Nanosized Semiconducting Stannous Oxide Thick Films Sensor for Some Oxidizing and Reducing Gases

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ABSTRACT

The present study deals with the fabrication of stannous oxide nanomaterial prepared by co-precipitation method and followed by preparation of thick films by conventional screen printing method. The stannous oxide is excellent semiconducting material possessing approximately 3.5eV band gap, which can be exclusively used for sensing phenomenon. The SnO2 nanoparticles were characterized by XRD, SEM, and EDX .The nanoparticle size calculated by Scherer formula for SnO2 found to be 36nm. The scanning electron microscopy shows microspores and mesopores of heterogeneous texture with greyish black background. EDX analysis confirms the fundamental elemental composition of stannous oxide material. Designed SnO2 thick films found to be sensitive towards ammonia, ethyl alcohol, H2S, and NO2 gases.

Keywords: SnO2; Gas sensitivity; XRD; SEM; EDX.

INTRODUCTION:

The recent emergence of concern over environmental pollution and accidental leakages of explosive gases have increased awareness for efficient detection and constant monitoring of such gases. To meet this demand, considerable research into the development of different types of sensors with novel design using tailored material properties is under way. A great deal of efforts has been put into developing new sensing materials with improved sensor properties. Metal-oxide-semiconductor (MOS) is a more suitable material for the fabrication of gas sensors due to long-term cyclic stability in air atmosphere, simplicity, low-cost, and compact size. Metal oxides possess a broad range of electrical, chemical and physical properties that are often highly sensitive to changes in their chemical environment [1]. Because of these properties, metal oxides have been widely studied and most commercial sensors are based on appropriately structured [2].The enhancement in the gas sensing performance of metal oxides by electron [3].

Now a days tremendous efforts are being directed towards the development of nanometer sized materials and finding applications of these materials. Nanometer-sized materials have recently attracted a considerable amount of attention due to their unique electrical, physical, chemical, and magnetic properties; these materials behave differently from bulk semiconductors. With decreasing particle size the band structure of the semiconductor changes; the band gap increases and the edges of the bands splits into discrete energy levels. These so-called quantum size effects occur [4-8], and stimulated great interest in both basic and applied research.

SnO_2 is a remarkable n-type semiconductor material having wide band gap (3.5 eV) and is sought for a wide variety of applications. It has been used as solid state sensor mainly due to its sensitivity towards different gaseous species [9, 10].

H_2S is a very toxic gas, it has no colour, but it smells like rotten eggs. In larger amounts H_2S quickly blocks the sense of smell and can irritate the eyes, nose, throat, lungs and even halt the breathing center in the brain, which can cause death. H_2S is often found in oil and natural gas deposits, and in some mineral rock. It may also form when organic material such as manure or vegetable matter breaks down without oxygen. It also produce at a by-product in the making of pulp and paper, fertilizers, glues, dyes, plastic wrap, and other products[11].Hence, it has always been a big challenge to measure H_2S accurately with the least amount of bias under field conditions. In the present work the fabrication and characterization of crystalline SnO_2 nanoparticles powder by precipitation method and its sensitivity for H_2S gas at low temperature was studied.

MATERIALS AND METHODS:

All the chemicals used in synthesis of SnO_2 are of AR grade purchased from Modern lab, Nasik and used without further purification.

Synthesis of nanoparticles of stannous oxide by co-precipitation method:

Dissolve 0.01 moles of stannous chloride in 80 ml of double distilled water to get a clear solution. Add to it 0.05 moles of liquor ammonia (30ml), drop wise with continuous stirring on magnetic stirrer with heating at 70 ^{0}C for 30 minutes. A white precipitate will separate out, which is allowed to settle for 2 hours. Filter the precipitate by whatman filter paper 01 and washed the residue two to three times with hot water. The dried residue was calcined for 600 ^{0}C up to 6-8 hours, the light cream whitish color nanoparticles of SnO_2 are obtained. [12].

Fabrication of thick films of SnO_2 by screen printing method:

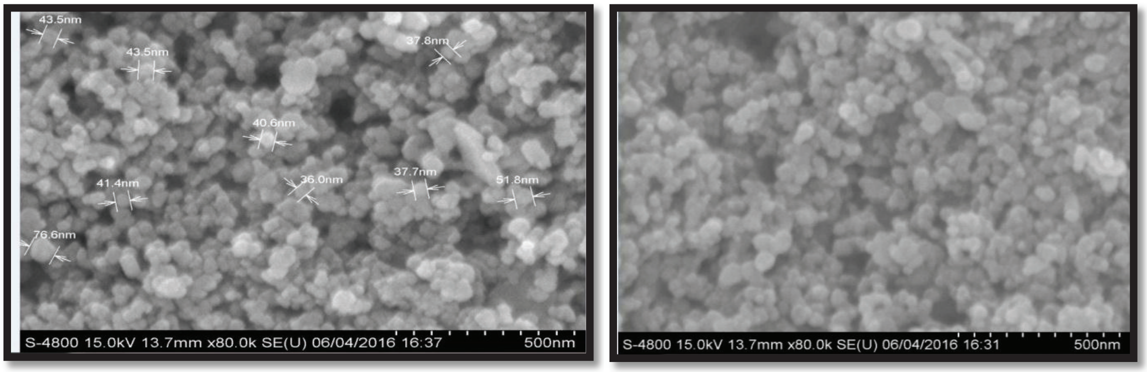
The powder of stannous oxide converted into paste form was used to prepare thick films by screen printing method by maintaining the inorganic to organic materials ratio at 70:30.The inorganic part consist of nanoparticles (SnO_2). The organic part consisted of 8% ethyl cellulose (EC) and 92% butyl carbitol acetate (BCA).The SnO_2 oxide with ethyl cellulose (EC) were mixed throughout in an acetone medium with mortar and pestle. A solution of BCA which was added drop wise until proper thyrotrophic properties of the paste achieved. The paste was then coated on glass substrate by using standard screen -printing technique. The SnO_2 film was dried under IR lamp for 60 minutes to remove the organic volatile impurities and then fired at 400 ^{o}C for 2 hours in muffle furnace. The prepared thick films are now ready for characterization and further electronic application. [13, 14]

RESULT AND DISCUSSION:

Electron microscopy: SEM Analysis:

The microscopic analysis exclusively used for surface characterization, study of morphological features and porosity of ceramic materials. SEM analysis, showed the homogeneous, grayish blacked surface texture with microspores of stannous oxide nanoparticles. The varied size of nanoparticles ranging from 36.0 nm to 76.6 nm as depicted in fig.1

Fig.1: SEM images of prepared SnO2 nanoparticles.



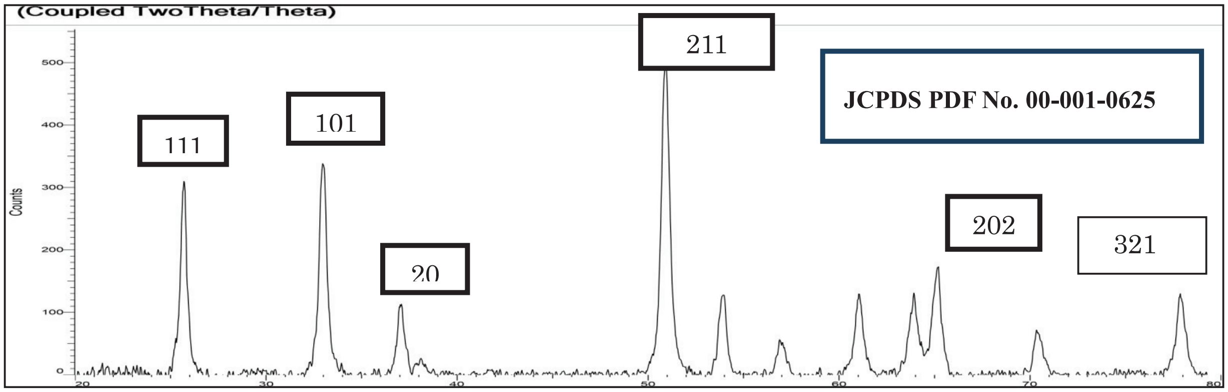
Average particle size analysis by XRD :

The stannous oxide nanoparticles were characterized by XRD [BRUKER, Cu Kα radiations of wavelength 1.54 A ^{0}] showed the main two theta peaks for various diffraction at 25.69^{0} 32.980^{0}, 37.06^{0}, 53.90^{0}, 63.90^{0}, 77.89^{0} calcined at 600 ^{0} C. The XRD spectrum for prepared SnO_2 thick films is as shown in fig.2.form which the calculated size of stannous oxide nanoparticles by using Scherrer euation was found to be 36.5 nm .SnO_2 is a part of Cassiterite mineral which has a tetragonal crystal system.

$D = K\lambda/\beta \cos\theta$ ……………. Scherer equation.

Where K=constant (0.89 to1.39), λ=Radiation of wavelength (1.54 A^0) β=FWHM (Full Width Half wave Maxima), θ=Bragg angle in degree, D=Particle Size.

Fig.2: XRD spectra of SnO_2 Thick Films

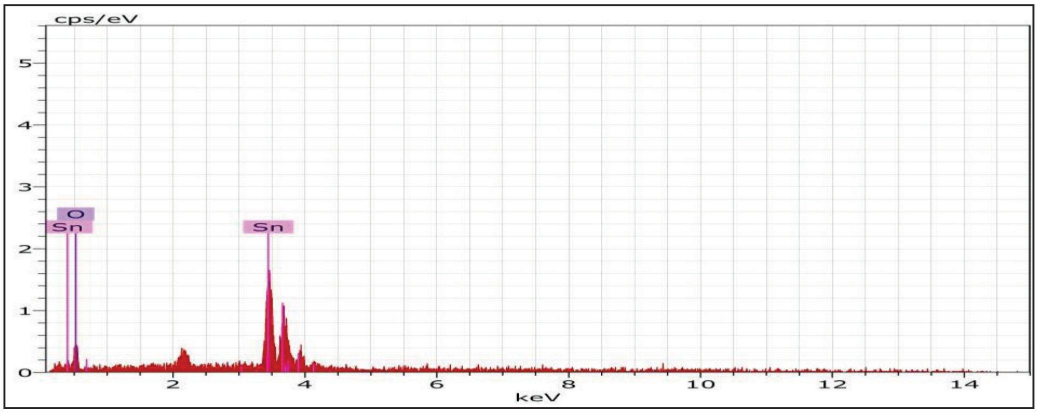


2 Theta (Coupled Two Theta/Theta) WL =1.54060

Electron Dispersive X-Ray Spectroscopy (EDX) Analysis:

The prepared stannous oxide material was subjected for EDS study shows the perfect percentage of elemental atoms present in the synthesized stannous oxide nanoparticles. The EDS spectrum of prepared nanoparticles of SnO_2 is as shown in fig.3.

Fig.3: EDS Image of prepared SnO_2 thick films



The percentage of prepared SnO_2 nanoparticles is as shown in table 1

Table1: Percentage of elements & its elementary atom weight in synthesized SnO_2

S.N	Element	% of elementary atom in prepared SnO_2
1	Tin	61.47
2	Oxygen	38.53

Electrical Characterization:

The electrical characterization of thick films of prepared SnO_2 nanoparticles was achieved by measuring the D.C.resistance of the films by means of half bridge method as a function of temperature in a home built measurement system. Which consist of glass chamber of 25 liters and -12 inch diameter & heater (1000W) of nichrome wire (Resistance -120ohm at room temperature). The heater was used to change the film sample temperature from room temperature (RT) to 350^0C by changing its voltage using dimmer stat (maximum current limit up to -8A). The high resistance of the sample film was determined by using the half bridge method The resistance of the sample was measured in air atmosphere as well as in the presence of gas (at ppm level) of interest at different operating temperatures. The resistance (Ra) of the sample in air and (Rg) in gas atmosphere was measured by using half-bridge method, measured to evaluate the gas response (*S*) given by the relation, S = Ra-Rg/Ra.

Electrical resistance and effect of temperature on SnO2 Thick Films:

Fig. 4: showing graph of Electrical resistance V/s Temperature for SnO_2 thick films.

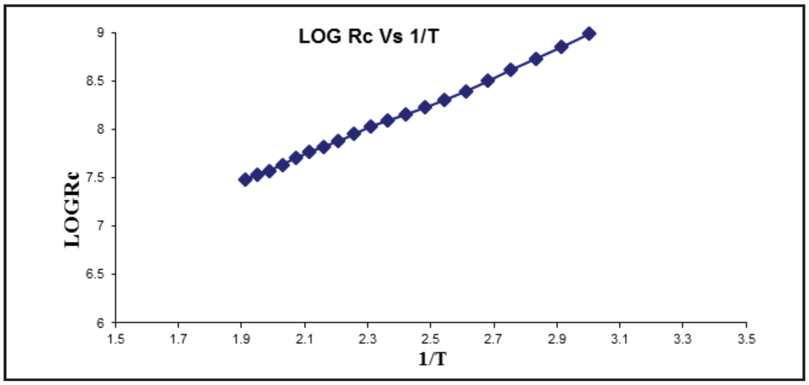


Fig 4 showing the typical curve of electrical resistance against temperature for prepared thick films of SnO_2 .The graph shows typical semiconducting behavior for prepared material of SnO_2 as the electrical resistance is decreasing with increase in temperature, showing a typical NTC semiconducting behavior. [15, 16]

Gas Response for SnO_2 thick films:

The gas response for the SnO_2 thick films for various gases is as shown in following fig.5, 6, 7, 8.The optimum response shown by SnO_2 is around 29 % for NO_2 gas at 500 ppm of gas concentration.

Fig. 5 Ammonia gas response for SnO2 thick films

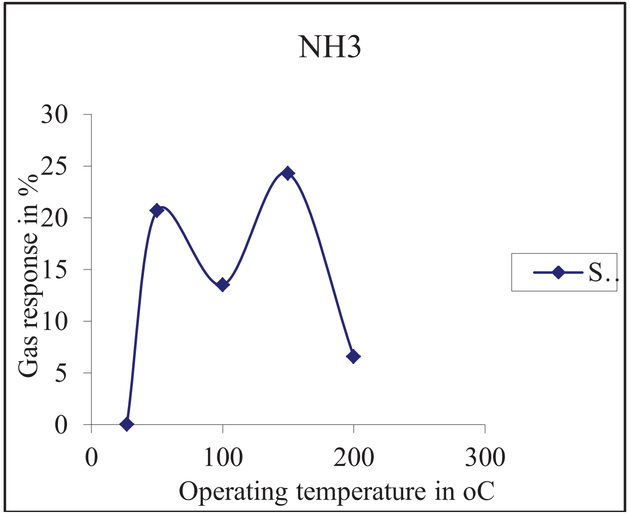


Fig. 6 Ethanol gas response for SnO2 thick films:

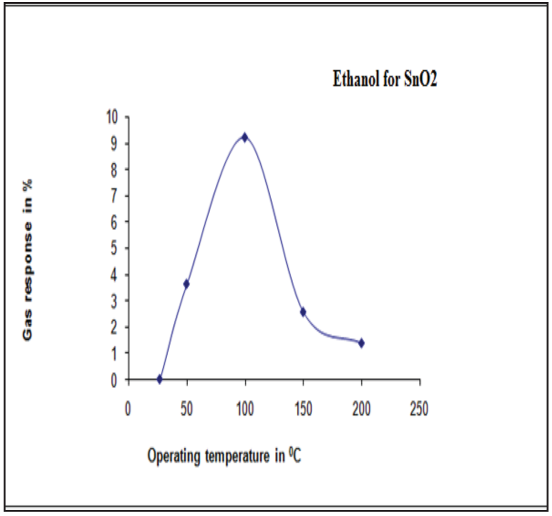


Fig. 7: H_2S gas response for SnO2 thick films

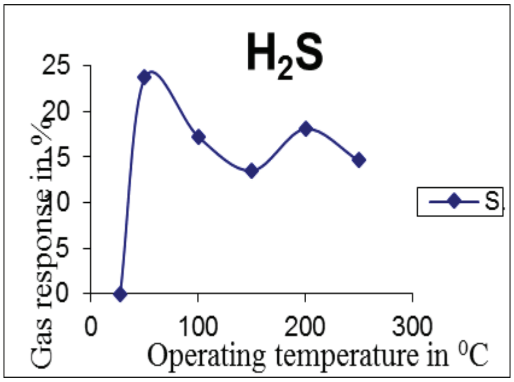
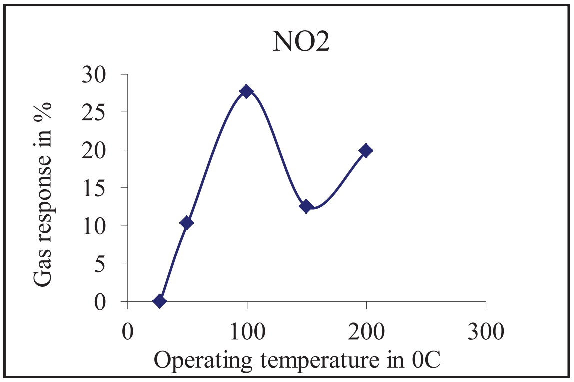


Fig. 8: H_2S gas response for SnO2 thick films:



CONCLUSIONS:

1) The SnO_2 nanoparticles were successfully synthesized by Co-precipitation method.
2) The thick films of SnO_2 are prepared by Screen printing method
3) The SnO_2 thick films were characterized by XRD, SEM, EDS.
4) The calculated size of SnO_2 material from Scherer equation found to be 36 nm
5) The electrical characterization of prepared SnO_2 thick films were carried out by typical gas sensing apparatus for knowing the semiconducting behavior of SnO_2 .The graph as depicted in fig.4 showed a typical behavior of semiconductor as the resistance of the SnO_2 films found to decreasing with increase in temperature.
6) The thick films of SnO_2 show highest sensitivity to H_2S gas at room temperature. The sensitivity of stannous oxide films to H_2S was observed as 23.73% at room temperature (40^0C).At the same time the SnO_2 films found to sensitive for ethyl alcohol, methyl alcohol, and ammonia gases.

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