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Synthesis and characterization of ZnO nanoparticles for efficient gas sensors

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ABSTRACT

In the present work zinc oxide nanoparticles were synthesized using simple chemical method. The prepared nano zinc oxide was characterized using XRD and UV-Visible spectroscopy, S.E.M..T.E.M., The optical band gap was calculated from UV-Visible absorption measurement. The particles size was estimated using XRD pattern. Gas response of Zinc oxide films are checked for different concentration of reducing and oxidizing gases. The sensitivity measurement for selective ammonia gas with varying concentrations and stability studies have been carried out.

INTRODUCTION

Many metal oxides are used to detect reducing and oxidizing gaess by conductive measurement .the metal oxides are divided into following two classes .(8)

1] Transition metal oxides
2] Non transition metal oxide

Semiconductor nanomaterials have received been received great attentions. Among these various semiconductor oxide nanomaterialss zinc oxide is a versatile material because of its physic-chemical properties such as mechanical, electrical, optical, magnetic and chemical sensing properties. It has a wide band gap of 3.3 eV and it is used in various applications electronic devices, biomedical field, verity of sensors, etc.

Now a days, various routes have been used for the synthesis of ZnO nanomaterials, such as sol–gel synthesis [1], hydrothermal/solvothermal methods [2,3], microemulsion method [precipitation [and physical vapor deposition Sol-gel method gives homogenous, high-purity, and high-quality nanopowders . The morphology of the nanoparticles can be changed by changing the solvents.

Zinc oxide is an important n-type semiconductor with a direct band gap of 3.37 eV. Zinc oxide nanoparticles are widely used in various applications such as optical devices , catalysis, light emitting diodes, photo detectors, solar cells and gas sensors (9)(10). In recent days thick film(11)(12) and thin film have been performing(13)(14)(15) .Zinc is an essential nutrient in humans and animals for many physiological functions, including immune and antioxidant function, growth, Skeleton development, skin growth, appetite, wound healing and reproduction . Zinc oxide (ZnO), a safe source for Zn supplementation and it is commonly used to fortify foodstuff in the food industry. ZnO will decompose into Zn ions after consumption. A variety of methods have been used for the synthesis of zinc oxide nanoparticles such as direct precipitation, homogeneous precipitation, solvothermal method, sonochemical method, reverse micelles, sol gel method , hydrothermal, thermal decomposition, and microwave irradiation. In the present study, a simple and cost effective sol–gel method was used to prepare ZnO nanoparticles, using zinc acetate as a precursor, acetic acid the complexing agent and triton X-100 as a surfactant. The optical properties, particle size, and crystallinity, of the final ZnO nanoparticles were investigated.

MATERIALS AND METHODS

Experimental detail

The ZnO nanoparticles were prepared by sol-gel method at room temperature. Zinc acetate ($Zn(CH_3COO)_2.2H_2O$), and Triton X-100 were used as starting materials. 0.2 M zinc acetate solution was prepared by dissolving 1 g of zinc acetate in 25 mL of water. The solution was stirred at room temperature, and then the 5mLTriton X-100 was added to the solution and again stirred for 3 hour at room temperature. After the 1 hour slightly precipitation observed then ammonia solution was added for complete precipitation. Then the residue was filtered, washed with water and then dried at 353 K for an hour. The dried residue then calcined at 673 K in an electric oven.

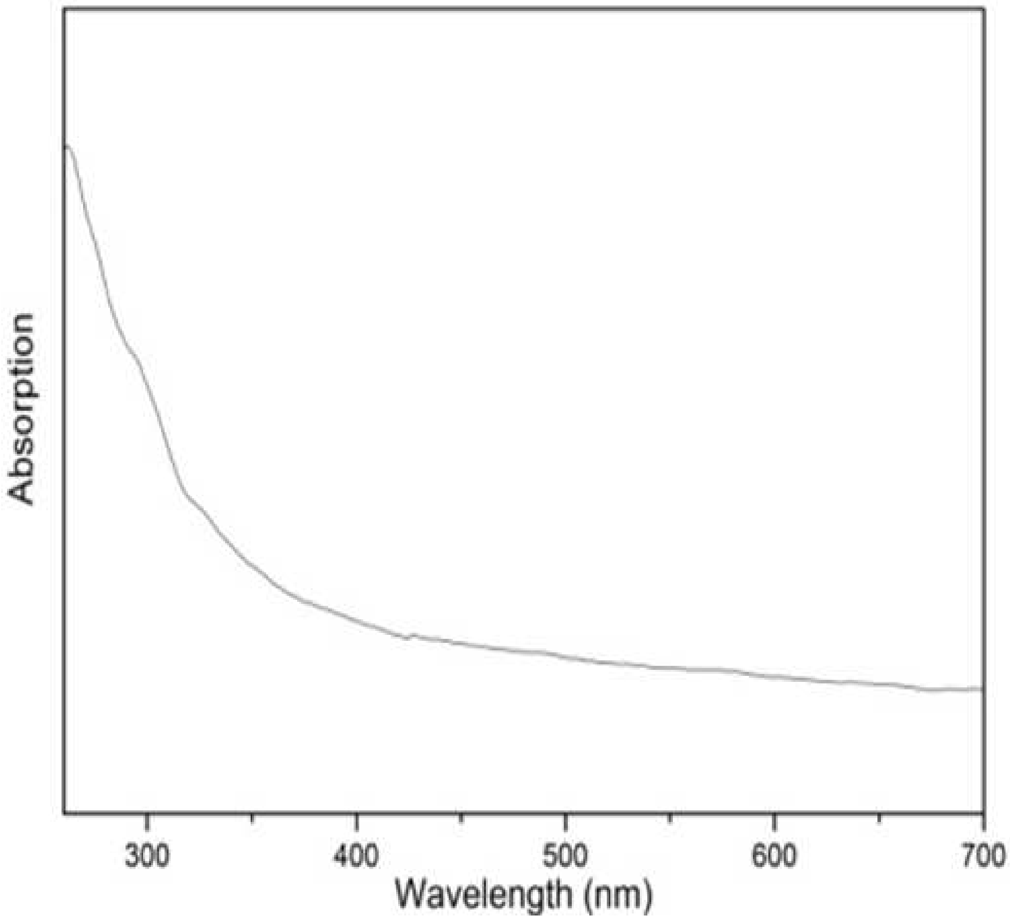

Fig UV-V 1(a) is spectra of ZnO nanoparticles

The structure morphology of the prepared ZnO nanoparticle was characterized by Bruker D-8, powder X-ray diffraction (Cu Kα=1.5406 Å). The UV-Vis absorption measurement was measured over the range of 200–800 nm by a Bio-age UV-Vis spectrophotometer. FTIR spectra of the samples were recorded on BRUKER Alpha FT9–Infra–Red spectrometer.

Substrate cleaning :
In thin film deposition process substrate cleaning has great importance .which affects the smoothness uniformaly , adherence, and porosity of the films . in the substrate cleaning process the bond between substrate and contaminant breaks without damaging the substrate . substrate cleaning is depends upon nature of substrate . the glass substrate 1.35 mm thick were used for the deposition of films.

1) Substrate is washed with AR grade hydrochloric acid
2) Then it is washed with detergent
3) Washed with distilled water to remove detergent powder residue
4) Then substrate ultrasonically cleaned for 15 min.
5) Finally substrate were dried and degressed with AR grade acetone .and finally kept in to dust free chamber.

RESULTS AND DISCUSSION

UV–Visible absorption studies
Figure 1(a) shows the UV-Vis spectra of ZnO nanoparticles. UV–Vis absorption of ZnO nanoparticles was measured and it is observed in the wavelength range of 250-400nm.

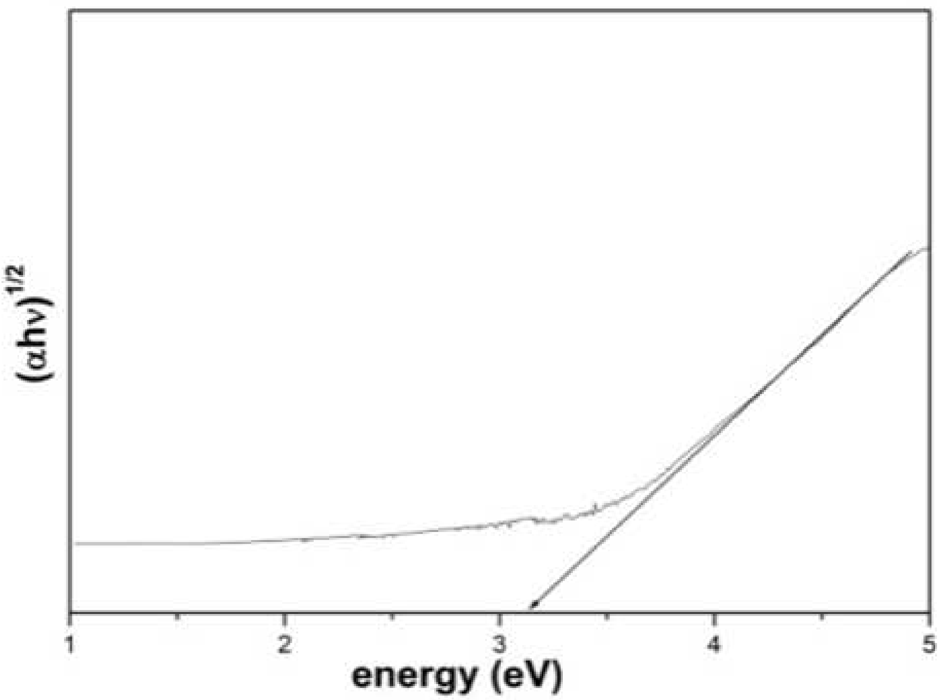

Fig 1 (b) Band gap measurement

Figure 1(b) Shows the plot of 1/2 vs. photon energy hν of ZnO nanoparticles. The band gap energy value for ZnO samples was calculated from this plot. The wavelength of 380 nm corresponds to the bulk band-edge of 3.2 eV for ZnO. The absorbance at wavelength of 370 nm indicates a blue shift, which should be due to the quantum confinement effect from the small particles size of 10 nm as found in XRD analyses.

1 (b) Band gap measurement
XRD studies
The XRD spectra shows well defined diffraction peaks showing good crystanility.The XRD pattern of ZnO nanoparticles calcined at 673 K is shown in Figure 3. The XRD pattern shows of ZnO. All XRD diffraction peaks of ZnO powders are shown in a good agreement with hexagonal structure of zincite phase reported in JCPDS File Card No.05-0664. No peaks of impurity are observed, indicating that the high purity ZnO was obtained.The particle size calculated using Debye–Scherrer formula D = 0.94λ / (βcosθ), where λ the X-ray wavelength, β the peak width of

half-maximum, and θ is the Bragg diffraction angle. The average crystallite size D is 10 nm calculated using the Debye–Scherrer formula. It is observed that as the annealing temperature increased the crystalline size increased.

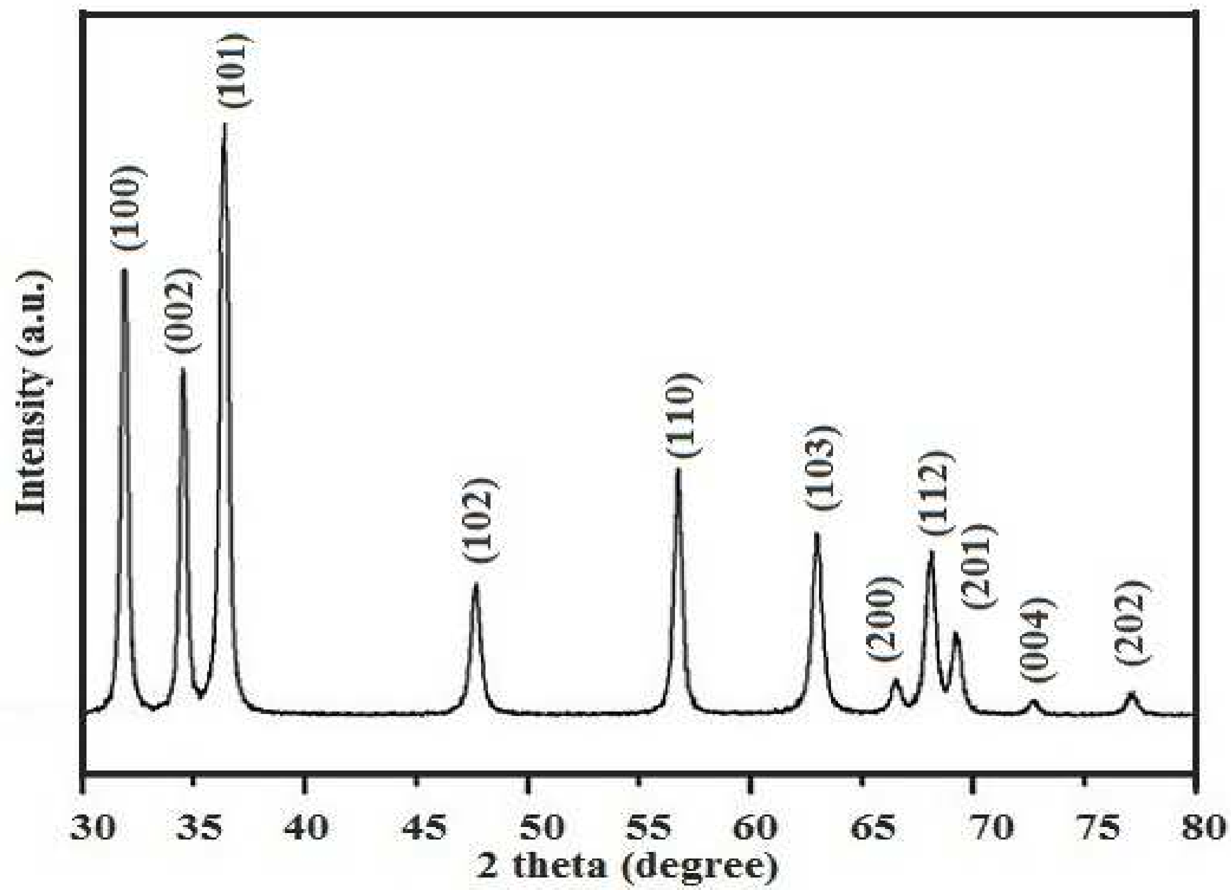

Fig XRD pattern of ZnO nanoparticles

From fig. nine prominent peaks corresponding to the (100) phase (2 theta =31.65), , (002) phase(2 theta =34.65), (101) phase (2 theta =37.18), (102) phase(2 theta =47.25), (110) phase (2 theta =56.45), (103) phase(2 theta =63.75), (200) phase (2 theta =67.73), (112) phase(2 theta =68.43), (201) phase (2 theta =69.68), xrd peaks were observed and it is concluded that all it is concluded that all the films were polycrystalline with hexagonal wurtzite structure,

Gas sensing studies :

Gas sensing properties of ZnO thin films is fabricated by the high temperature gas sensors. In this article the gas sensing studies towards oxidizing and reducing gases is reported .since in the s.e.m. images it shows spherical shapes consisting of fine nano particle with porous space between them.

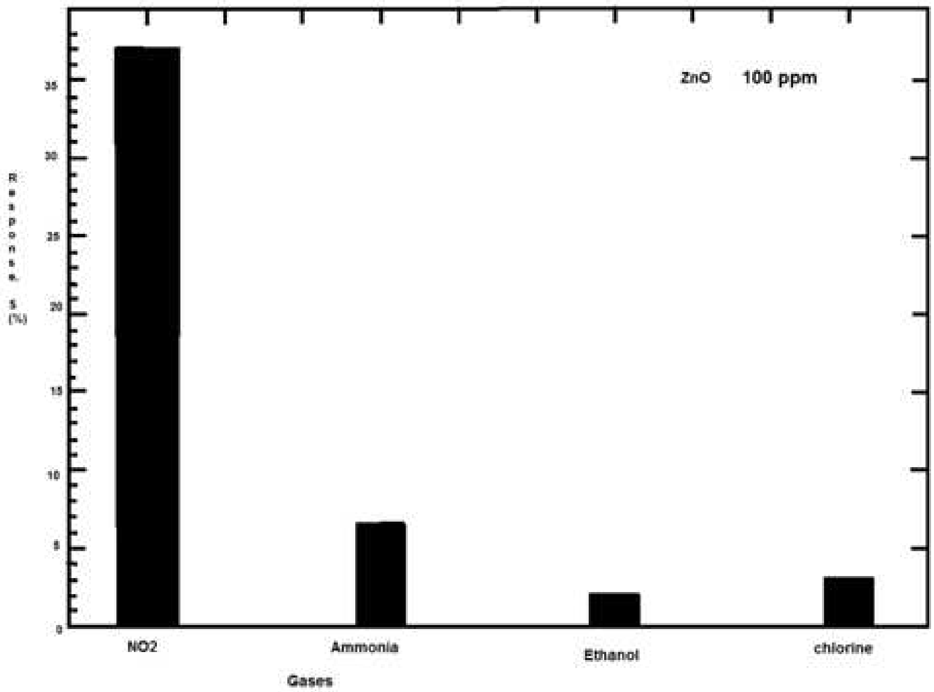

Fig Gas responses of ZnO sensors films to 100 ppm of NO_2, NH_3, Ethanol, Chlorine

From figure the ZnO sensors offered maximum response to NO_2 , NH_3,Chlorine,Ethanol. The zinc oxide film shows more selectivity for NO_2 over other three gases .The operating temperature is about 200^0C. poor selectivity for chlorine gas.

Mechanism of NO_2 gas sensing:
Generally metal oxide are of p- type and n-type . the ZnO is an n-type of semiconductor which is carrier of electron . NO_2 is toxic gasby inhalation but at low concentration will anaesthetize the nose thus creating a potential for over exposure . long time exposure to NO_2 at different concentration causes adverse health effect(27). The important source of NO_2 are I.C. Engines , power stations (28).

When an n-type of semiconductor gas sensors is present in the air chemisorptions of O_2 molecules could happen on the surface in the form of O_2^-,O_2^{2-},and O^{2-} ions by capturing electrons from the conductance band . since the electronegativity of oxygen molecules is bigger than semiconductor ,the oxygen species capture conductionelectron from the materials this leads to decrease in electron concentration. The junction between ZnO grains, the depletion layer and potential barrier leads to the increasing of the electrical resistivity value. This value is strongly dependant on the concentration of absorbed O_2 ions of the surface . the reaction in an NO_2 oxidizing gas

$$NO_2 + e^- \longrightarrow NO + O^-$$

Sensitivity
Effect of operating temperature and NO_2 concentration
The sensor response reached maximum at 200ocC and then decreased .it is well known that at low temperature speed of chemical reaction restricred the response. The sensitivity of sensors increases with the increase in the temperature and reaches amaximu value .but after some time temperature is increases but the sensitivity is decreses. This behavior explained by mechanism of gas adsoption and desortion.

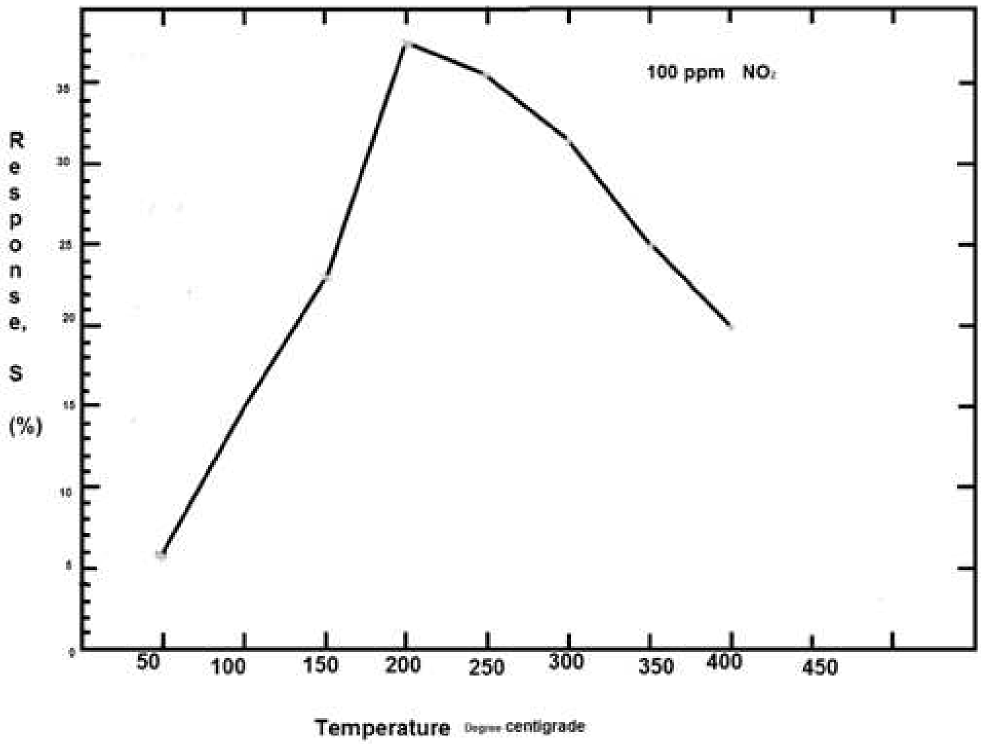

Fig Response of ZnO films at 100 ppm of NO_2 gas at operating temperature

Variation in concentration of No_2 at operating temperature .
Fig .shows the response of zinc oxide films as a function of NO_2 concentration increased from 10 to 100 ppm.

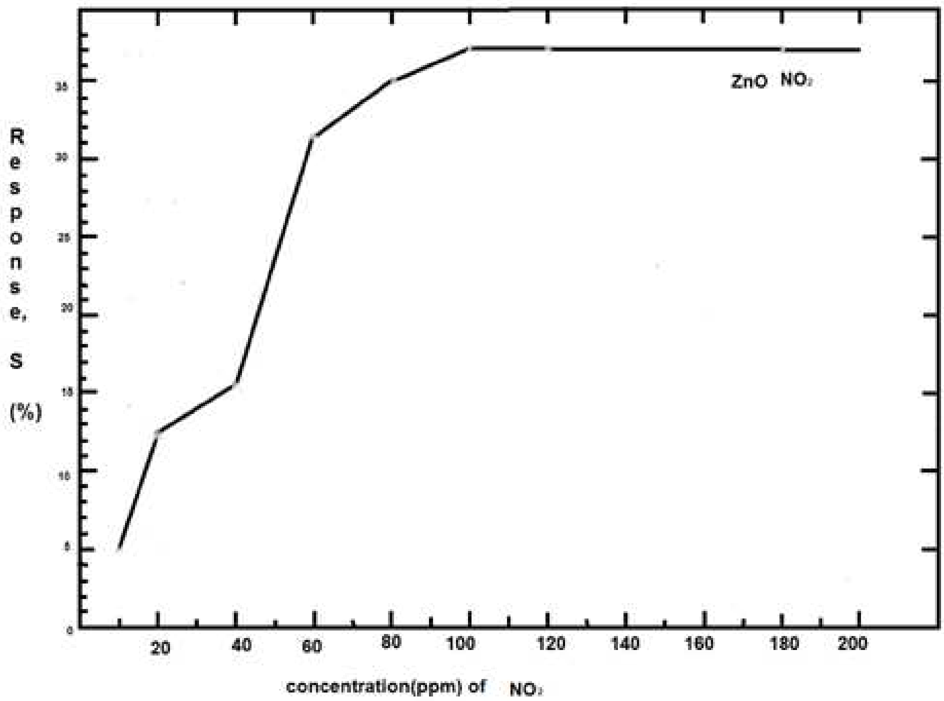

Fig Variation in concentration of No_2 at operating temperature

From fig**.** it shows that from 90 ppm it shows saturation of No2 due to increased in surface reaction.

Zinc oxide sensors stability:
for check the stability the response zinc oxide film at fix concentration of 100 ppm is observed for 50 days by the interval of 5 days at temperature 200^0c .from the first day zinc oxide shows maximum response but it decreases sreadealy, from days 25-50 it shows stable response .

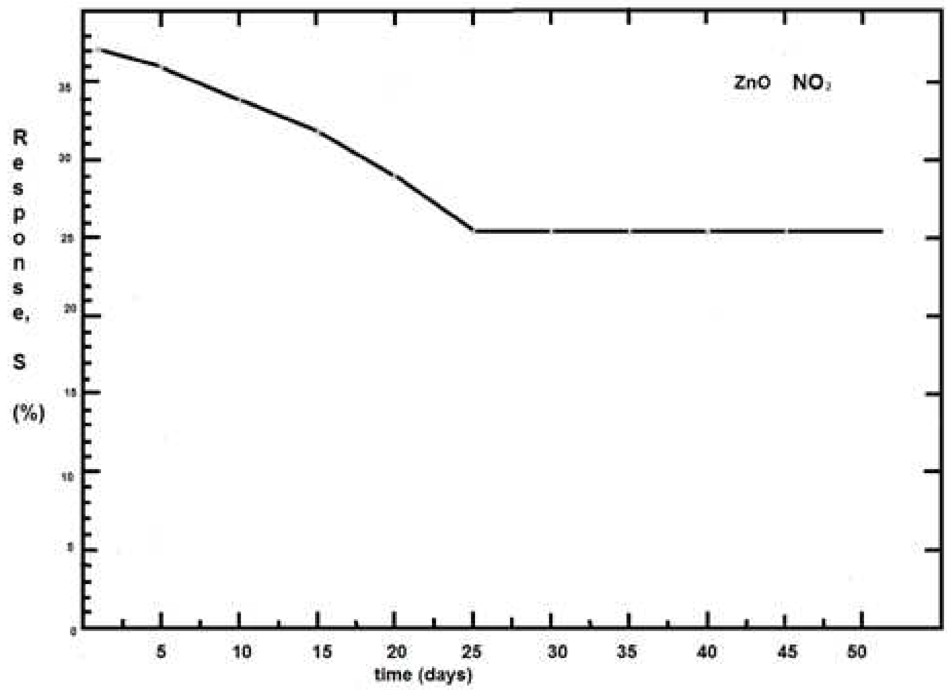

Fig sensing stability of ZnO film at 200^0 c

From this it proves that 75 % stability of zinc oxide at 200^0c.

Response and recovery characteristics of ZnO films:
Response and recovery time are two different and important parameters for sensors characterization. It is observe that response and recovery time are varies inversely with respect to concentration of gases. Response time is the time taken by sensors to attain ninety percentage of maximum resistance on exposure of target gas. recovery time as the time taken to get back ninety percentage of the maximum resistance when exposed to pure air.

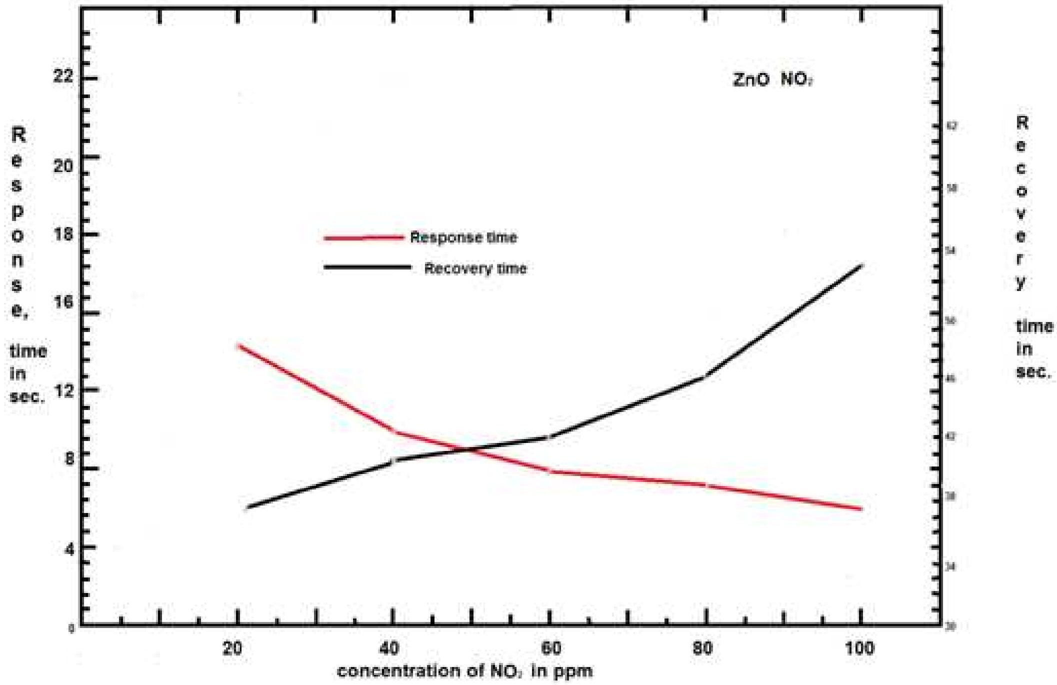

Fig response and recovery time of ZnO film at different concentration of NO2 and at operating temperature 200^0 c

CONCLUSION

ZnO nanoparticles have been sussesfully synthesized by simple sol-gel method at room temperature. The prepared ZnO nanoparticles were characterized using XRD and UV-Vis absorption measurement. The average particle size was found to 10 nm for ZnO nanoparticles calcined at 673K. ZnO offers tremendous potential in future applications of electronic, optoelectronic, and magnetoelectronic devices. The prepared ZnO nanoparticles may possibly applicable for photocatalysis, gas sensing, biomediacal devices and sun screens applications. The X.R.D. study reveals that the deposited thin film of zinc oxide has good nanocrystanilline hexagonal wurtzite structure. The zinc oxide film shows high sensitivity towards No2 gas at operating temperature 200 c. fast and high gas sensitivity for N02. The highest response is given as 36.3.it shows different response towards different concentration(10-100 ppm) of NO2.

The fast recovery and response are due to the high adsorption density of o- and O^2- due to high operating temperature. maximum gas response for 75 % at 200^{0}c.

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