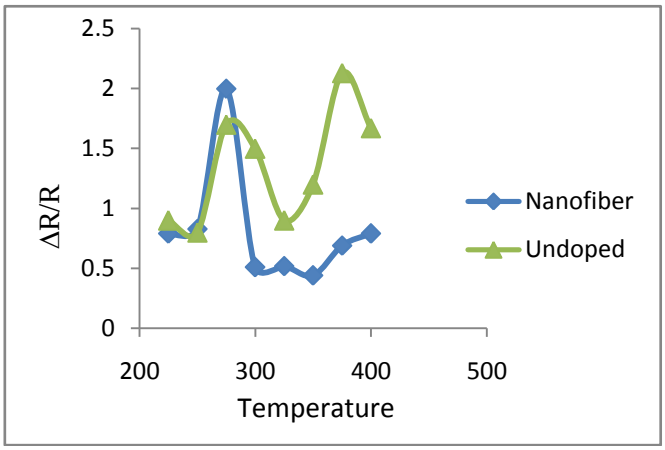

Fig13 sensor response towards ammonia at different temperature

3.3 FTIR Analysis

FTIR analysis of the nanofiber and SnO_2 are shown in the Fig.8 and Fig.9. in the case of nanofibers, Various well-defined peaks at 536, 802, 1400.32,1641 and313047 cm−1 were observed in the spectrum. The peak appeared at 536 cm−1could be attributed to the metal oxygen (SnO_2) bonds and verified the formation of doped $Sn0_2$. The spectra Ce doped Sn02 nanofiber showed broad absorption peak at 3388 cm-1 which corresponds to the O-H stretching vibration of water molecule.

3.4 Electrical Properties.

The electrical properties of the nanofiber and nanocone are shown above. The experiment is carried out with the help of the gas sensor chamber. The initial resistivity is allowed to stabilize and the value is measured and recorded. The resistance values with and without ammonia is been noted down.

Fig.10 shows the relation between change in electrical resistance and operating temperature. Here the maximum sensitivity of the nanofiber is obtained at 275^0C than that of normal SnO_2 at 350^0C. The resistance increase when the concentration increases but later falls down. from the figure we can infer that the nanofiber has highest sensitivity at lower temperature than the normal SnO_2

Fig.11 shows the relationship between the change in resistance with different operating temperature for fixed PPM(50ppm).During the test process 50 PPM ammonia was injected. For normal SnO_2 resistance increases slowly upto 325^0C and later steadily rises and falls after 350^0C.

Fig.12 shows relationship of nanoparticles for different ppm. Nanofibers increases linearly with different ppm concentration than normal SnO_2. From the figure we can say that nanofiber are favorable contender to detect low concentration of ammonia.

Fig.13 shows the sensitivity curve for Ce-doped SnO_2 and normal SnO_2. Ammonia gas sensing properties were studied within the temperature of 200^0C to 400^0C.The sensitivity was considered to be highly appreciable below 350^0C. In the case

of nanofibers the sensitivity increases with increase in temperature and later falls down. Nanofibers was found to be more sensitive than the normal SnO_2. At 275^0C the sensitivity of nanofiber was found to 50 percent more than higher and lower temperature. But in the case of the normal SnO_2 the highest sensitivity was recorded at 350^0C .From above experiment we came to conclusion that ammonia sensor based Ce-doped nanofiber gave good sensitivity at lower temperature.

4. CONCLUSIONS

In summary, Ce doped Tin oxide nanofiber and normal SnO_2 were synthesized by electrospinning and traditional sol gel technique and moreover particles were characterized by EDAX,SEM FTIR and XRD. It is found that the Ce-doped nanofiber exhibit good sensitivity, fast response, stable, low ppm detection than bounded nanocones. All these results shows that the Ce-doped nanofiber are the potential candidate for ammonia detection. The response of both Sensor towards ammonia gas at different concentration(50-500ppm) with different operating temperature (225^0C-400^0C) were studied. A new technique metal oxide semiconductor sensor for monitoring the gas leak in chemical industry has been developed

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