UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002.

Final Report of the work done on the Minor Research Project.

1. Project report No: **Final**

2. UGC Reference No. **File No: 47-2150/11(WRO)**

3. Period of report: **From 29/02/2012 to 23/ 09/2014**

4. Title of research project: **"Development of nanostructured SnO_2 thin film gas sensors".**

5. (a) Name of the Principal Investigator: **Dr. R.N.Mulik**

   (b) Deptt. and University/College where work has progressed:
   Department of Physics, DBF Dayanand College of Arts & Science Solapur
   and **School of Physical Sciences, Solapur University, Solapur.**

6. Effective date of starting of the project: **29/02/2012.**

7. Grant approved and expenditure incurred during the period of the report:

a. Total amount approved Rs**: 1, 95,000/- (for two years)**
b. Total expenditure **Rs: 1, 95,000/-**

Report of the work done: Separate sheet enclosed **Appendix – I**

Appendix – I

Project Title: "Development of nanostructured SnO_2 thin film gas sensors".

i) Objectives of the Project:

1. Preparation of nanostructured SnO_2 thin film on glass substrates by sol gel spin coating technique.
2. Devise phase diagram of properties of grown SnO_2 films and deposition parameters.
3. Device a SnO_2 gas sensor and study their gas sensing properties.
4. Analyze the result.

During first phase of project the following work was carried out;

Initially the project related literature survey has been carried out before starting the experimental work. After that nanocrystalline SnO_2 was synthesized by sol- gel method. Thin films of SnO_2 formed using spin coating method on glass substrate.

Structure, Morphology, Electrical transport and Optical properties were studied through X-ray diffraction, Scanning electron microscopy (SEM), Two probe technique and UV-visible spectroscopy.

1) X –ray diffraction analysis:

The structural and morphological investigations have been carried out due to their significant role in electrical and gas-sensing properties. The diffraction patterns show characteristic SnO_2 peaks with tetragonal structure (JCPDS No. 72-1147). The average crystallite size (d) calculated from Sherrer's formula is in the range of 10–15 nm.

$$D=0.94\lambda/\beta\cos\theta \quad (1)$$

where D is the average crystallite size, assuming particles to be spherical K = 0.94, λ is the wavelength of X-ray radiation, β is the full width at half maximum of the diffracted peak measured in radians and θ is the angle of diffraction. Fig. 1 shows the XRD patterns of SnO_2 without any impurity phase. The lattice parameters calculated for the tetragonal phase of SnO_2 using Eq. (2) has been calculated to be a = b = 0.47nm and c = 0.33nm which is in close agreement with the reported JCPDS No. 72-1147.

$$1/d^2 = h^2+k^2/a^2 + l^2/c^2 \quad (2)$$

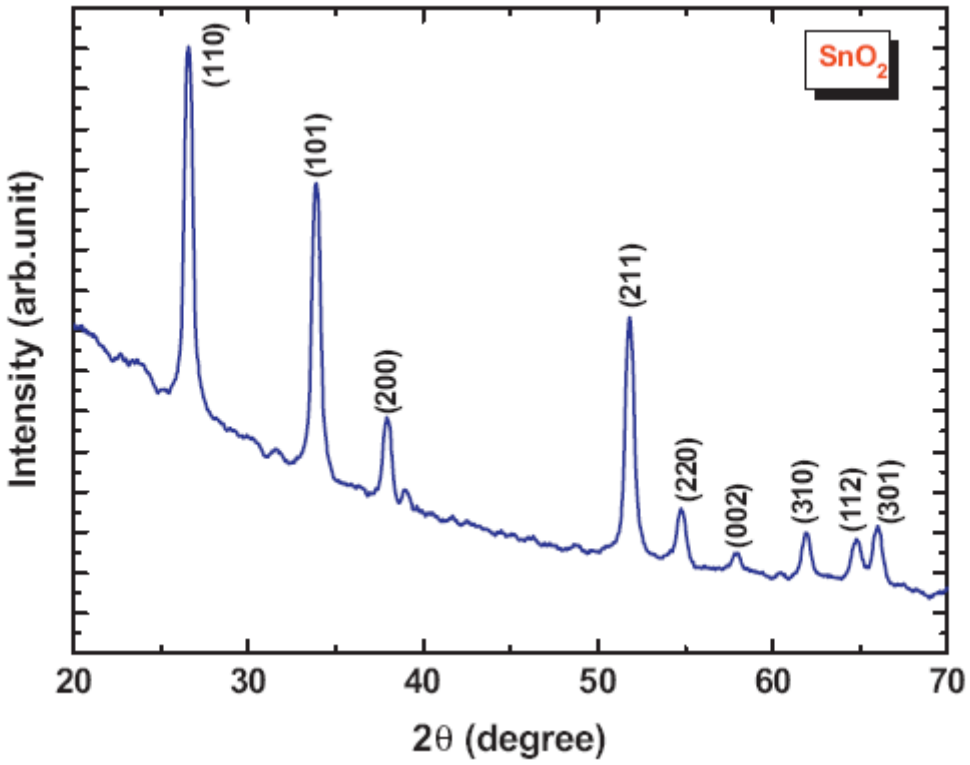

Fig.1. XRD pattern of SnO_2 calcinated at 700 °C.

2) FESEM analysis

The two-dimensional high magnification surface morphology of SnO_2 thin film processed at 700 °C was carried out using FESEM image (Fig. 2). From the FESEM image, it is seen that the film consists of nanocrystalline grains with uniform coverage of the substrate surface with randomly oriented morphology.

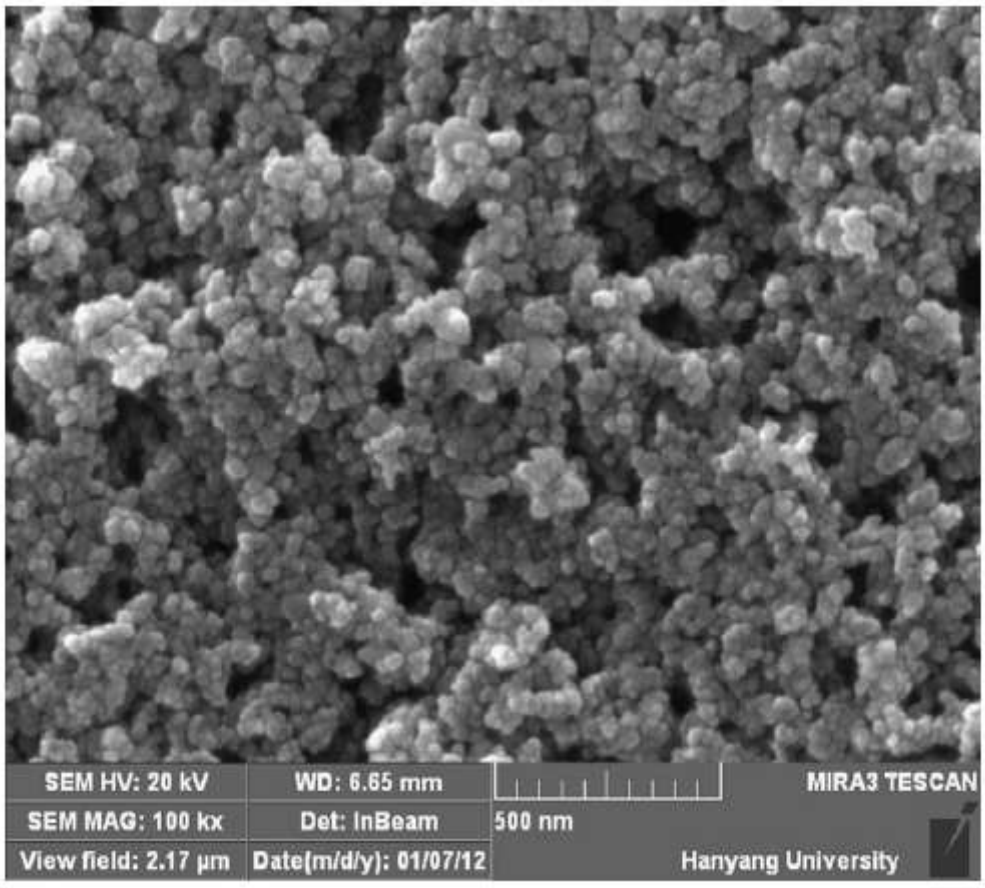

Fig.2. FESEM of SnO_2 thin films

3) Electrical conductivity measurement

The two-probe technique of dark dc electrical conductivity measurement was used to study the variation of electrical conductivity of film with processing temperature. The variation of log σ with reciprocal temperature (1000/T) is depicted in Fig. 3. From Fig. 3 it is observed that the conductivity of film is increases with increase in annealing temperature, further it is observed that conductivity obeys Arrhenius behaviour indicating semiconducting transport behaviour. The activation energies were calculated using

$$\sigma = \sigma_0 \, Exp \, (E_{a\sigma} / kT) \qquad (3)$$

Where, σ is the conductivity at temperature T, σ_0 is a constant, k is the Boltzmann constant, T is the absolute temperature and $E_{a\sigma}$ is the activation energy. The temperature dependence of electrical conductivity (Fig.3) showed two distinct conduction regions corresponding to two different conduction mechanisms; one, a grain boundary scattering limited and second a variable range hopping. The activation energies of an electrical conduction have been computed for the regions and it is observed that the activation energies is 0.423 eV,

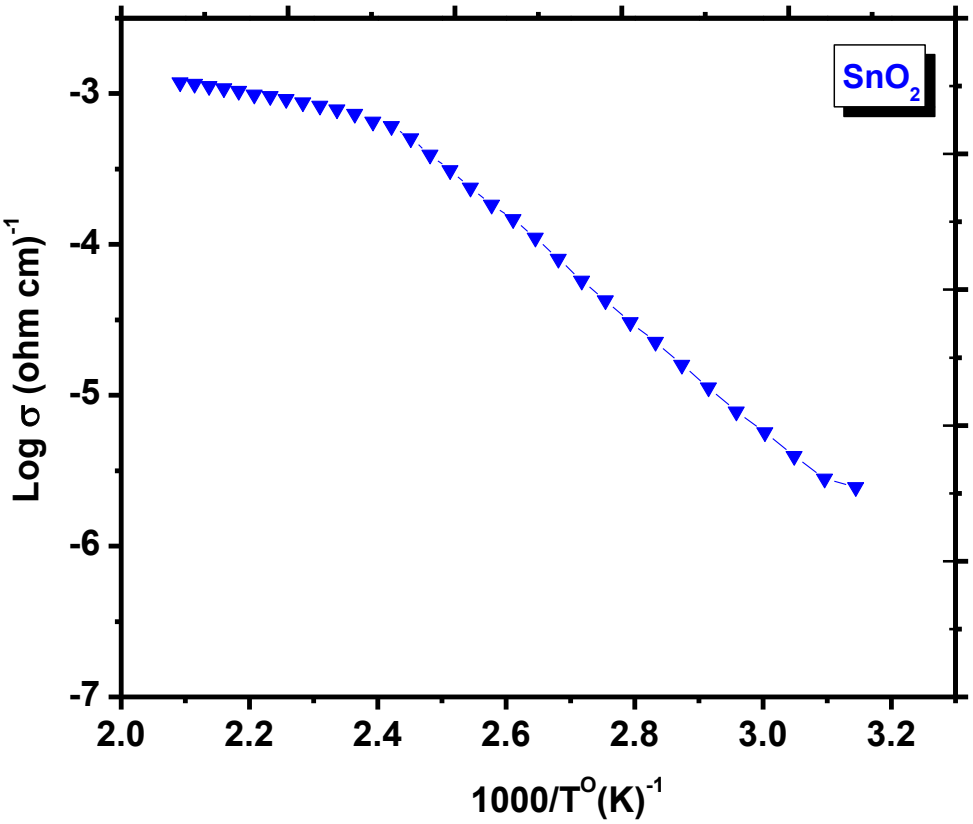

Fig. 3. The variation of log σ with reciprocal temperature (1000/T)

4) Optical studies

The SnO_2 thin films on glass substrate were used to study the optical absorption. The optical absorption of SnO_2 thin films in the wavelength range of 200–1100 nm has been investigated.

Fig. 4 shows plots of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) for SnO_2thin films Since the plot is almost linear, the direct nature of the optical transition in SnO_2 is confirmed. Extrapolation of these curves to photon energy axis reveals the band gap of SnO2.

The band gap of SnO_2 film was found to be 3.60 eV

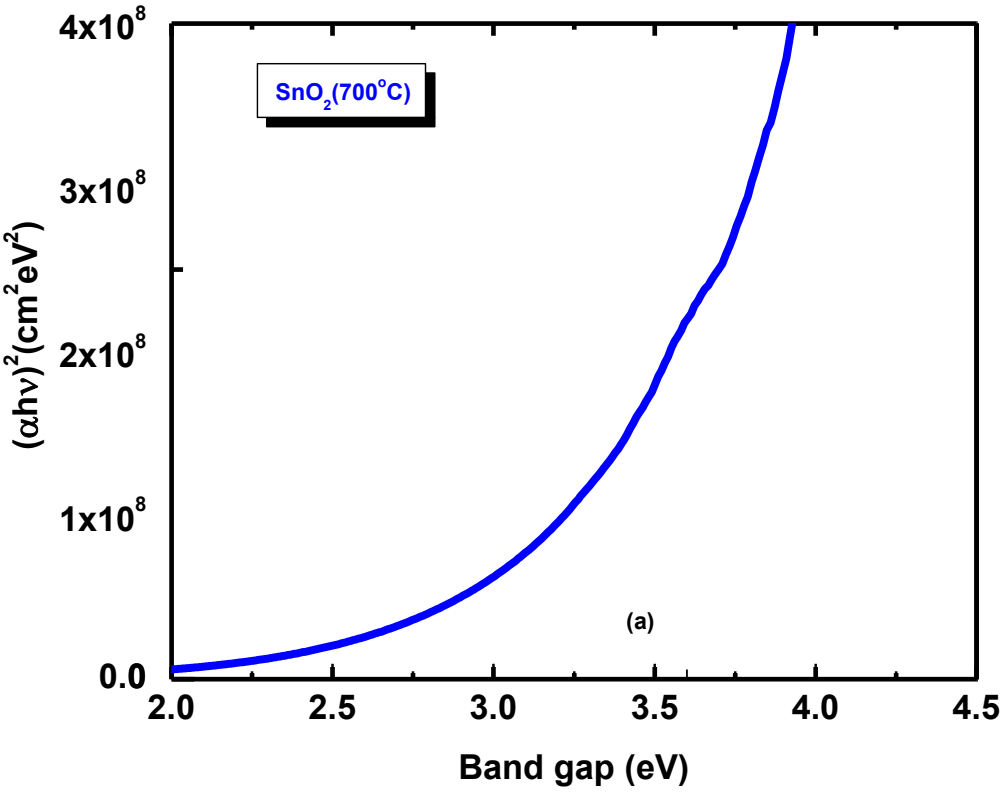

Fig. 4 shows plots of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) for SnO_2thin films

During second phase of project the following work was carried out;

5) Gas sensing properties

To study the gas-sensing properties of SnO_2, samples were made in the thin film form with thickness 0.92 μm. The gas response was measured after providing the ohmic contacts using silver paste. Films were subjected for studying sensitivity and selectivity towards the known amount of various test gases using the custom fabricated dynamic setup . The sensor film was kept in the insulated steel chamber. The known amount of test gas was introduced in the gas-mixing chamber so that the required ppm level was attended. The gas-sensing characteristics with reference to time, at different operating temperatures and concentrations were recorded using a programmable 6514 Keithley Electrometer. The gas response (S) for a given test gas is calculated as follows:

$S = R_a / R_g$

Where, R_a and R_g are the electrical resistances of the sensor in air and in test gas.

5.1 Stabilization of sensor resistance

Stabilization of metal oxide film resistance in ambient air prior to exposure of gas is very important, because it ensures stable zero level for gas sensing application . Because of that before exposing gas to SnO_2 films, the electrical resistance was allowed to be stable for 30 min and the behaviour of resistance was observed. Fig.5 shows the initial stabilization curve of the SnO_2 film at 200 ^oC. The decrease in resistance observed at the beginning of stabilization period can be attributed to the generation of electrons due to

thermal excitation [4, 5]. The resistance of the film decreases gradually from 1.60×10^9 Ω to 3.44×10^8 Ω at 200 °C in the first 3 min and for next 6.5 min, the resistance decreases slowly then it remains constant. After 30 min, the SnO_2 thin film attains a stable constant resistance of 4.95×10^8 Ω at 200 °C.

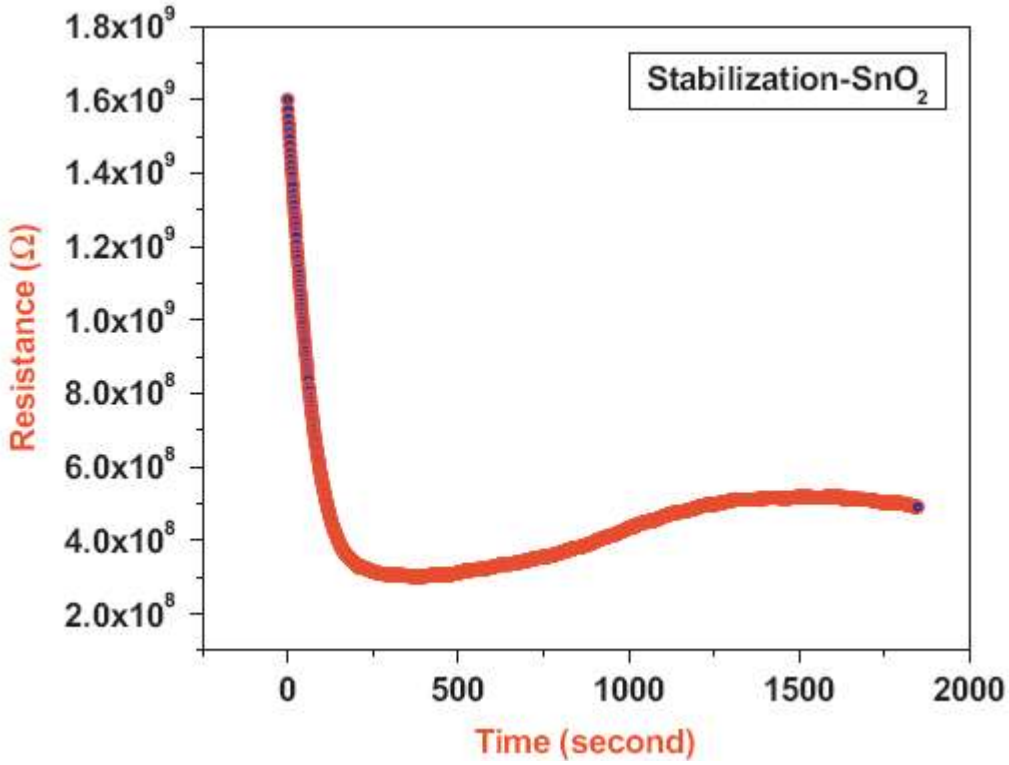

Fig. 5. Resistance stabilization curve with time for SnO_2 film at 200 °C

5.2. Selectivity of SnO_2 sensor

The ability of a gas sensor to response to a certain gas in the presence of other gases is known as selectivity. The selectivity of a sensor in relation to a definite gas is closely

associated with its operating temperature. Figure 6 shows the bar diagram of gas response of different gases at a fixed concentration of 100 ppm. From the bar diagram, it is revealed that the SnO_2 sensor offered maximum response to NH_3 (4%), H_2S (9%), and NO_2 (19 %) at 200 ^oC. The SnO_2 film showed more selectivity for NO_2 over H_2S compared to NH_3 (S_{NO2}/S_{H2S}=2.12, S_{NO2}/S_{NH3}=4.17) at an operating temperature 200 ^oC. It is revealed that NO_2 is the more selective against NH_3 and poor selective against H_2S. Once the operating temperature is fixed, the sensor response is studied at different NO_2 concentrations.

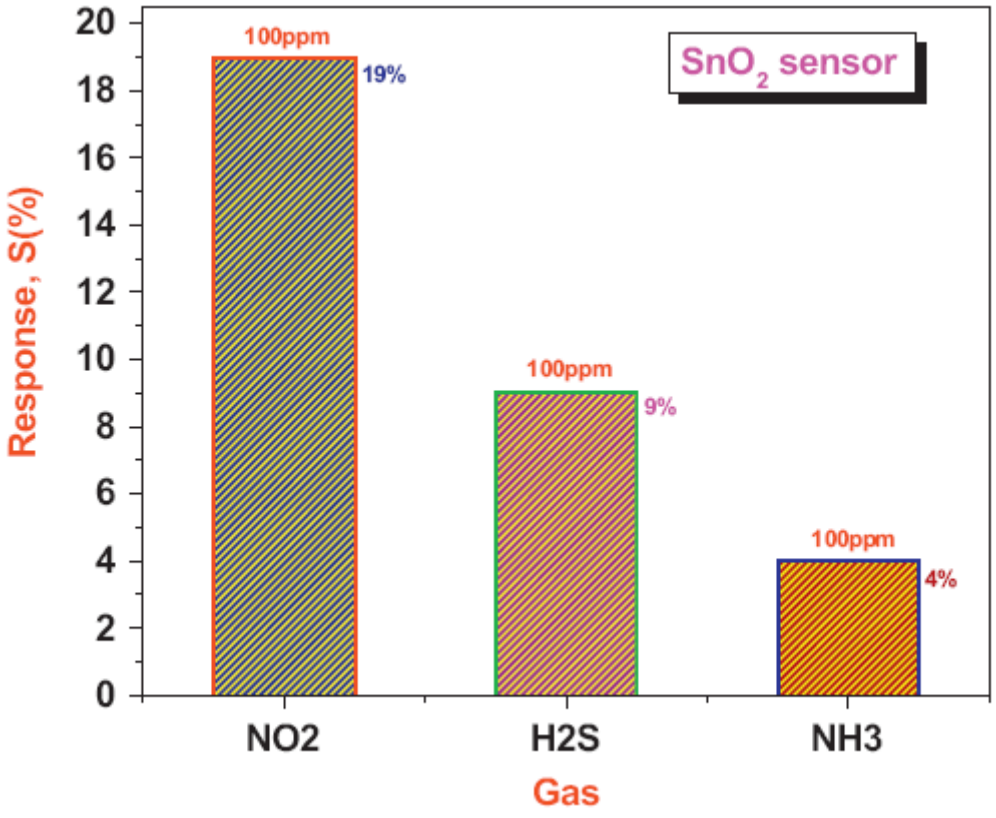

Fig.6. Gas response of SnO_2 sensor to 100 ppm of NO_2, H_2S and NH_3

Fig.7 shows the response of SnO_2 film as a function of NO_2 concentration. The response increased from 4 to 19%, as the NO_2 concentration increased from 10 to 100 ppm. The gas response showed saturation at NO_2 concentration more than 100 ppm due to increased surface reaction . The response of a sensor depends on removal of adsorbed oxygen molecules by reaction with a target gas and generation of electrons. For a small concentration of gas, exposed to a fixed surface area of a sample, there is lower coverage of gas molecules on the surface and hence lower surface reaction occurred. An increase in gas concentration increases the surface reaction due to larger surface coverage .

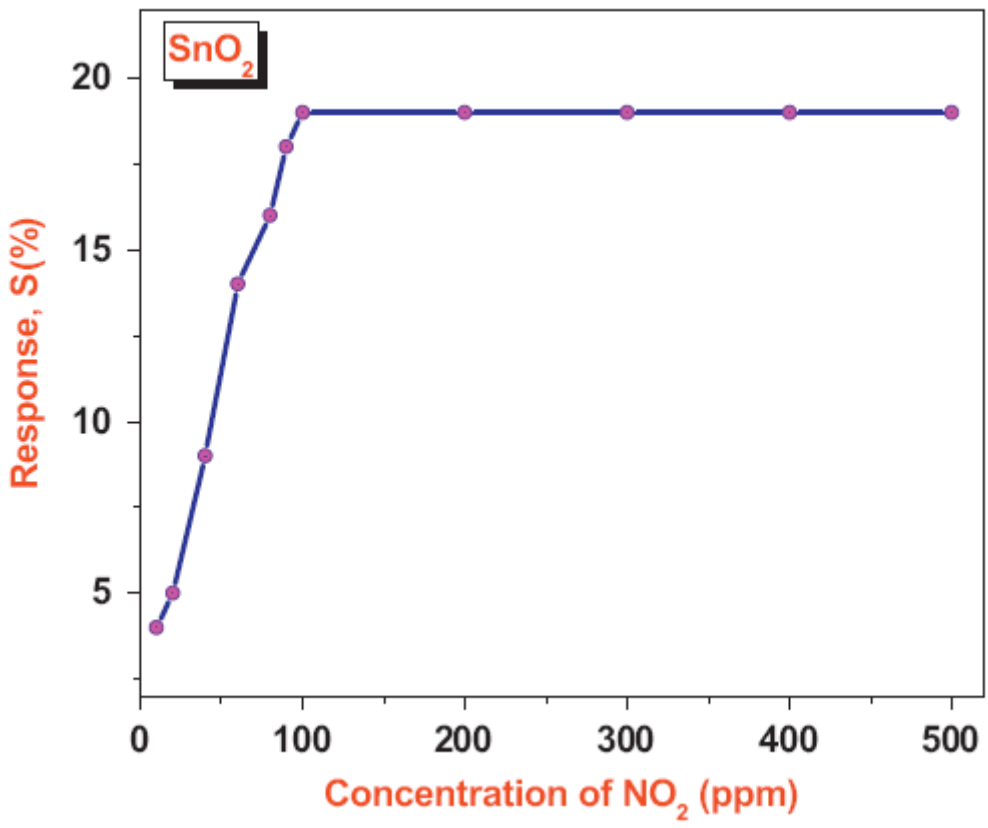

Fig.7. Variation of gas response of SnO_2 film with different concentration of NO_2

5.3 Dynamic response of SnO_2 thin films

Fig.8 shows the dynamic response of SnO_2 sensor with time at 10-100 ppm of NO_2 at 200 ^oC. From Fig. 8, it is observed that the response increased from 4 to 19 % with increasing the gas concentration of NO_2 from 10-100 ppm. At 100 ppm, the SnO_2 sensor showed the maximum response of 19%. Such a maximum response is due to interactions between the NO_2 gas and the surface of SnO_2 film. So, it is obvious that for the materials of greater surface area, the interactions between the adsorbed gases and the sensor surface are significant .

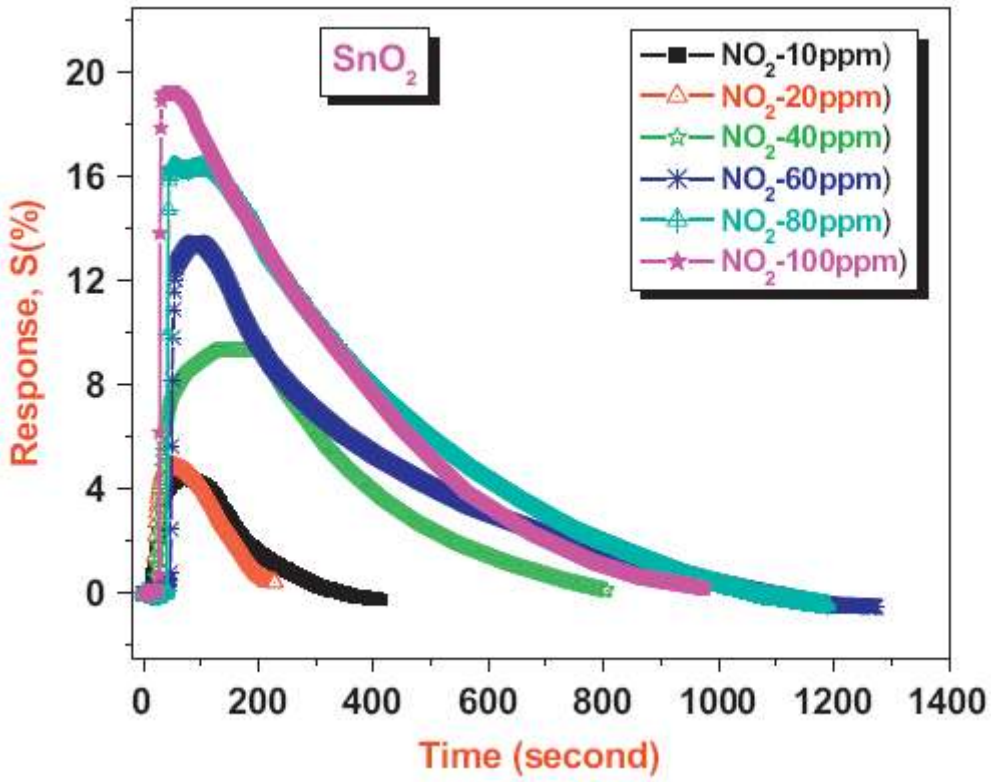

Fig.8. Dynamic response of SnO_2 sensor for 10-100 ppm NO_2

5.4 Reproducibility of SnO_2 sensor to NO_2

The sensor reliability is strongly dependent on the reproducibility and stability exhibited by the sensor material. The reproducibility of SnO_2 sensor was measured by repeating the response measurement a number of times. Fig. 9 depicts the dynamic response transients for different samples of SnO_2 towards NO_2. It is clear that response of the material is almost constant confirming the reproducibility of sensor material.

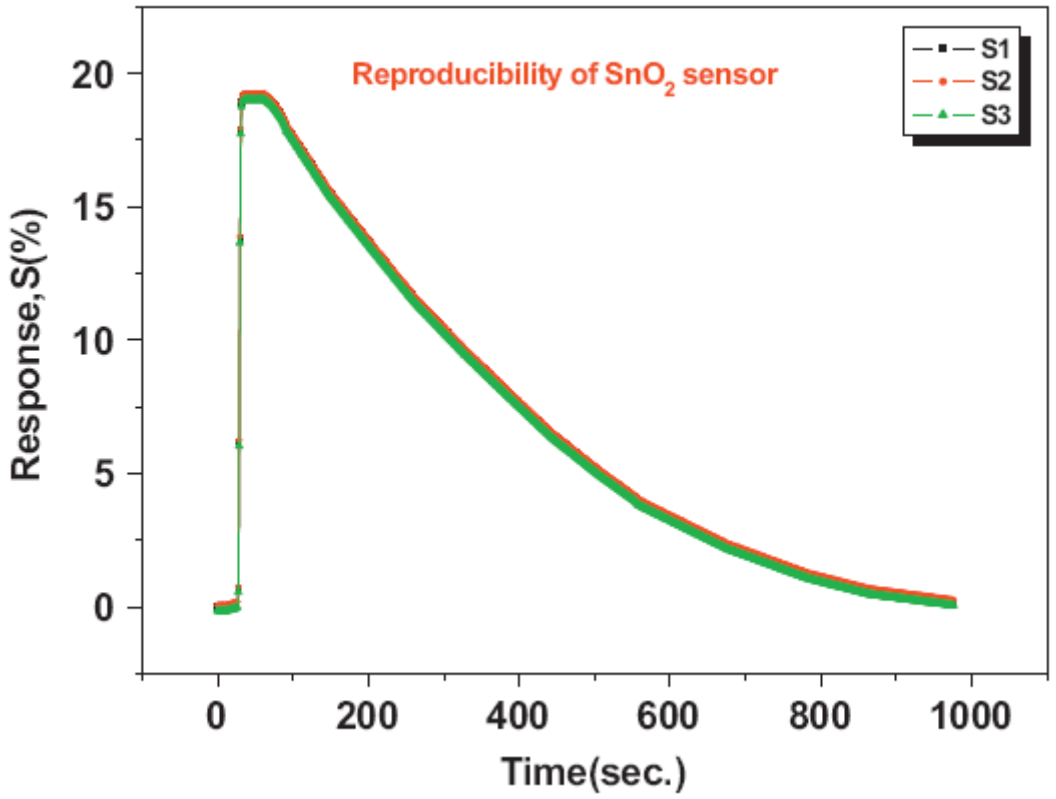

Fig.9. Reproducibility of SnO_2 thin film sensor

5.5 Stability of SnO_2 sensor

Reproducibility and stability of the SnO_2 sensor was measured by repeating the test many times. During the test, no significant variation was observed and is shown in fig.10. The obtained results show that both sensitivity and electrical conductance are reproducible. In order to determine the stability of SnO_2 sensor, the response of sensor was tested at fixed concentration of 100 ppm and temperature (200 ^oC) of NO_2 for 45 days in an interval of 5 days. Initially SnO_2 sensor shows relatively maximum response, however it is dropped from 19% to 14.8 % and stable response obtained after 15 days with 77.90% stability. This is because in the initial stage SnO_2 sensor may undergo interface modification during operation and then reaches to steady state indicating the stability of SnO_2 sensor operating at 200 ^oC temperature.

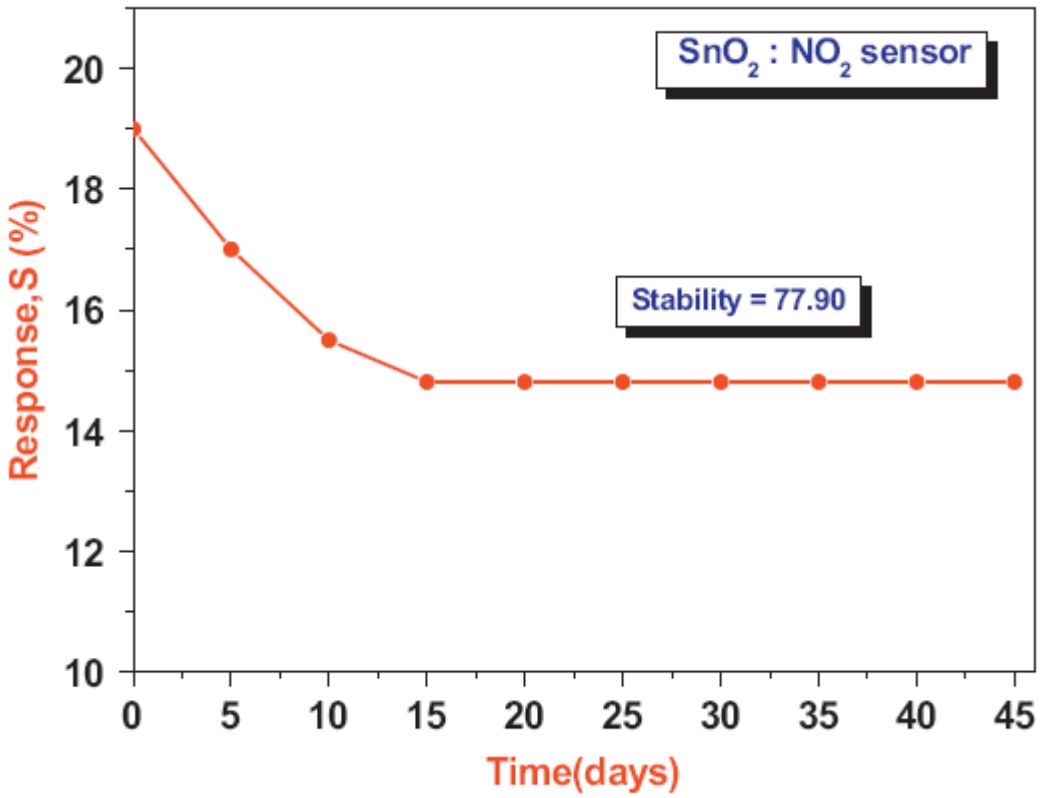

Fig.10. Stability of SnO_2 thin film sensor at 100 ppm NO_2

6. Conclusions

Sol-gel spin coating technique was employed for fabrication of nanostructured SnO_2 thin film sensor on glass substrate. This process is convenient, environment friendly and effective for making nanosized material. Structural studies revealed that the formation of tetragonal SnO_2. Microstructural analysis confirms nanostructured morphology suitable for gas sensing application. The gas sensing measurements at 200 ^oC showed that SnO_2

film is selective at low concentration of NO_2 gas. SnO_2 thin film sensor exhibits maximum response of 19 % with 77.90 % stability towards NO_2 gas. Impedance spectroscopy studies revealed that the change in resistance of the SnO_2 film after exposure to NO_2 is mainly contributed by intragrain region. The gas sensing characteristics viz, selectivity, response reproducibility and stability showed that SnO_2 would be a prospective candidate for the detection of NO_2 gas at low concentration (10-100 ppm) and at lower operating temperature.

Publications

Journal publications

1) Nanocrystalline SnO_2 thin films: Structural, morphological, electrical transport and optical studies,

R.D.Sakhare, G.D.Khuspe, S.T.Navale, **R.N.Mulik** , R.C.Pawar, C.S.Lee, M.A.Chougule and V.B.Patil

J. Alloys and compounds 563 (2013) 300–306

2)Nanostructured SnO_2 thin film for NO_2 gas sensing applications

G.D. Khuspe, R.D. Sakhare, S.T.Navale, M.A.Chougule, **R.N.Mulik**, R.C.Pawar, C.S.Lee, V.B. Patil

Ceramic International, 39(2013)8673–8679

Conference publications:

1) Fabrication of Nanostructured SnO_2 Thin Film sensor for NO_2 Monitoring,

G.D. Khuspe, R.D. Sakhare, M.A. Chougule, **R.N. Mulik** and V.B. Patil, National Conference on Physics of Nanomaterials & Applications (NCPNA-2012), 14-15 December 2012, Department of Physics, DBF Dayanand College of Arts & Sciences, Solapur.