

**DESIGN AND FABRICATION OF NO₂ GAS SENSOR USING
NANOSTRUCTURED METAL OXIDES THIN FILM WITH
POLYMERIC MATERIALS**

**THESIS SUBMITTED FOR THE AWARD OF THE DEGREE
OF**

Doctor of Philosophy

In
Applied Physics

BY

Rakesh Kumar Sonker

Enrollment No. 583/12

Under the Supervision of

Dr. Bal Chandra Yadav



**DEPARTMENT OF APPLIED PHYSICS
SCHOOL FOR PHYSICAL SCIENCES
BABASAHEB BHIMRAO AMBEDKAR UNIVERSITY, LUCKNOW,
(U.P.) INDIA – 226025**

May, 2016

ABSTRACT

Over the past two decades, a great deal of research efforts has been made towards the development of gas sensing devices for practical applications ranging from toxic/inflammable gas detection to continuous environmental monitoring. Air pollution is one of the major consequences which continuously causing increasing threats to living beings and vegetation. Air pollution may be defined as any atmospheric condition in which certain substances are present in such concentrations that may produce undesirable effects on human beings and ecosystem. These substances include gases (sulphur dioxide, nitrogen oxides, carbon monoxide, hydrocarbons, etc.), particulate matters (smoke, dust, fumes, aerosols, etc), radioactive materials and many others. Amongst various air pollutants, nitrogen oxide (NO_2) is an important pollutant. It contributes to the formation of photochemical smog, which can have significant impacts on human health.

Gas sensors play a pivotal role in domestic and industrial fields and also help to keep a cleaner environment by giving an early warning of leakage of toxic gases. Nitrogen oxides (NO_x), a mixture of nitric oxide (NO) and nitrogen dioxide (NO_2), are produced from natural sources, motor vehicles and other fuel combustion processes. Nitrogen dioxide (NO_2) is an intermediate product in the industrial synthesis of nitric acid, millions of tons which are produced every year. Nitrogen dioxide is harmful to vegetation, can fade and discolor fabrics, reduce visibility, and react with surfaces and furnishings. Vegetation exposure to high levels of nitrogen dioxide can be identified by damage to greenery, decreased growth or reduced crop yield. This reddish-brown toxic gas has a characteristic sharp and pungent odor. NO_2 is the main air pollutant in the combustion exhaust gases of automobiles, industrial, combustion of fossil fuels or domestic heater/burners. As a matter of fact, NO_2 associated with other pollutants like volatile organic compounds (VOCs) are responsible for the formation of ozone in lower atmosphere (troposphere) when interacts directly with sun rays and smog in urban areas. Ground level ozone is severe irritant, responsible for the choking, coughing and burning eyes. Also chemical reaction of NO_2 gas with water vapour in atmosphere causes acid rain. NO_2 is also a precursor to nitrates, which contribute to increase the irrespirable particle levels in the environment. Constantly increasing level of NO_2 gas is harmful to living

beings as it is irritating to the upper respiratory tract and lungs even at low concentrations. Immediately dangerous to life or health Concentrations (IDLHs) of NO₂ gas has been declared to be 20 ppm by Occupational Safety and Health Administration, USA. Thus it is very important to accurately monitor and control the increasing level of NO₂ gas using efficient sensors.

Semiconducting metal oxides are best suited for fabrication of gas sensors. However, obtaining high response for low concentration of target gas, good selectivity with fast response and recovery time and low operating temperature simultaneously are the major concern which are not yet reported in literature. The modulation of electronic properties of sensing layer with suitable catalyst/modifier or development of novel sensor design such as n-n or p-n heterojunctions are expected to improve the response characteristics to a great extent, which can be easily attained using thin film technology. Metal oxide semiconductors SnO₂, ZnO, Fe₂O₃ and PANI are extensively utilized for the detection of various gases due to their high chemical stability. Thus in the present work, an effort has been made to develop an efficient sensor based on SnO₂, ZnO, Fe₂O₃ and PANI thin film for detecting trace level of NO₂ gas with enhanced response. The SnO₂, ZnO, Fe₂O₃ and PANI thin films are prepared by sol-gel method. Structural and optical properties of SnO₂, ZnO, Fe₂O₃ and PANI thin films are found to be highly dependent on the film thickness. NO₂ gas sensing properties of SnO₂, ZnO, Fe₂O₃ and PANI doped nanocomposite thin films are studied.

In present investigations synthesis and characterization of n and p-type semiconducting metal oxides like Tin oxide (SnO₂), Zinc Oxide (ZnO), Ferric Oxide (Fe₂O₃) and Polyaniline (PANI) have been carried out. Thin films of various thickness and on various substrates have been fabricated using sol-gel method. For the purpose of gas sensing thick as well as thin films were fabricated.

Nitrogen Dioxide (NO₂) is a reddish-brown toxic gas with a sharp characteristic, biting odor and is a prominent air pollutant. Present paper reports the synthesis of α -Fe₂O₃-PANI and its application as NO₂ gas sensor operable at low temperature. For this purpose the iron oxide-polyaniline (α -Fe₂O₃-PANI) films were prepared by spin coating method on various corning glass substrates over Pt inter digital electrodes (IDEs) and characterized for

structural and morphological properties by means of X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM). The sensing mechanism pertains to a change in the depletion region of the p-n junction formed between PANI and α -Fe₂O₃ as a result of electronic charge transfer between the gas molecules and the sensor. The sensing mechanism of α -Fe₂O₃ materials to NO₂ was presumed to be the synergism of α -Fe₂O₃ with NO₂ gas molecules. The prepared nanostructured α -Fe₂O₃-PANI film showed a high sensing response $\sim 2.29 \times 10^2$ towards 20 ppm of NO₂ gas. Besides giving the higher sensing response towards NO₂ gas, α -Fe₂O₃-PANI sensor structure was found to be highly selective and exhibited the poor gas sensing response towards other interfering gases including 2000 ppm of Acetone, IPA, NH₃, LPG and CO₂ gases ranged from 0.98 to 1.29.

In the present chapter zinc oxide has been prepared by using two different methods and their characterizations were carried out using SEM, AFM, XRD, UV and FTIR. Sensing performances of each samples were investigated and found that hexagonal ZnO nanocrystals were more sensitive responsive than ZnO nanopetal structures.

In the present work, the comparative investigations on NO₂ gas sensing properties of the hybrid nanocomposite thin films of Polyaniline (PANI), ZnO and PANI-ZnO towards NO₂ gas at room temperature have been reported. Effect of concentrations of PANI in the composite thin films on the NO₂ gas sensing has been investigated. Structural and surface morphological characterizations have been carried out by using X-ray diffraction (XRD) and scanning electron microscope (SEM) respectively. The presence of 5% PANI in composite film was found to give maximum sensing response of $\sim 6.11 \times 10^2$ towards to 20 ppm NO₂ gas having fast response and recovery time of about 2.16 min and 3.5 min respectively.

The highly sensitive low temperature operated nitrogen dioxide (NO₂) gas sensor has been fabricated using SnO₂ thin film doped with different catalysts (Pt, Ag and CuO) using chemical route. Amongst all the prepared sensor structures, Pt-doped SnO₂ thin film based sensor (SnO₂-Pt) was found to give maximum sensing response of about 1.83×10^2 towards low concentration of (20 ppm) of NO₂ gas at a lower operating temperature of 90°C with very fast response (~ 6 sec) and recovery (~ 13 sec) time. The structural, microstructural and

optical properties of the prepared sensor have been studied using X-ray diffraction (XRD), Scanning electron microscope (SEM) and UV-Visible spectroscopy and the results have also been correlated with the observed gas sensing properties.

A novel sensor structure has been fabricated by incorporating polyaniline (PANI) into SnO₂ sensing film using chemical route and exploited for room temperature detection of NO₂ gas. Amongst different concentration of PANI incorporated into SnO₂ thin film, 1% PANI was found to give maximum sensing response ($\sim 2.58 \times 10^2$) at room temperature towards 20 ppm of NO₂ gas with modulated response and recovery time of about 5.8 min and 4.55 min respectively. The structural, morphological and optical properties of the prepared sensor structures have been revealed by X-ray diffraction (XRD), Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), Fourier transform infrared spectroscopy (FTIR) and UV-Visible spectroscopy.

Nitrogen dioxide (NO₂) is a typical automotive air pollutant that causes many environmental and health problems. Detection of low concentrations of NO₂ is becoming very important now a day and various approaches have been used for the same. SnO₂ and ZnO are the two widely explored semiconductor materials for the detection of a number of toxic and harmful gases. Thus, in the present work an effort has been made to synthesize nanocrystalline composite thin films of Zinc oxide and Tin oxide (ZSO) using chemical route for the efficient trace level detection of NO₂ gas at lower operating temperature. Thin film of SnO₂-ZnO (ZSO) composite was prepared onto the surface of Pt IDEs/corning glass and has been exploited for studying the gas sensing response characteristics towards NO₂ gas. The prepared ZSO sensor structure showed a high sensing response of about 3×10^2 towards 20 ppm of NO₂ gas at operable room temperature with an average response and recovery time of 10.23 and 11.75 min. respectively. The structural, optical and surface morphology properties of the ZSO composite thin film have been studied by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), UV-Visible spectroscopy, Scanning electron microscope (SEM) and have also been correlated with the observed enhancement in gas sensing properties of prepared sensor structure.

We report the synthesis of SnO₂-polyaniline (PANI)-ZnO composite thin film for NO₂ sensor was fabricated from SnO₂-ZnO porous nanostructure and PANI by a predictable spin coating method. The SnO₂-ZnO composite porous nanostructure was prepared by a sol-gel method. It was found that the composite sensor has high selectivity and response to low concentration NO₂ gas. Furthermore, the composite sensor also showed high stability to NO₂ over a long period at operable at room temperature (30 °C). As experiment results show that both the pore structures of SnO₂ and porous nanostructure of ZnO had effects on the sensor response of SnO₂-PANI-ZnO (SPZ) nanocomposites sensor response calculate 995 at 20 ppm NO₂ operable at room temperature. The response and recovery times of SnO₂-PANI-ZnO composite sensor (SPZ) were calculated as about 3.8 and 2.2 min to 20 ppm NO₂ at room temperature, respectively.