



A Review Article on SnO₂ based Thick Film Gas Sensors

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Abstract: Pollution has raised its ugly head high in the global environment. It created tremendous disasters of global warming. To face such disasters is very challenging for mankind. Many gases released by vehicles and industries contribute the pollution and ultimately global warming. Gases beyond a certain limit can affect living beings. So, there is a need to detect the gaseous pollutants in the environment, even at trace levels. Many researchers are already working to detect hazardous gases in the environment and develop gas sensors at their best level. Researchers are well known about the hazards of different gases released by any means in the open environment. Still, the action has not been initiated in the desired proportion to save the environment from pollution and its hazards. Also, the researchers have the responsibility to the aware society of pollution hazards. The aim of the present study is, to well acquaint ourselves with the thick films of SnO₂ and their nanocomposite gas sensors. Gas sensors can be fabricated and developed by utilizing the pure and surface activated SnO₂ and their nanocomposites so that, they could be able to detect various gases at trace levels (ppm / ppb).

Key Words: SnO₂, Synthesis, Thick Films, Gas sensors, Characterizations, Polluting Gases, etc.

1. INTRODUCTION:

The concentration of gas in the environment which produces an undesirable and disastrous change in the physical, chemical, or biological characteristics of air, soil, and water that can harmfully affect living beings is called pollution. Heavy industrialization, uncontrolled urbanization, and careless application of technology can cause pollution [1-6]. There are three major types of pollution: air pollution, water pollution, and soil pollution. Out of these, air pollution is a major threat to modern society. Current burning issues are global warming, the cruellest episodes like Bhopal gas tragedy, leakage from the Ukraine atomic reactor plant, and the blackening of world heritage places like Taj Mahal and Ajanta caves are the effects of air pollution. Along with this, some domestic threats are also occurring all over the world. The main culprits behind all such hazards are toxic, inflammable, and explosive gases. Gases play a key role in many industrial or domestic activities. In the last twenty years, the demand for gas detection and monitoring has increased. Particularly, the awareness of the need to protect the environment has grown. This century is the century of automation. It requires fast, simple, safety control and reliable measurement technology of the physical quantities.

1.1. POLLUTING GASES AND THEIR HEALTH HAZARDS:

Various gases above a certain concentration pollute the environment and can cause undesirable and disastrous effects on living beings [7-22]. The various polluting gases and their toxic effects are discussed elsewhere [17].

Over the past few decades, tin oxide-based films are widely used as gas sensors due to their high sensitivity in the presence of trace amounts of some gases of interest viz. carbon monoxide, ethanol, methane, LPG, LNG, etc. Allied to this advantage is the low cost, simple, easier, fast response and recovery, selective nature to a particular gaseous species among the mixture of gases, and the possibility of miniaturization of these devices [23-30]. The variation of the conductance measured under specific gases depends on many parameters such as intrinsic resistance, grain size [31], grain boundary barriers, detection temperature [32], etc.

Higher concentrations of gases containing sulfur led to bronchitis and lung cancer. These gases containing sulfur destroy plant cells and interfere with chlorophyll synthesis. Leaf blotching and reduction in crop yield occur even at a concentration of less than 1 ppm. Exposure of gases containing sulfur can also affect nonliving things viz. stone leprosy, increase in the rate of corrosion of metals, retardation of drying of paints, etc.

H₂S sensor model TGS 825 is already available in the market and is manufactured by Figaro Engg. Inc. Ltd. But TGS 825 is an expensive model. So, it is a need to fabricate low-cost sensors for large applicability.



H₂S is a colourless gas with the characteristic foul odour of rotten eggs. H₂S is one of the major pollutants, hazardous and toxic [27-28] in nature, which is also released from industries and laboratories. H₂S has also been liberated in volcano eruptions like natural events along with some manmade processes. So, it is a need to detect it even at very low concentrations (ppm / ppb / sub-ppb level). The aim of the present work is to develop low-cost H₂S sensors by utilizing the easily available material to a large extent and modifying the material to enhance the H₂S sensing performance. Thick films of pure and modified SnO₂ are tested and developed, which could be able to detect the H₂S at trace levels (below TLV).

1.2. APPLICATIONS OF GAS SENSORS AND THEIR NEED:

A gas sensor is a device that when exposed to the gaseous species, produces a proportional output signal corresponding to its odour, concentration, contents, etc. The gas sensor detects the odour and concentration of gases, below the detection limit of human sense organs. The output signal produced by the gas sensor may be in the form of electrical, mechanical, or magnetic in nature. Gas sensors find applications in numerous fields, viz. fire detectors, gas leakage detectors, controllers of ventilation in cars and planes, alarm devices for hazardous gases in workplaces, etc. The detection of volatile organic compounds (VOCs) or smells generated from food or household products has also become increasingly important in the food industry, in indoor air quality, and in multisensory systems. Gas sensors are popularly referred to as electronic noses.

There are many more applications of gas sensors, viz. Safety, Environmental Control, Automobiles, Food Fresheners, Medicine, etc.

Metal oxide-based solid-state gas sensors are the best selection for the development of commercial gas sensors for a wide range of applications. The great interest in industrial and domestic solid-state gas sensors comes from their versatile advantages like portable size, high sensitivity in detecting very low concentrations (ppm, ppb, or sub ppb level) of a wide range of gaseous chemical compounds, and low cost. On the other hand, traditional analytical instruments are expensive, complicated, and bulky. Solid-state chemical sensors have been widely used but they also suffer from limited measurement accuracy and problems with long-time stability. Recent advances in nanotechnology, as far as the synthesis of materials is concerned, produce novel classes of nanostructured materials with enhanced gas-sensing performance. This technology dramatically increases the performance of solid-state gas sensors. Gas sensors are needed to; minimize health hazards, avoid the hazards of global warming, avoid the cruelest episodes, and detect and control the pollutants in the environment in the form of gas or moisture.

The technological progress made by mankind has changed and shaped the world. But this progress has several side effects, the major being related to the environment. Industrial development all over the world is generating toxic solid, liquid, and gaseous wastes. Hazardous gases like CO, NO_x, H₂S, etc. are polluting the air blanket of the earth which is creating several health issues for human beings. The health issues include several diseases like respiratory tract diseases (bronchitis, asthma, nausea, shortness of breath), lung cancer, reduction in haemoglobin, impairment of the nervous system, mental retardation, disorders of the digestive system, disorders of blindness, reproductive system, hypertension, forgetfulness, headaches, etc. It has, therefore, become the need of an hour to keep watch and monitor the air quality with the help of gas sensors. Such monitoring can be made outdoors as well as indoors. The detection of gas pollution with the help of sensors can help in the elimination of these polluting gases and thus improve air quality. These gas sensors can be seen as security equipment for environmental security. The pollutant gases are of various types, and they originate in different physical conditions like temperature, radiation, etc. The sensor should work and provide accurate results irrespective of the environmental conditions where they are installed i.e., there should be no compromise in stability, selectivity, sensitivity, etc. [15].

A lot of research and development is in progress to design portable and affordable gas sensors which possess the highest response, produce ability at trace levels of gaseous species, have selective nature among the mixture of various gases, long-term stability, low cost, large applicability, etc.

1.3. PERFORMANCE MEASUREMENT OF SENSORS:

The characteristics that are desirable to measure the sensing performance of any sensor are as follows.

- i) **Gas Response (S):** The gas response is defined as the ratio of the change in conductance of the sensor in the presence and absence of target gas to the conductance in absence of target gas (air). The gas response (S) is given by the relation,

$$S = \frac{G_g - G_a}{G_a}$$

Where, G_g and G_a are the conductance of sensor in air and in a target gas medium, respectively. The percentage gas response is given by the relation,



$$\% S = \frac{G_g - G_a}{G_a} \times 100\%$$

ii) **Selectivity:** Selectivity is defined as, the ability of a sensor to respond to certain gas in the presence of a mixture of the number of gases. Selectivity is also termed as, specificity. A good gas sensor should be very much selective for a particular gas in presence of some other gases or a mixture of gases, even at high concentrations.

iii) **Selectivity Factor (K):** The selectivity factor of one gas over another is defined as, the ratio of the maximum response of the target gas to the maximum response of the other gas at optimum conditions, viz. temperature, gas concentration, etc.

$$K = \frac{S_{\text{target gas}}}{S_{\text{gas}}}$$

iv) **Response Time (RST):** The time taken for the sensor to attain ninety percent of the maximum increase in conductance on exposure to the target gas, is known as response time.

v) **Recovery Time (RCT):** The time taken by the sensor to get back ninety percent of the maximum conductance when the flow of gas is switched off, is known as recovery time.

vi) **Sensitivity:** The sensitivity of a sensor is defined as the change in output of the sensor per unit change in the parameter being measured.

vii) **Repeatability:** The ability of the sensor to produce a stable response upon the number of successive exposures of a target gas is called repeatability.

viii) **Long-Term Stability:** The ability of the sensor to produce a stable response over a longer time span, irrespective of the number of target gas exposures is called long-term stability.

ix) **Detection Limit:** It is the lowest concentration of the gas (ppm / ppb) that can be detected by the sensor under given conditions, particularly at a given temperature.

x) **Resolution:** The lowest value of the difference in gas concentration (ppm / ppb), that can be distinguished by the sensor is called resolution. It is measured in ppm.

xi) **Linearity:** It is the relative deviation of an experimentally determined calibration graph from an ideal straight line.

xii) **Operating Temperature:** It is usually the temperature that corresponds to the maximum response to a particular gas.

2. LITERATURE REVIEW:

Jun Zhang *et al.* [33] carried out the large-scale synthesis of highly ethanol sensitive SnO₂ nanoparticles. They used a metal alkoxide hydrolysis route for the synthesis process and obtained SnO₂ nanoparticles in the range of 5 to 15 nm sizes. SnO₂ nanoparticles were characterized by transmission electron microscope (TEM), selected area electron diffraction (SAED), and X-ray diffraction (XRD). A gas sensor was fabricated from SnO₂ nanoparticles. It was applied to test ethanol as well as some other gases. High sensitivity, quick response, and good selectivity to ethanol were observed at the operating temperature of 220°C.

Ansari S. G. *et al.* [34] worked on the characterization of SnO₂-based sensors for different gases. A simple screen-printing technique was used for obtaining the thick films of pure SnO₂. The films were characterized for sensing H₂ and CO₂ gases using a static measurement setup. At 400 ppm, samples showed the highest sensitivity for H₂ and CO₂. Peak response was observed at 210°C and 160°C for CO₂ and H₂ gas respectively. They also carried out cross-sensitivity measurements.

N. Barsan *et al.* [35] developed and studied the model for interaction between CO and SnO₂ surface by the role of water vapour. They observed the presence of water vapour in the ambient atmosphere enhances the interaction between the atmospheric O₂ and SnO₂ surface. From the electronic point of view, the density of chemisorbed oxygen is increased i.e., more electrons can pass into the conduction band. Thus, the activation energy increases. This suggests that water acts as a catalyst. The operating temperature is about 600°K.

S. Matsuura [36] studied new developments and applications of gas sensors in Japan. He predicted how gas sensors are needed in the modern era. Starting from the historical development and applications of gas sensors he studied the research and development of gas sensors in Japan. The newly developed sensors are given in the discussion in which energy-saving sensors, operated for an extended time of battery are the main considerations. He focused on the importance of CO₂ detectors, NO detectors, and optical gas sensors. Some commercial sensors were also discussed like Figaro Eng. Inc. and Cosmos Electric Co. Ltd. In the application area, domestic gas leak detectors, air purifiers, microwave ovens, odour checkers, alcohol checkers, and oxygen sensors are also discussed in brief.

Yasuhiro Shimizu *et al.* [37] prepared thermally stable Im- SnO₂ powders (mean pore diameter ≈ 4 nm) by employing SnCl₂.H₂O as an Sn source and the self-assembly of a triblock copolymer as a surfactant to sense H₂ gas. Thick film sensors were fabricated by applying the paste of phosphoric acid large mesoporous tin oxide (PA-Im-SnO₂)



powders on alumina substrates with pair of platinum electrodes. The gas response of the sensor was measured to 1000 ppm H₂ balanced with air in a flow apparatus at 250-550°C.

Azam Anaraki Firooz *et al.* [38] successfully carried out their research work on synthesis and gas sensing properties of nano and mesoporous MoO₃ doped SnO₂. By ultrasonic spray pyrolysis method, nano and mesoporous SnO₂ doped with and without 1-10 wt % MoO₃ powders were synthesized. Well-developed nano and mesoporous structures of SnO₂ by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and X-ray photoelectron spectroscopy were realized. Thick films of the synthesized material were fabricated by the screen-printing technique. The gases, viz. NO₂, C₂H₅OH, and H₂ were tested at room temperature. The conclusion of the work is, doped thick films showed a high response and selectivity to 5 ppm NO₂ gas. Also, the presence of Mo species in SnO₂ lattice can improve sensor response and selectivity of NO₂ gas.

E. A. Makeeva *et al.* [39] worked on the synthesis, microstructure, and gas-sensing properties of SnO₂/ MoO₃ nanocomposites. SnO₂/ MoO₃ nanocomposites containing up to 82 mol % MoO₃ were synthesized in a broad composition range through chemical precipitation. Microstructural analysis was carried out by X-ray diffraction. The gas sensing of lower alcohols (C_nH_{2n+1}OH, n=1-4) was carried out by in situ conductance measurement.

M. S. Wagh *et al.* [40] successfully prepared SnO₂ thick films using RuO₂ as a surfactant for the detection of LPG. A simple, low-cost screen-printing technique was used to fabricate thick films. Response of SnO₂ by surface customized using RuO₂ was found to be larger than the responses of pure and RuO₂-doped SnO₂ to 1000 ppm LPG. The operating temperature of the modified SnO₂ sensor (300°C) was lower than the unmodified SnO₂ sensor (350°C). Surface customization using ruthenium as a surfactant was observed to enhance the gas response and selectivity to LPG.

L. A. Patil *et al.* [41] innovated a hetero-contact type CuO- modified SnO₂ sensor for the detection of a ppm level H₂S gas at room temperature. Thick films of pure SnO₂ by screen printing technique. By dipping process, the films were surface modified with Cu²⁺ for different intervals of time and fired at 550°C for 24 h. The p-type CuO grains around n-type SnO₂ grains formed n-SnO₂/p-CuO heterojunctions. The outcome of this innovation is that the sensor showed a very high response to H₂S gas. The response was of the order of 10⁵ to 300 ppm and 10³ to 1 ppm H₂S gas at room temperature. The sensor was highly selective to a trace amount (1 ppm) of H₂S gas from thousand times concentrations of the other toxic gases.

John S. Suehle *et al.* [42] fabricated SnO₂ gas sensor using CMOS micro-hotplates and in-situ processing. A monolithic SnO₂ gas sensor has been produced by micromachining a custom CMOS chip fabricated through the MOSIS (Metal Oxide Semiconductor Implementation Service) foundry system and then sputter depositing a SnO₂ sensing film. A maskless micromachining technique was used in realizing a micro-hotplate array structure on the CMOS chip. The sensor exhibits a fivefold conductance change in response to H₂ and O₂ exposures in a vacuum, with a response time of less than 200 S. This is a low-cost CMOS based gas sensor system. The gas sensor responses of pure SnO₂ films to H₂ and O₂ with an operating temperature of 350°C were reported.

U. Brunsmann *et al.* [43] investigated high-resolution readout of metal oxide gas sensors using time-to-digital conversion. The method was evaluated by exposing metal oxide gas sensors to very low carbon monoxide concentrations. By combining CMOS technology with micro-electro-mechanical systems (MEMS) technology, monolithically integrated circuits with hot plates and control and measurement electronics on a single chip was presented, which detect a noise equivalent CO concentration of 30 ppb, compared with the commercially available MEMS design specified up to 50 ppb CO. the measurements were performed at 25°C gas temperature and at a gas flow rate of 200 ml/min at a total pressure of 10⁵ Pa.

Ganesh E. Patil *et al.* [44] successfully carried out the synthesis, characterization, and investigated gas sensing performance of SnO₂ thin films to H₂S gas. The SnO₂ films were synthesized by spray pyrolysis method using SnCl₂·2H₂O. The resulting SnO₂ films were characterized by X-ray diffraction and SEM. The average particle size obtained from SEM images was 56.1-68.3 nm, from XRD data, the average grain size changed from 40-56.1 nm, and from the absorption spectrum band gap values was in the range from 3.62-3.5 eV for increasing the annealing temperature from 550°C-950°C. The maximum sensitivity was obtained at an operating temperature of 100°C for the exposure of 80 ppm of H₂S gas.

Liang-Dong Feng *et al.* [45] successfully prepared strontium doped SnO₂ thick film for liquefied petroleum gas (LPG) down to several ppm levels using the screen-printing technique. Characterizations were carried out by XRD, XPS and DTA-TGA analysis. The sol-gel setup for the preparation of Sr-doped tin oxide films was based on the use of stabilized solutions containing the semiconducting material precursors. In the present work sensitivity, selectivity, sintering temperature, and static and dynamic measurements were investigated. The measurements showed that the sensor exhibited high sensitivity and selectivity at 210-300°C for domestic LPG gas.

B. Licznarski [46] developed thick-film gas microsensors based on tin oxide. The SnO₂ powders were prepared with Okazaki method, by doing some modifications in it. The powder was annealed at 600°C and then it was



mixed with an organic carrier to provide the desired rheological properties. The average size of crystallites determined by X-ray analysis was about 30 nm. The sensors were printed on 250 μm alumina substrate printed with gold electrodes to their gas sensing sides. This sensor was used to sensitize CO, C₂H₅OH, and CH₄ gases. They reported operating temperature requirements for all these gases were in the range of 400-600°C. The study reveals the fact that the SnO₂ thick film gas sensors are suitable for the detection of explosive and toxic gases and vapours. Improvement in selectivity has been achieved due to microelectronic technology.

Jianwei Gong *et al.* [47] fabricated micromachined nanocrystalline SnO₂ chemical gas sensors for an electronic nose. SnO₂ gas sensor based on the polymeric sol-gel method has been developed to detect H₂ gas. Observed very fast response time of about 2 S, quick recovery time about 10 S and reported the operating at about 100°C. Low power consumption, low thermally induced signal shift, and safe detection in certain environments are the salient features of this invention.

Sandipan Ray *et al.* [48] investigated the electrical and optical properties of sol-gel prepared Pd-doped SnO₂ thin films and studied the effect of multiple layers and their use as a room-temperature methane gas sensor. SnO₂ thin films of multiple layers were prepared from SnCl₂.2H₂O inorganic salt by sol-gel method. A comparative study of both undoped and Pd-doped SnO₂ thin films was carried out. Electrical and Hall measurements were carried out and it has been found that undoped SnO₂ showed poor response to methane gas at room temperature. However, if the number of layers increased and if SnO₂ was doped with palladium, the increase in sensitivity was observed for methane gas at room temperature.

Smitesh D. Bakrania *et al.* [49] carried out the synthesis of SnO₂ nanoparticles by a specific type of sintered-combustion method. Fabricated the thick films of synthesized nanostructured SnO₂ material by two types of film deposition methods, viz. binder-paste method and dispersion-drop method. In both methods, materials were deposited on the alumina substrate with the use of Pt electrodes. The dispersion-drop sensors yielded excellent repeatability as compared with the binder-paste sensors. Screen printing is necessary for sensors made using the binder-paste method. On the other hand, high-quality films, in terms of structure and uniformity and resulting sensor performance, can be achieved using dispersion-drop method. Sensor performance at a fixed operating temperature of 330°C was evaluated for CO gas in both methods.

Bee-Yu Wei *et al.* [50], fabricated a hybrid SWCNTs/SnO₂ gas sensor operating at room temperature to detect NO₂ gas by adding single-walled carbon nanotubes (SWCNTs). The technique involves giving out the heat treatment to the SWCNTs/SnO₂ layer, which was fabricated by spin coating using an organometallic solution dispersed with SWCNTs. The main purpose of utilizing SWCNTs was to improve the efficiency of SnO₂ gas sensor operable at room temperature to detect NO₂ gas. According to this study, the sensor exhibited much higher sensing sensitivity and recovery properties in detecting NO₂ gas at room temperature than the blank SnO₂ sensor.

Kamalpreet Khun Khun *et al.* [51], investigated room temperature ammonia gas sensors by SnO₂ thick films. The porous nano-sized powder has been synthesized by a simple non-aqueous sol-gel method using SnCl₂.2H₂O and C₂H₅OH as precursors. Characterizations, viz. XRD, FESEM, and TEM were carried out to investigate the microstructural properties of the synthesized SnO₂ material. On average 35 nm-sized particles were found by using TEM micrographs of SnO₂ powder. Thick films by screen printing were obtained on the glass substrate. The sensing response of SnO₂ sensor towards ammonia was comparatively higher than acetone and ethanol at room temperature was reported.

Paisan Setasuwon [52], prepared SnO₂ films from sol-gel by spinning on the substrate, with various dopants, viz. Al, La, Nd, Mn, Ni, Cu, Sb, In, Pd, Pt, Nb, Si and Fe at 0.5-4 mole%. The effects of these dopants on the alcohol sensitivity of SnO₂ gas sensor were investigated. Only four dopants, Al, Pt, Pd, and Si, have shown an improvement in alcohol sensitivity. 2% Al, 1% Pt, 2% Pd and 4% Si doping increased the maximum sensitivity to alcohol at 100°C. Si-doping seems to be highly effective.

Bienchetti M. F. *et al.* [53] reported a nanocrystalline pure SnO₂ thick film gas sensor for H₂ gas. The SnO₂ was synthesized by a precipitation method followed by calcination at different temperatures. The mean crystallite size measured by XRD was 5-6 nm. Thick films of this material on alumina substrate were obtained by the screen-printing technique. Measurements were carried out in synthetic and dry air + H₂ mixtures. A hydrogen sensor detecting mixtures from 5 ppm H₂ in the air was reported. The highest sensitivity was found at an operating temperature of 200°C.

H. C. Wang *et al.* [54] reported fast response thin-film SnO₂ gas sensors operating at room temperature. Thin film SnO₂ gas sensor prepared by the hydrolysis and low temperature annealing of SnCl₄. An anti-smudge (as) prepared precursor solution was dip-coated onto a glass substrate by using the automatic dip-coating machine. The gas sensing characteristics of the thin film SnO₂ sensor were investigated by recording online the electrical response of the sensor to periodical changes between dry air (dried with silica gel) and saturated vapours of alcohols (methyl, ethyl, isopropyl, and butyl alcohol) using a simple electric circuit at room temperature. A gas sensor was obtained by heating an as-coated sensor at 150°C in the air for 2 h. The sensor has an ultra-fast, reversible, and reproducible response to methyl alcohol



vapours at room temperature. It was found that the particle size of the hydrolyzed SnCl_4 affects the sensitivity of the sensor.

Nguyen Van Hieu *et al.* [55] highly sensitive NH_3 gas sensor operating at room temperature based on SnO_2 /MWCNTs composite fabricated by thin film microelectronic technique. The composite thin films were prepared by using both commercially available multi-walled carbon nanotubes (MWCNTs) and nano-sized SnO_2 dispersion. Microstructural analysis was carried out by X-ray diffraction and FE-SEM. The response of this sensor strongly depends on MWCNTs content, MWCNTs diameter, thermal treatment conditions, and film thickness. The composite thin films with MWCNTs content of 15%, MWCNTs diameter of 60-100 nm, calcination temperature of 530°C under vacuum of 10^{-2} Torr, and a film thickness of 400 nm are the optimum conditions. This sensor is found to have a very good response and recovery to NH_3 gas at room temperature.

Yong Sahn Choe *et al.* [56] achieved the patent for their work on a process for producing thin film gas sensors with dual ion beam sputtering. The present innovation provides processes for making stoichiometric, highly electrically resistant, and crystalline gas sensing layers of SnO_2 thin films for stable detection of reducing gases. It also provides processes for making stoichiometric and crystalline thin film CuO catalytic layers for the detection of dilute sulfur compound gases. The catalytic layer was made using dual ion beam sputtering, where an argon ion beam sputters targets comprising Cu or its oxides, and a pure or highly concentrated oxygen ion beam was simultaneously deposited on a substrate. The effect of the oxygen-assisted ion beam and the resulting stoichiometric, dense, and crystalline thin films are important parts of the present innovation.

P. Ivanov *et al.* [57] successfully detected ammonia and benzene via zeolite films deposited on SnO_2 /Pt- SnO_2 thick film gas sensors. Pt-doped SnO_2 covered with zeolites was used to sense CO , NH_3 , C_6H_6 , ethanol, and humidity at an operating temperature of 250 - 300°C . Sensors were fabricated by thick film technology on an alumina substrate. Screens and pastes with different properties were used for the fabrication process. Synthesis of commercially available tin oxide material was carried out by ball mill technique. To increase the selectivity of the sensor, two different zeolite films were tested onto pure and Pt-doped SnO_2 thick film layers. EDX showed that the percentage of Pt doping was nearly 1.5% in wt. SEM analysis revealed that the particle size of tin polycrystalline oxide layers was nearly 150 nm. The gas sensing results clearly showed that a suitable zeolite layer strongly increases sensor selectivity. The results of the present work indicate the potential of zeolite-based sensors to achieve a higher selectivity in gas sensing applications.

Chi-Hwan Han *et al.* [58] developed F-doped SnO_2 by surface modification with SiO_2 and enhanced H_2 -sensing properties of the sensor. F-doped SnO_2 was synthesized by the sol-gel method. Surface-modified F-doped SnO_2 with SiO_2 , as well as unmodified F-doped SnO_2 microsensors, were fabricated on the silicon-based substrate with Pt electrodes and a heater. SEM photographs predict the particle size of F-doped SnO_2 was in the range of 15-30 nm. After surface chemical treatment with sodium silicate, due to slight aggregation, particle size increased up to 45 nm. The sensor was used to test the gases like H_2 , CH_4 , C_3H_8 , and CO for the 100 to 600 ppm concentrations. A better response was observed for the F-doped SnO_2 micro sensor to H_2 gas ($S=175$), which was more than 40 times higher than that of the unmodified sensor ($S\approx 4.2$). The low energy-consuming sensor is a salient feature of the present work, as maximum hydrogen sensitivity was recorded at a heater voltage of 0.7 V operating at 320°C .

Gerald Frenzer *et al.* [59] investigated gas-sensing applications by chemically synthesizing thick, porous oxide films. The method is based on the robot (Packard Multiprobe II EX) controlled application of unstable metal oxide suspensions on an array of electrodes placed on an alumina substrate. SnO_2 , WO_3 , ZrO_2 , TiO_2 , CeO_2 , In_2O_3 , and Bi_2O_3 were used as base materials and were optimized by doping or mixed oxide formation. Thick, porous films within the range of 10-20 μm have been developed. After exposing suitable sensor libraries containing doped base oxides with the selected set of test gases (H_2 , CO , NO , NO_2) in synthetic air, the materials were evaluated for their sensor properties with the help of complex high throughput impedance spectroscopy (HT-IS). 250 - 400°C was the range of temperature required to test these gases for all the mixed oxides. The study revealed that optimization in the materials to increase performance is still required.

Ching-Liang Dai *et al.* [60] achieved a nanoparticle SnO_2 gas sensor with a circuit and microheater chip fabricated using CMOS-MEMS technique. The gas sensor is composed of a polysilicon resistor and CO gas sensing film. The polysilicon resistor is the polysilicon layer of the CMOS process. SnO_2 was prepared by the sol-gel method. The micro heater was used to provide a working temperature of the gas sensor. When adsorbs the CO gas, the gas sensor changes its resistance. An amplifier circuit is used to convert the resistance of the sensor into the voltage output. The experimental result showed that the sensitivity of the CO gas sensor is about 1 mV/ppm.

Frank Rettig *et al.* [61] presented their investigation on direct thermoelectric hydrocarbon gas sensors based on SnO_2 . The design of the direct thermoelectric gas sensing device was optimized with respect to low internal film resistances. SnO_2 material has been used in the present investigation. The film thickness of this material was about 20-



40 μm , achieved with the help of the screen-printing process. The sensor showed a very reproducible behaviour with an internal resistance of about 0.5 M Ω at 400°C. The repeatability and reproducibility of thermoelectric gas sensors with an adapted design were also compared to the conductometric gas sensors. The operating temperature for sensing hydrocarbons using this thermoelectric gas sensor was about 400°C.

Jing Wang *et al.* [62] successfully fabricated a formaldehyde (CHOH) gas sensor with a composite of nanostructured tin oxide and functionalized multi-wall carbon nanotubes (MWCNTs). The sensitivity of the composite SnO₂/MWCNTs to formaldehyde gas was much improved using this technique than the techniques which were innovated earlier. Formaldehyde is harmful to human eyes, nose, etc. Other gases, viz. acetone, and toluene were also tested by this sensor. The report reveals that formaldehyde showed higher sensitivity among all of them.

Il Jin Kim *et al.* [63] invented indium-doped nanocrystalline micro semiconductor tin oxide gas sensors to detect carbon monoxide gas. The precursors of SnO₂ nanocrystalline powders doped with In₂O₃ were prepared by the sol-precipitation method. The precursors were calcined at temperatures from 200 - 900°C in the air for 2 h to produce SnO₂ and In₂O₃/SnO₂ nanocrystalline rutile powders with different average particle sizes. A high-performance CO sensor based on a simple device utilizing SnO₂ or In₂O₃/SnO₂ nanocrystalline material with PdO_x was fabricated. The sensor showed a high response and good sensitivity to CO at an operating temperature of 200°C. The response time was 8 s and the recovery time was less than 10 s in presence of 50 ppm CO gas.

Sardar M. Ayub Durrani [64] obtained thin films of tin oxide by electron beam evaporation method. The thickness of the films was in the range of 220-400 nm. The effects of the sensor biasing voltage and film thickness on the CO sensing of SnO₂ thin films were investigated. The current-voltage resistance characteristics of the sensor in the air have shown the formation of Schottky barrier at the metal-semiconductor interface. The maximum sensitivity was obtained at an operating temperature of 350°C. It was also reported that; the sensitivity of the films strongly depends on sensor biasing voltages and thickness of the films. Maximum sensitivity was observed at lower biasing voltages and higher thicknesses of the films.

Matthias Batzill [65] carried out the review on surface science studies of SnO₂ gas sensing material. This study gives an overview of how surface science studies can contribute to a fundamental understanding of metal oxide gas sensors. The tin oxide was used as a specimen system for metal oxide gas sensor materials surface science studies of single crystal SnO₂ have been reviewed. The composition, structure, and electronic and chemical properties of (110) and (101) surfaces were discussed. Finally, it was concluded that the chemical and gas-sensing properties of the materials strongly depend on the surface composition.

Jung Y. Kim *et al.* [66] designed a smart gas sensor system for room air cleaners of automobiles using thick film metal oxide semiconductor gas sensors. Selected the semiconductor gas sensors with different ranks (sensor resistances) from Figaro Eng. Inc., Japan. Using the thick-film technique, the sensor material (metal oxide semiconductor) was printed on suitable electrodes which were printed on the alumina substrates. The main sensing material used was the like SnO₂. The sensor is used to recognize the air quality of the passenger space of automobiles.

Xing Jianping *et al.* [67] obtained the metal oxide SnO₂, ZnO thin film sensors by a powder sputtering technique. According to their study, this method is likely to become popular in the field of gas sensors. The main procedure was depositing the gas sensing layer by powder sputtered method with steady doping. ZnO thin film is another gas-sensing material that can be developed besides SnO₂. The gases under test were CO, C₂H₅OH, and gasoline with the operating temperature ranging from 260-370°C.

Akira Fujimoto *et al.* [68] proposed a method to distinguish smells using a SnO₂ gas sensor. A commercially available conventional gas sensor was used. The sample gases used were alcoholic gases. Four carboxylic gases were also used to compare with alcoholic gases. A simple electrical circuit was used to measure the response of SnO₂ gas sensor. The sensor was operated under heater modulation with triangular and rectangular pulse currents to distinguish smells. Four kinds of alcoholic gases have different delay outputs. These results showed that a smell-distinguishable system can be realized using SnO₂ gas sensor.

J. K. Srivastava *et al.* [69] studied CuO-Doped SnO₂-based thick film gas sensors for the detection of H₂S gas. This review focuses on commercial and experimental gas sensors that uses metal oxide semiconductors.

R. S. Pandav *et al.* [70] investigated nanocrystalline manganese substituted nickel ferrite thick films as ppm-level H₂S gas sensors. The nanocrystalline manganese substituted nickel ferrite dry powders were synthesized by a simple sol-gel auto-combustion technique.

Thixotropic pastes of as prepared ferrite powders were formulated, and screen printed on glass substrates to form thick films, followed by firing at 450°C. The characterizations were carried out by XRD, SEM, TEM, etc. The gas sensing behaviour of the samples was characterized by exposing the films to various inflammable and toxic. A sensor having an equivalent amount of Fe and Mn ions ($x = 1$) exhibits high selectivity and the most sensitivity towards 20 ppm of H₂S

gas at 350°C. The effect of operating temperature, gas concentration, type of gases, etc. on gas response were studied and discussed.

G. B. Shelke *et al.* [71] carried out the work on the synthesis, characterizations, and gas sensing performance of $Zr_{(0.50)}Sn_{(0.50)}O_4$ nanocomposite material. The material was prepared by using synthesized ZrO_2 and SnO_2 powders by taking their 1:1 proportion. Thick films of nanostructured pure $Zr_{(0.50)}Sn_{(0.50)}O_4$ powder were fabricated by the screen printing technique. These films were surface functionalized by SrO_2 . The surface morphology, chemical composition, and the crystal structure has been investigated by FESEM, EDAX, XRD, etc. Electrical and H_2S gas sensing performance of the thick films were also studied along with other parameters, viz. Response, recovery time, and the long-term stable nature.

G. B. Shelke *et al.* [72] studied the surface functionalized $Zr_{(0.75)}Sn_{(0.25)}O_4$ by SrO_2 thick films as H_2S gas sensors. Pure $Zr_{(0.75)}Sn_{(0.25)}O_4$ thick film was almost less sensitive to H_2S . Among various additives tested, SrO_2 in $Zr_{(0.75)}Sn_{(0.25)}O_4$ is outstanding in promoting H_2S sensing. Surface modification by activation is one of the most suitable methods of modifying the surface of thick films. The sensor has good selectivity to 5 ppm H_2S gas against LPG, NH_3 , O_2 , CO_2 , Cl_2 , H_2 , and C_2H_5OH at room temperature.

3. MATERIAL SYNTHESIS AND THICK FILM FABRICATION:

Tin is principally found in the ore cassiterite (tin oxide). It is obtained commercially by reducing the ore with coal in a furnace. SnO_2 is a wide band gap semiconducting oxide having an energy gap of 3.6 eV. It crystallizes in the rutile structure. Its unit cell contains two tin and four oxygen atoms. It has tetragonal symmetry. Each tin atom is surrounded by a distorted octahedron of six oxygen atoms and each oxygen atom has three tin nearest neighbors at the corners of an almost equilateral triangle. SnO_2 is used as a polishing powder and is sometimes known as putty powder. Tin oxide is used for ceramics and gas sensors. In gas sensors, the sensor area is heated to a constant temperature (a few hundred degrees Celsius), and in the presence of a test gas, the electrical resistivity drops. SnO_2 wires are commonly used as the detecting element in carbon monoxide detectors [15].



Fig. 1 (a): Disc type ultrasonicator

Fig. 1 (b): Microwave treatment following the centrifuge technique

Fig. 1 (a) shows disc type ultrasonicator and Fig. 1 (b) shows microwave treatment following the centrifuge technique. Nanostructured SnO_2 powder was synthesized by disc-type ultrasonicated microwave treatment followed by centrifuge technique [71,72], by hydrolysis of AR grade tin oxychloride in aqueous-alcohol solution. An initial aqueous-alcohol solution was prepared from distilled water and propylene glycol in the ratio of 1:1. This solution was then mixed with 1M aqueous solution of tin oxychloride in the ratio 1:1. The special arrangement was made to add dropwise aqueous ammonia (0.1 ml / min.) with constant stirring until the optimum pH of the solution becomes 7.9. After complete precipitation and centrifugation, the hydroxide was washed with distilled water until chloride ions were not detected by $AgNO_3$ solution. Then the precipitate was allowed for ultrasonication and then kept in a microwave oven for 10 minutes with continuous on-off cycles, periodically, followed by calcination at 500°C for 2 hrs in a muffle furnace. The dried precipitate was ground by agate pestle-mortar to ensure sufficiently fine particle size and recalcined in a muffle furnace at 500°C for 2 hrs, to eliminate the organic impurities, if present. Thus, the dry white powder of nanostructured SnO_2 has been prepared to use.

3.1 THICK FILM FABRICATION TECHNIQUE:

The use of thick film technology in the production of chemical sensors has opened up the possibility of manufacturing sensors in a cost-effective manner. Such properties of a thick film sensor are highly desirable for chemical

applications. Furthermore, thick film technology can produce sensors from nano-scaled materials. This is an advantage because a minute sample volume is required. Also, the portability of the interface instrument for the sensor can be realized.

Thick film technology based on glass and ceramic compositions is very stable in severe conditions such as high temperatures or corrosive environments. Deposition of the layers is mostly carried out by using screen printing for high-volume and low-cost production. Each layer is printed with a paste comprising a functional material and a temporary organic vehicle. After deposition, the solvent was removed by drying followed by firing, to eliminate the organic binder and sinter the materials. Glass frits are commonly used alone for over-glazes and as a permanent binder in thick film technology. Commonly ceramic substrates made of mostly alumina (Al_2O_3), silicon, glass-ceramic, and sapphire with appropriate surface finish are used. The change in resistance for thicker films is large as compared to thinner ones. Thick film technology involves screen printing methodology and thick film fabrication.

Screen-printing is a simple method that allows the production of low-cost and robust oxide thick film sensors with good reproducibility, provided that, the starting materials are well controlled. It involves printing the thixotropic paste through a mesh screen which defines the desired pattern on the substrate. The thixotropic paste of the semiconducting material contains finely divided particles of basic sensor material and additives along with organic binders, whereas the substrate is usually made up of ceramic, steel, glass, etc. The sensor material has a relatively high viscosity but when forced through the screen mesh by the squeegee blade, the paste undergoes sheer thinning which allows it to penetrate through the screen mesh which defines the desired pattern on the substrate. Upon contact with the substrate, the sensor material returns to its viscous state forming the desired pattern. The pattern thus formed using screen printing technology have a thickness that ranges from 30 to 40 μm and is thicker than those obtained by other printing techniques. Thus, printing such films using screen printing is called, 'Thick Film Technology'.

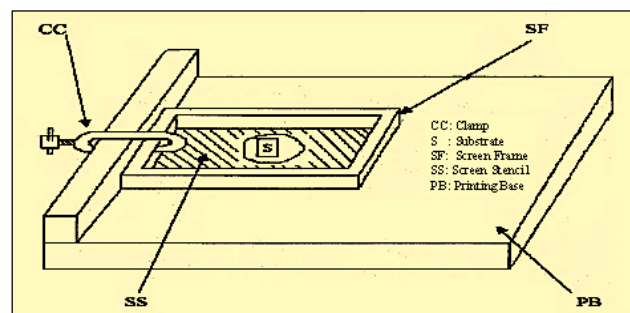


Fig. 2: Screen-printing set-up board

As shown in Fig. 2, the screen-printing setup contains a screen base, frame, stencil, squeegee, and substrate. The screen stencil is made up of a fine mesh of polyester, and nylon material which is stretched and mounted on preferably a wooden frame. The photosensitive emulsion is spread over the mesh and with the help of the photographic method, the desired pattern is obtained. The squeegee is a flexible polyurethane blade (sometimes neoprene) held in a rigid mount or handle. It is used to spread the thixotropic paste evenly over the screen so that the paste oozes down through the pores (open areas) of the screen mesh onto the substrate. A detailed procedure was adopted for making stencil, cleaning the substrates, and screen printing [71,72].

Stencil preparation and cleaning of the substrates:

- A four times larger piece of chromline film (than the required pattern to be developed) was taken.
- This piece was pasted with a solution comprising of thick film coating lotion and sensitizer mixed in the ratio 20:1.
- The chromline film was allowed to dry and remove the protective layer on the top of chromline film.
- The mask was placed with the required pattern in contact with chromline film and exposed to solar radiation for an appropriate time interval (~ 2 min.).
- The screen was washed in a water bath and the portion which was not exposed to light dissolved in water.
- The windows for sensor patterns are ready to print.
- The substrates were kept in chromic acid for 15 min.
- The substrates were washed thoroughly in water to remove the acid.
- The washed substrates were immersed in a soap solution for 5 min.
- Substrates were finally cleaned in an ultrasonic cleaner and dried under an IR lamp for 30 min.

These samples are then subjected to a temperature in the range of 70-130°C for drying under an IR lamp. Curing is done to avoid the blistering of the film. It has two steps: removal of organic binder and high-temperature curing / firing. In the first step, the residues of the organic binder (even after the drying process) are eliminated by heating at a low temperature. In the second step, the film is subjected to a furnace under controlled conditions. The chemical reactions that take place, give the required electrical and physical properties of the film.

3.2 STATIC GAS SENSING SYSTEM:

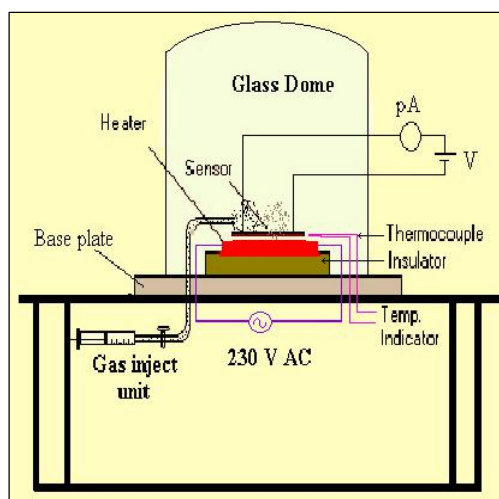


Fig. 3: Block diagram of static gas sensing system

Fig. 3 shows the block diagram of the static gas sensing system. The sensor element, heating unit, dc power supply, gas inject unit, temperature measuring unit, current meter (pico-ammeter), glass dome, and steel base plate are the major components of a static gas sensing system. The heating unit is fixed on the base plate. It provides the desired temperature to the sensor for its proper performance. The sensor sample to be tested was mounted above the heater. Cr-Al thermocouple is mounted to measure the temperature. The output of the thermocouple is connected to the temperature indicator. An inlet gas port was fitted at one of the ports of the base plate. Gas concentration inside the static system is achieved by injecting a known volume of test gas by a gas inject syringe. 0-30 V d. c. is applied to the sensor element constantly for measurement of I-V characteristics and 30 V d. c. for gas sensing and the current is measured by pico-ammeter [71,72].

4. CONCLUSIONS:

A review of the existing literature suggests that the modified and unmodified SnO₂ thick films possess several important areas of applications of modern microelectronic techniques, because of their uses in the production of advanced infrared detectors and sensors for sensing toxic gases. The parameters, on which the performance of the gas sensor depends, can be optimized for better performance of the sensor. Operating temperature, additive concentration (doping concentration in wt % and dipping time), calcination temperature, etc. are the parameters of the sensor to be optimized. The review also reveals that many researchers studied SnO₂ thick films. Also, very few attempts have been made to study the dipping time variation with the response of gas. Hence, it is the need to study the effect on structural, electrical, and gas sensing properties by changing dipping time. There is a great space to work for the development of SnO₂-based gas sensors.

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