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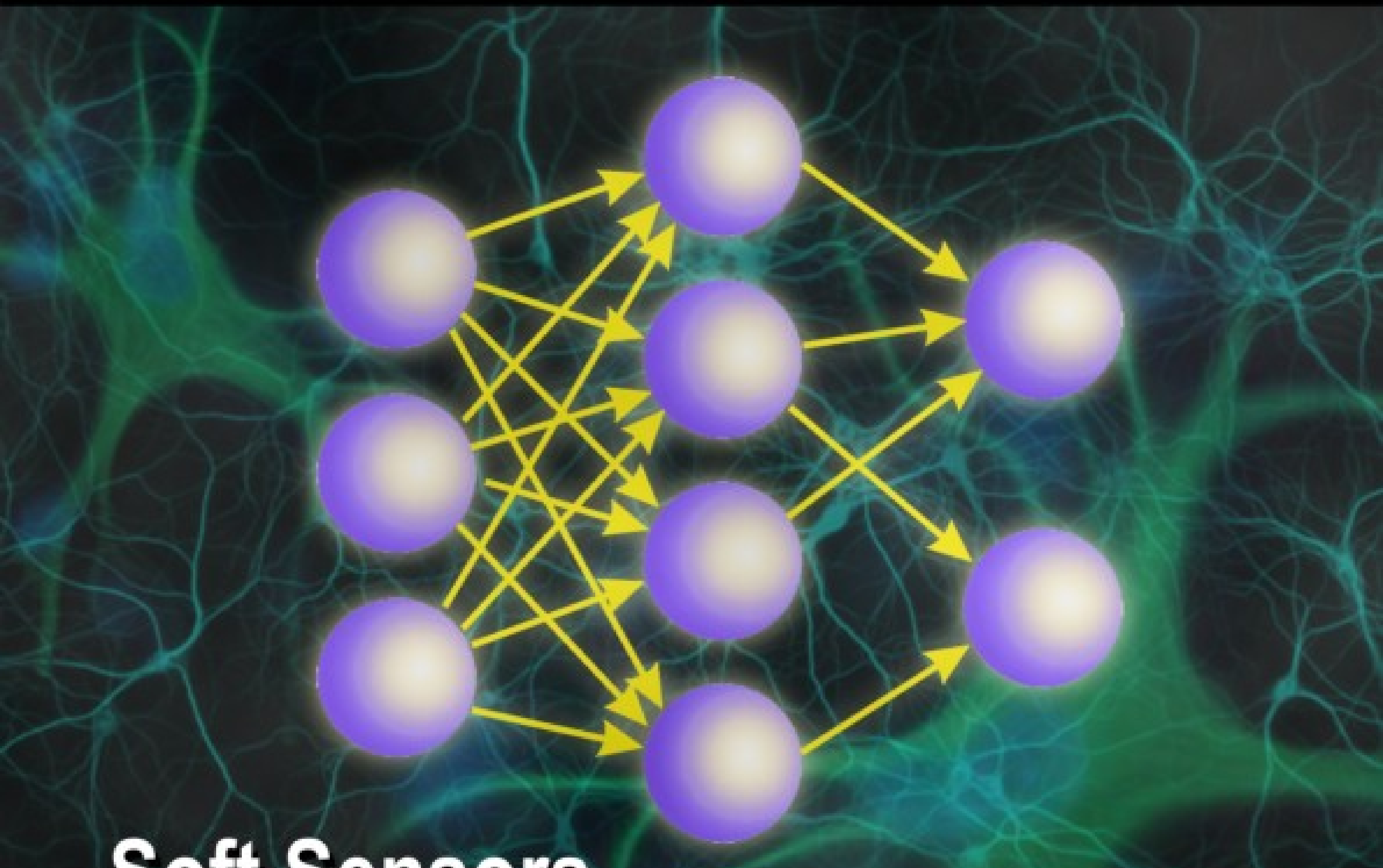

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Al_2O_3- BSST Based Chemical Sensors for Ammonia Gas Sensing

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Abstract: Gas sensing behaviour of pure and modified $(Ba_{0.9}Sr_{0.1})(Sn_{0.5}Ti_{0.5})O_3$ (BSST) thick films is reported in this article. The surface of the BSST thick film was modified by dipping it into aqueous solution of $AlCl_3$, for different intervals of time. These films were then dried at 500 ^{0}C for 24 hours in air ambient for transformation of $AlCl_3$ into Al_2O_3, for the evaporation of organic binders and also to improve the texture of the film. The gas response, selectivity, response and recovery time of the sensors were measured and presented. The role played by the aluminium species to improve the gas sensing performance of the sensors is discussed. *Copyright © 2009 IFSA.*

Keywords: BSST, Thick film, Surface modification, Al_2O_3 modified films, Ammonia sensor

1. Introduction

The gas sensors using metal oxide semiconductors were first reported by Seiyama et al and Taguchi [1, 2]. Nowadays, increased awareness over the need to monitor the toxic gases for environmental pollution and efficiency in a combustion process has stimulated substantial research and development in the field of gas sensors. Such sensors are n-type semiconductors where loss of oxygen on heating results in the generation of oxygen vacancies, leading to electron donor states.

Ammonia is produced and utilized extensively in many chemical industries, fertilizer factories, refrigeration systems, food processing, medical diagnosis, fire power plants etc. A leak in the system can result the health hazards. Ammonia is harmful and toxic [3-9] in nature. The exposure of ammonia causes chronic lung disease, irritating and even burning the respiratory track, etc. Environmental pollution [10-13] is a burning global issue; pollution has raised its ugly head high in the global environment. Therefore, all industries working on and for ammonia should have an alarm system detecting and warning for dangerous ammonia concentrations. It is therefore, necessary to monitor ammonia gas and to develop the ammonia gas sensor. Efforts are made to develop the BSST based NH_3 gas sensors.

2. Experimental

2.1. Powder and Paste Preparation

The $(Ba_{0.9}Sr_{0.1})(Sn_{0.5}Ti_{0.5})O_3$ powder was synthesized by mechanochemical process. The AR grade powders of $Ba(OH)_2.8H_2O$ and $Sr(OH)_2$) in the ratio 9:1 and SnO_2 and TiO_2 in the ratio 1:1 are mechanochemically mixed. The mixture was ball milled to mix thoroughly, followed by sintering at 800 ^{0}C for 12 h. The resulted white powder was termed as Barium Strontium Tin Titanate (BSST). The BSST thick films were printed on a glass substrates using screen printing technique [14-21]. The films were fired at 550 ^{o}C for 30 min.

2.2. Surface Modification of Thick Films

Thick films prepared were surface modified by dipping them into a 0.01 M aqueous solution of $AlCl_3$ for different intervals of time and were dried at 90 ^{0}C under an IR lamp, followed by firing at 500 ^{0}C for 24 h in air ambient. The $AlCl_3$ dispersed on the films would be oxidized in firing process, and sensor elements with different mass % of Al_2O_3 were obtained. Silver contacts were made by vacuum evaporation for electrical measurements.

2.3. Thickness Measurement

Thickness measurements were carried out using a Taylor-Hobson (Talystep, UK) system. The thicknesses of the films were observed to be in the range from 40 to 45 μm. The reproducibility of the film thickness was achieved by maintaining the proper rheology and thixotropy of the paste.

2.4. Details of Gas Sensing

Fig. 1 represents the schematic diagram of the system to test the sensing performance of the sensors. There are electrical feeds through the base plate. Heater is fixed on the base plate. A sample under test can be mounted on the heater. The Cr-Al thermocouple is mounted to measure the operating temperature. The output of the thermocouple is connected to a temperature indicator. A gas inlet valve is fitted at one of the ports of the base plate. The gas concentration inside the static system is achieved by injecting a known volume of a test gas with a gas – injecting syringe. Constant voltage is applied to the sensor and the current is measured by a current meter.

3. Results

3.1. X-Ray Diffraction Studies

The structure of the films was analyzed with X-ray diffractogram (RIGAKU DMAX 2500) using CuK_α radiation with a wavelength 1.5418 Å. Figs. 2 (a-c) show the X-ray diffractograms of the pure and Al_2O_3-modified BSST films (30 and 60 min). The observed peaks are matching well with ASTM reported data of BSST. The sharp peaks of the XRD pattern correspond to BSST material and are observed to be microcrystalline in nature**.** No peaks corresponding to Al_2O_3 are observed. It may be due to its very small mass % dispersed on the surface of BSST. The average grain size was determined using Scherer's formula and was estimated to be of 272 nm.

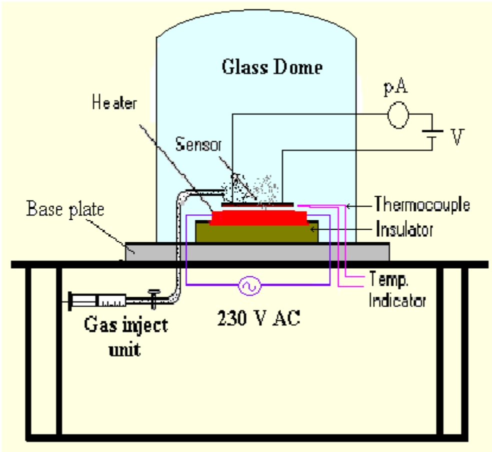


Fig. 1. Schematic diagram of the system to test the sensing performance of the sensors.

3.2. Microstructure-SEM

The microstructure and chemical composition of the films were analyzed using a scanning electron microscope (JOEL JED 2300) coupled with an energy dispersive spectrometer (6360 LA). Fig. 3 depicts the SEM images of pure BSST and Al_2O_3-modified BSST thick films. Unmodified BSST film (Fig. 3a) consists of randomly distributed grains with broader size and shape distribution. Fig. 3 (b) depicts the microstructure of a most sensitive Al_2O_3-modified BSST film. It consists of grains of uniform size with narrow size distribution. This film is more porous, giving largest effective surface area. This enables larger surface for the gas to react giving higher response. Fig. 3 (c) consists of non uniform grain size and relatively broader particle size distribution of grains as compared to the grains associated with Fig. 3 (b). The porosity of this film is also smaller. Due to larger dipping time interval, larger amount of Al_2O_3 would be expected to percolate up to deeper portion of films. The effective surface area to react the gas would therefore be smaller. It may therefore give smaller gas response.

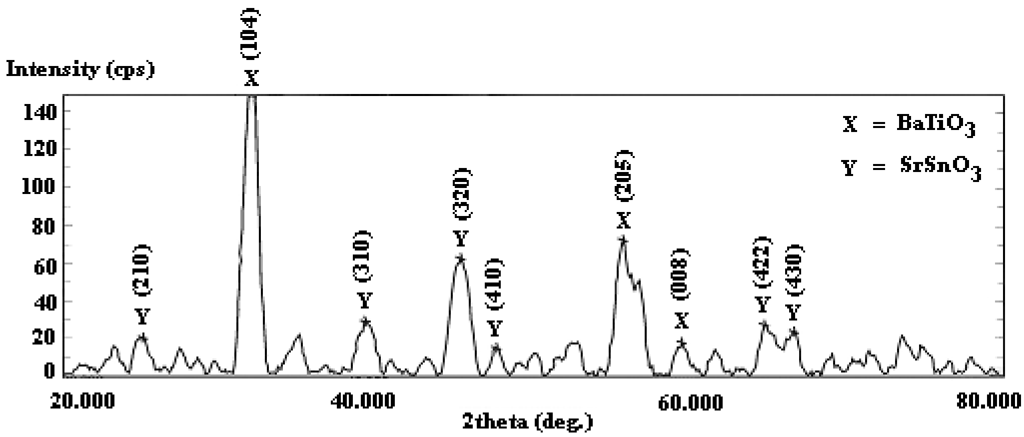
4. Gas Sensing Performance

4.1 Definition of Sensing Characteristics

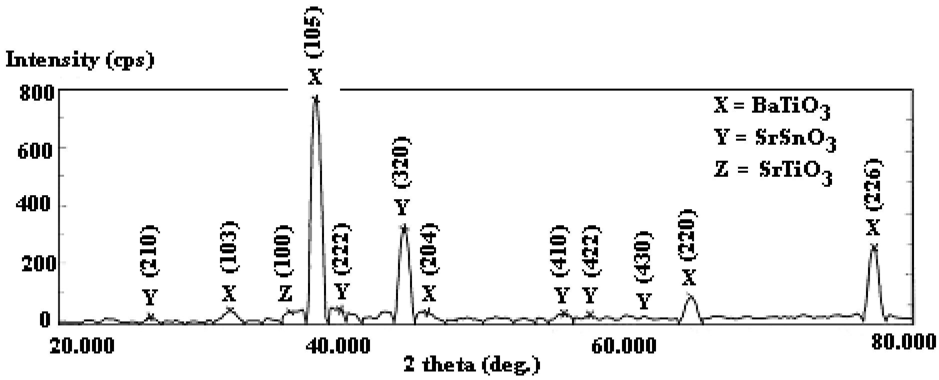
Gas response of a sensor is defined as the ratio of the conductance change upon exposure to a test gas to the conductance in air.

$$\text{Gas response} = (Gg - Ga) / Ga,$$

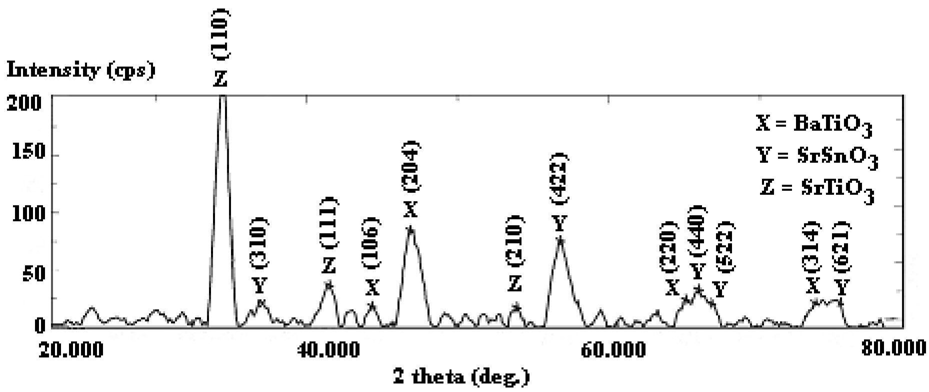
where Gg and Ga are the conductance of a sample in the presence and absence of a test gas respectively.



(a)



(b)



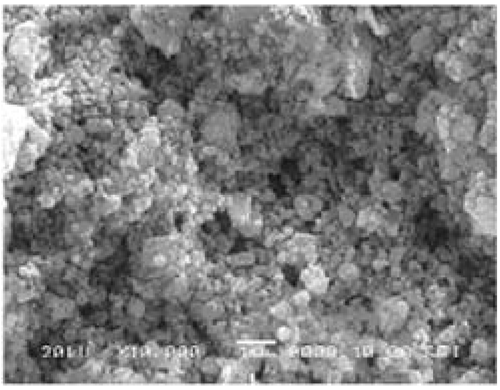
(c)

Fig. 2. XRD of (a) Pure, (b) Al_2O_3-modified (30 min) and (c) Al_2O_3-modified (60 min) BSST.

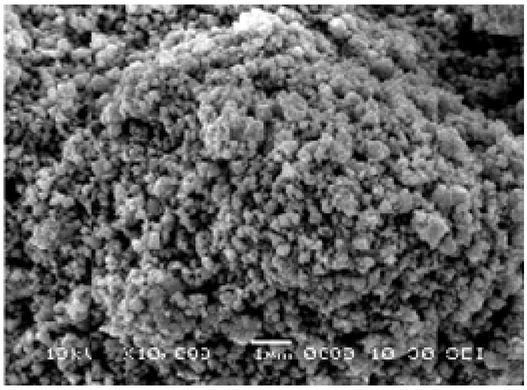
4.2. Unmodified BSST: NH_3 Sensor

4.2.1. Gas Response and Operating Temperature

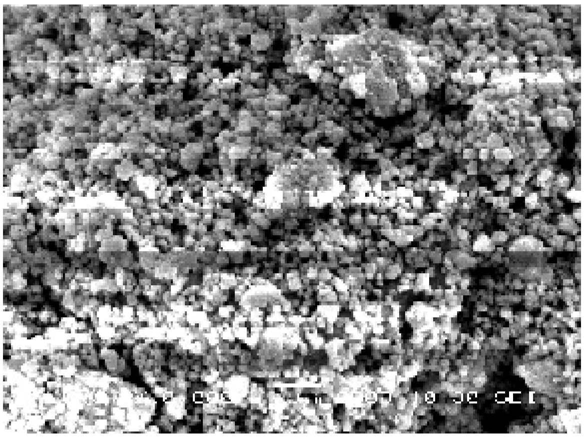
Fig. 4 shows the variation of gas responses of unmodified BSST thick films to 1000 ppm of various gases such as LPG, NH_3, CO_2, C_2H_5OH, H_2, Cl_2 and H_2S with operating temperatures. Pure BSST shows highest sensitivity to NH_3 as compared to other gases at 300 ^{0}C. The response of each gas goes on increasing with operating temperature, reaches to maximum at 300 ^{0}C and then decreases with further increase in temperature.



(a)



(b)



(c)

Fig. 3. Micrographs of (a) Pure, (b) Al_2O_3-BSST (30 min), (c) Al_2O_3-BSST (60 min) thick films.

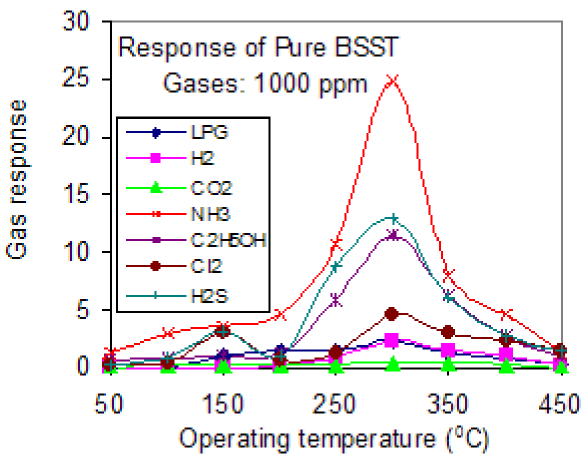
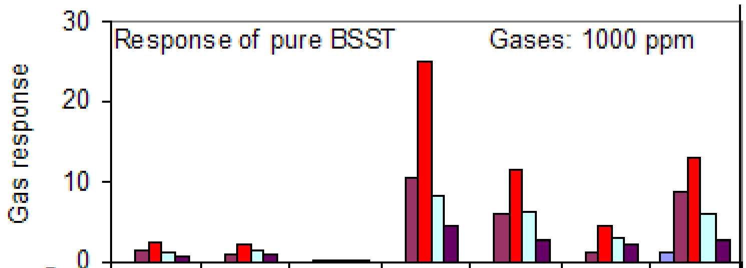


Fig. 4. Gas responses-operating temperature.

4.2.2. Selectivity

It is observed from the Fig. 5 that the pure BSST is most sensitive to NH_3 gas (1000 ppm) at 300 ^{0}C. It is clear from histogram that the sensor is selective to NH_3 in presence of other gas.



Gases	LPG	H2	CO2	NH3	C2H5OH	Cl2	H2S
R. T.	0.1	0.06	0.02	0.01	0.12	0.11	1.3
250	1.5	0.85	0.23	10.54	5.88	1.15	8.65
300	2.3	2.2	0.41	24.89	11.39	4.63	12.9
350	1.3	1.45	0.34	8	6.2	2.92	6.05
400	0.73	0.96	0.27	4.54	2.8	2.21	2.7

Fig. 5. Selectivity of pure BSST thick film.

4.3. Al_2O_3-modified BSST: NH_3 Sensor

4.3.1. Active Region of the Sensor

The variation of gas response of Al_2O_3-modified (30 min) BSST sample with NH_3 gas concentration is represented in Fig. 6. It is clear from figure that the gas responses go on increasing linearly with gas concentration up to 300 ppm and then saturate. Thus, the active region of the sensor would be up to 300 ppm.

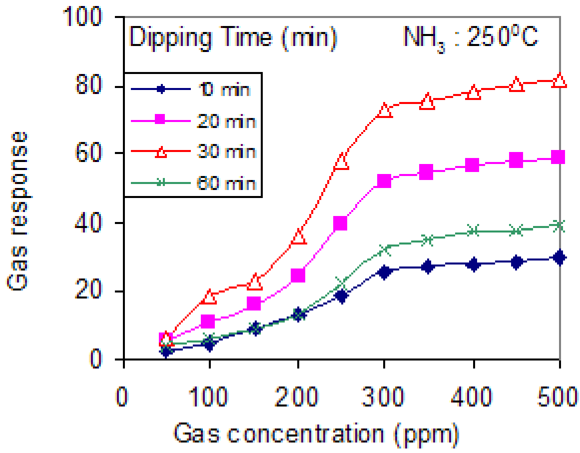


Fig. 6. Variation of gas response with NH_3 gas concentration.

4.3.2. Response and Operating Temperature

Figs. 7(a) through 7(g) depict the variation of modified (5, 10, 20, 30, 60) films to responses of LPG, NH_3, CO_2, C_2H_5OH, H_2, Cl_2 and H_2S with operating temperatures. Al_2O_3 modified film (for the interval of 30 min) is most sensitive to NH_3 (S=73) at 250 ^{0}C.

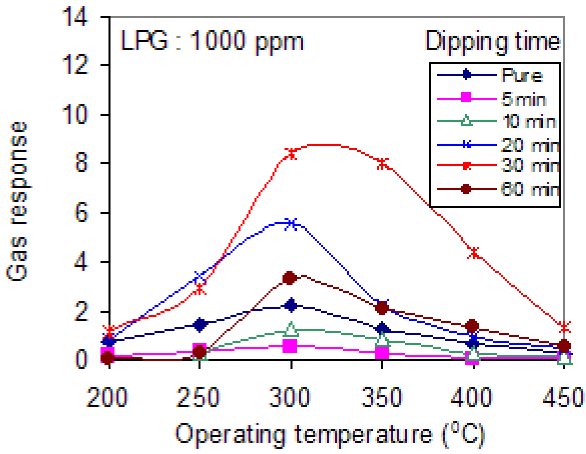


Fig. 7 (a). LPG response-operating temperature.

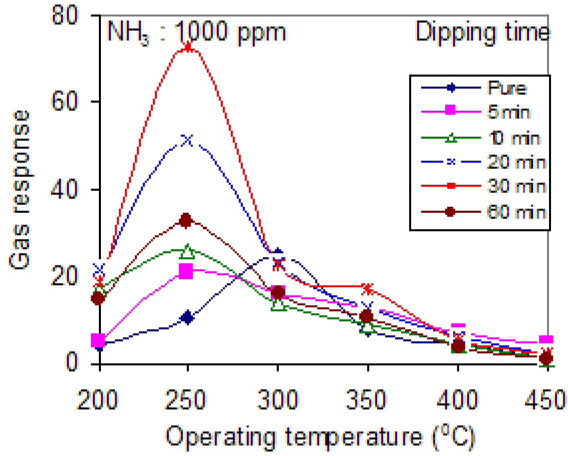


Fig. 7 (b). NH_3 response-operating temperature.

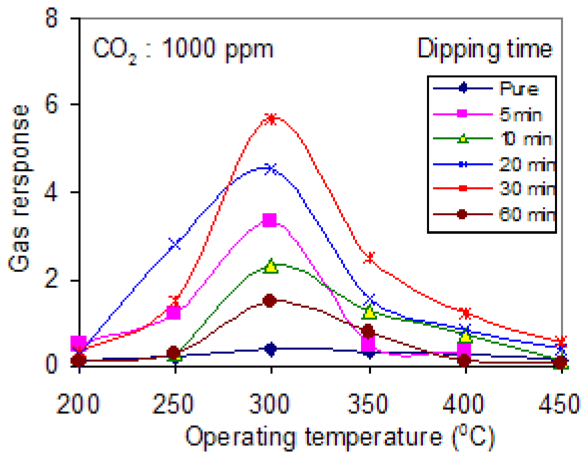


Fig. 7 (c). CO_2 response-operating temperature.

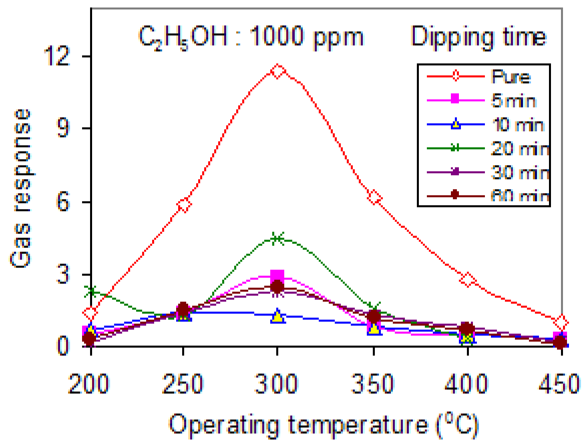


Fig. 7 (d). C_2H_5OH response-operating temperature.

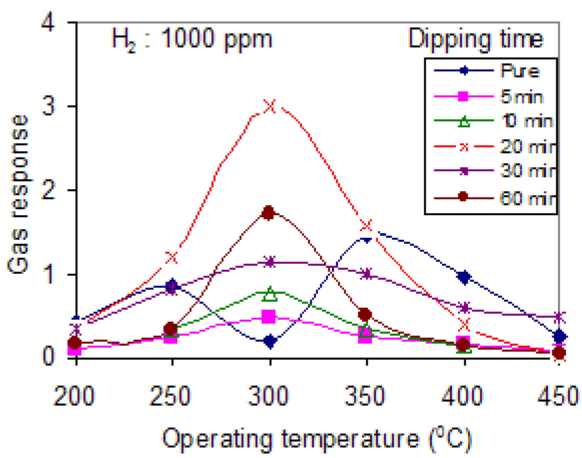


Fig. 7 (e). H_2 response-operating temperature.

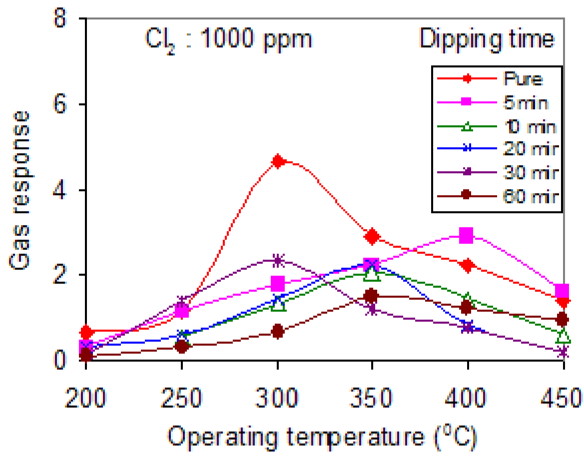


Fig. 7 (f). Cl_2 response-operating temperature.

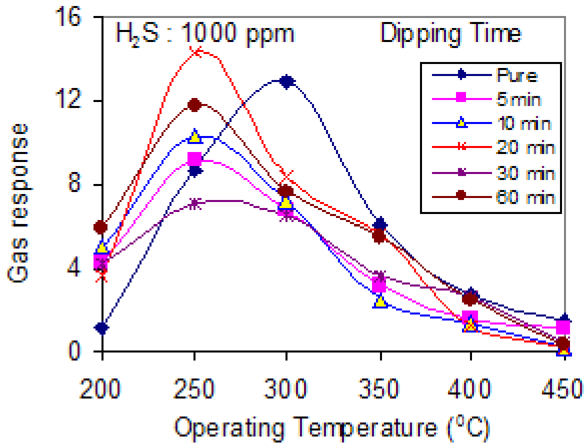


Fig. 7 (g). H_2S response-operating temperature.

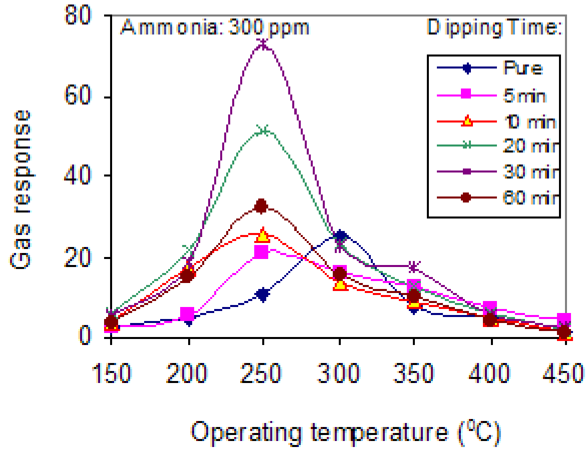
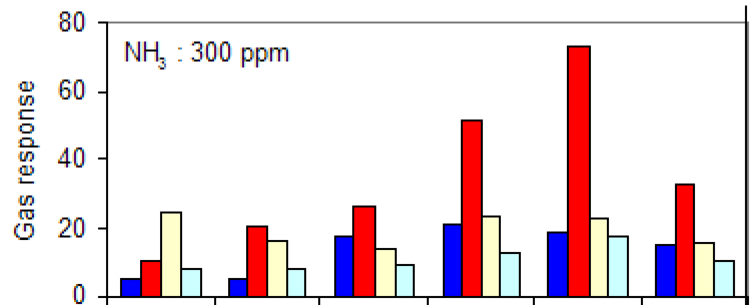


Fig. 7 (h). Gas response-operating temperature.

4.3.3 Effect of Dipping Time

Fig. 8 is the histogram indicating the NH_3 gas (300 ppm) response as a function of dipping time. The sensor with 30 min dipped in $AlCl_3$ was observed to be most sensitive at 300 ^{0}C.



Dip Time (min)	0	5	10	20	30	60
200	4.59	5.17	17.2	21.4	18.56	14.66
250	10.54	20.7	25.66	51.4	72.65	32.5
300	24.89	16.23	13.88	23	22.61	15.75
350	8	8	9	12.5	17.25	10.33

Fig. 8. Response values of different Al_2O_3-modified samples.

4.3.4. Selectivity for NH_3 Against Various Gases

Fig. 9 shows the histogram indicating the gas response of various samples tested at 250 ^{0}C. The sensor showed high selectivity for NH_3 and could distinguish the NH_3 among all the gases, such as LPG, CO_2, C_2H_5OH, NH_3, H_2S, H_2 and Cl_2.

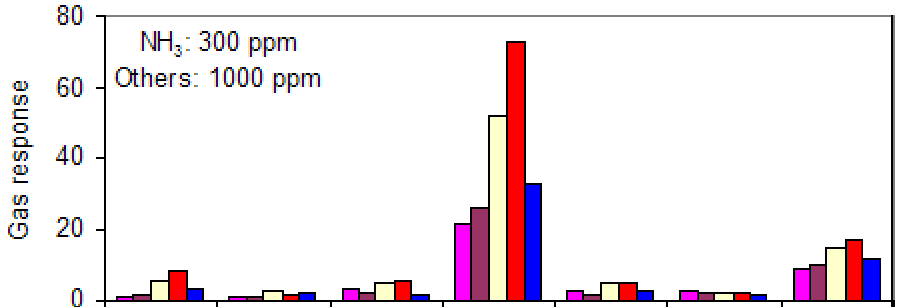
5. Discussion

Gas sensing mechanism is generally explained in terms of change in conductance (Fig. 10) either by adsorption of atmospheric oxygen on the surface and/or by direct reaction of lattice oxygen or interstitial oxygen with the test gases. In case of former, the atmospheric oxygen adsorbs on the surface by extracting the electrons from conduction band, in the form of super oxides or peroxides, which are mainly responsible for the detection of the test gases. At higher temperature, it captures the electrons from conduction band as:

$$O_{2\,(air)} + 2\,e^{-}_{(cond.band)} \rightarrow 2\,O^{-}_{(film\ surface)}$$

It would result in decreasing conductivity of the film. When ammonia reacts with adsorbed oxygen on the surface of the film, it gets oxidized to nitrogen oxide gas and water vapors as the products liberating free electrons in the conduction band. The following possible reaction would take place.

$$2\,NH_3 + 7\,O^{-}_{(film\ surface)} \xrightarrow[300^{0}C]{\Delta} 2\,NO_2\uparrow + 3\,H_2O\uparrow + 7\,e^{-}$$



Gases	LPG	H2	CO2	NH3	Ethanol	Cl2	H2S
5 min	0.54	0.5	3.33	20.7	2.9	2.91	9.1
10 min	1.32	0.77	2.3	25.66	1.35	2.07	10.33
20 min	5.6	3	4.54	51.4	4.5	2.25	14.25
30 min	8.44	1.14	5.71	72.65	4.57	2.33	17.12
60 min	3.31	1.72	1.5	32.5	2.5	1.5	11.75

Fig. 9. Selectivity of NH_3S gas from mixture of gases.

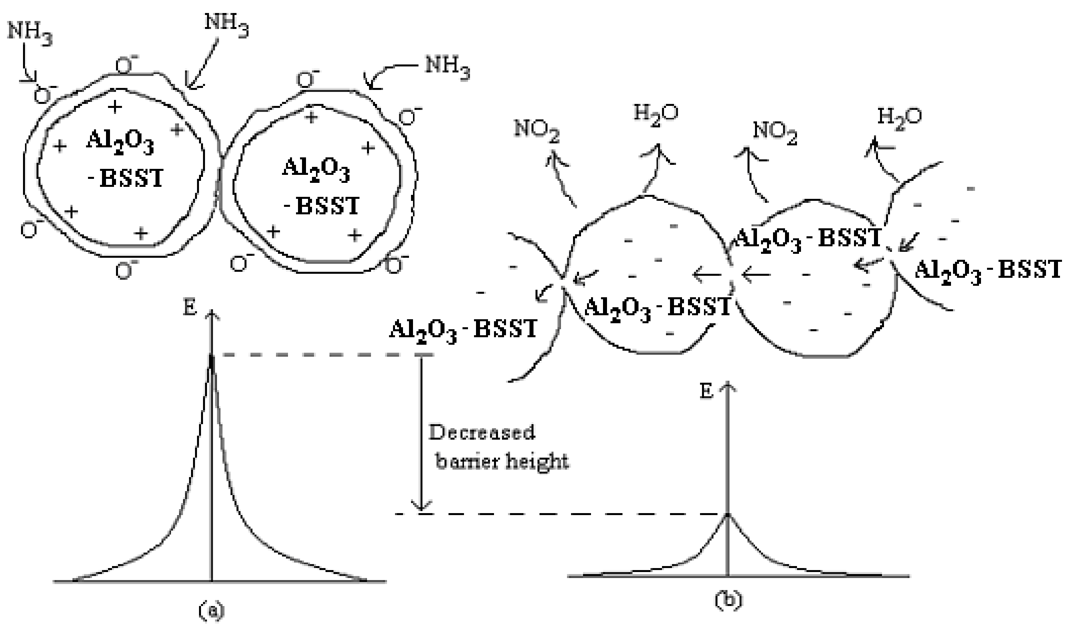


Fig. 10. NH_3 gas sensing mechanism of ironated BSST films at 350 ^{0}C.

This shows n-type conduction mechanism. Thus generated electrons contribute to sudden increase in conductance of the thick film. The Al_2O_3 misfit regions dispersed on the surface of the BSST film would enhance the ability of the material to adsorb more oxygen species giving high resistance in air ambient. On exposure to the NH_3 containing atmosphere, the resistance was observed to decrease in large extent. Therefore, the high response was obtained to 300 ppm NH_3 gas. As NO_2 and water vapors are released from the film surface, the sensor recovers back to its original chemical status, which would result in fast recovery.

The surface is the region where periodicity of the crystal is interrupted. Because of this, localized energy levels are formed in the forbidden gap. Such energy levels can either capture electrons or give up electrons. In case of semiconductor like pure or Al_2O_3–modified BSST, the surface oxygen ions give up electrons (act as donors). The donor levels are completely ionized if they are near the conduction band; however, if the donor levels are little below the conduction band, then these levels are not completely ionized at room temperature but ionized at higher temperature.

The response could be attributed to the adsorption-desorption type sensing mechanism. The largest response may be due to the higher amount of oxygen adsorption occurred at higher temperature. Oxidation of gas depends upon the amount of oxygen species ($O_2^- \rightarrow 2O^- \rightarrow O^{2-}$) adsorbed on the surface. It is observed that the oxygen adsorption on the BSST surface occurs at different temperature ranges. The conversion is as follows:

$$O_{2\,(RT)} \xrightarrow{\text{upto } 150^0C} O_2^- \xrightarrow{\text{upto } 450^0C} 2O^- \xrightarrow{\text{Above } 450^0C} O^{-2}$$

During oxidation of the gas, the electrons are released soon and become free to carry the current. At lower temperature, the smaller amount of oxygen would be adsorbed causes weak oxidation of target gas, resulting in smaller gas response. At higher temperature (> 300 ^{0}C), the adsorbed oxygen species may start to desorbed from the surface of the film, causing the less oxidation of ammonia gas, which in turn decreases the ammonia response of the sensor. Another reason of decreasing the ammonia response at higher temperatures (> 300 ^{0}C) may be attributed to the oxidation of ammonia before reaching the surface at higher temperatures (> 300 ^{0}C). Therefore, the gas response decreases further with increasing temperature.

6. Summary

From the results obtained, following statements can be made for the sensing performance of γ-Al_2O_3-modified BSST sensors.

1. Pure BSST thick films showed poor response to NH_3 gas.
2. Surface properties of the films were conveniently customized (without affecting bulk properties) by dipping BSST thick films in aluminium precursor.
3. γ-Al_2O_3-modified BSST (30 min) sensors showed better response to NH_3 gas at 250 ^{0}C than unmodified films.
4. The sensor was highly selective to NH_3 gas (300 ppm) from other toxic gases of higher concentrations (1000 ppm).
5. The sensor showed very rapid response (~ 4 s) and recovery (~ 12 s) to NH_3 gas.

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Guide for Contributors

Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually. *Sensors & Transducers Journal* is indexed and abstracted very quickly by Chemical Abstracts, IndexCopernicus Journals Master List, Open J-Gate, Google Scholar, etc.

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Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

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- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
- Signal processing;
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- Microsystems;
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