GAS SENSING PROPERTIES OF ALKALI AND RARE EARTH ELEMENTS DOPED TIN DIOXIDE

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SYNOPSIS

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Semiconducting Metal Oxide (SMO) based sensors are extensively used for toxic and combustible gas detection at low concentration of test gases due to their several advantages such as less production cost, high response and long-term stability. The various physico-chemical properties of sensor materials in the view of sensing behavior and size effects of semiconducting metal oxides have been investigated for their possible sensing applications. For chemo resistive types of sensors the sensing mechanism is governed by the electrical resistance change of SMO materials as a result of adsorption/desorption process of gaseous species on the sensor surfaces. The charge transfer process induced by surface reactions governs the resistance of the SMO materials. When the SMO based sensors are exposed to ambient atmosphere, atmospheric oxygen (O\textsubscript{2}) gets ionosorbed in the form of (O\textsuperscript{-}, O\textsuperscript{2-} or O\textsubscript{2-}) species on the sensor surface, which leads to a change in resistance due to a loss or gain of conduction band electrons as a result of adsorbed oxygen species reacting with the test gas. In case of n-type metal oxide semiconductor, the resistance increases in the presence of oxidizing gases (e.g. as nitric oxide (NO), nitrogen dioxide(NO\textsubscript{2}), ozone(O\textsubscript{3})), whereas in presence of reducing gases (e.g carbon monoxide(CO), methane(CH\textsubscript{4})) the resistance decreases. On the other hand in case of p-type metal oxides semiconductors the resistance decreases in the presence of reducing gas, whereas it increases in case of oxidizing gases. The amount of change in electrical resistance is a measure of concentration of the test gases.

The sensor performance is strongly dependent on the sensing material properties. Several semiconducting metal oxides such as zinc oxide (ZnO), tin oxide (SnO\textsubscript{2}), tungsten oxide (WO\textsubscript{3}), maghemite (\gamma-Fe\textsubscript{2}O\textsubscript{3}) and titanium dioxide (TiO\textsubscript{2}) have been extensively investigated in the field of gas sensor. Amongst various semiconducting metal oxides tin oxide (SnO\textsubscript{2}) is an extensively used for the fabrication of solid state gas sensors in various forms as pellets, thick films, thin films and heterojunction. Pristine and doped SnO\textsubscript{2} thick film sensors were studied by several researchers for toxic and combustible gas sensing applications. However, it has several critical limitations to be used as the commercial sensors such as higher operating temperatures and poor selectivity. There are several reports for improving the sensor performance in the view of operating temperature and selectivity such as addition of metal/metal oxides. The addition of noble metal catalysts (Pt, Pd etc.) on the
sensor surface improves the sensitivity of the sensor. The catalyst increase the active surface site on the sensor surface for the adsorption of test gases as well as lowers the activation energy required for the sensing reactions to take place and in turns improves its sensing performance.

In the present study of pristine, we have undertaken pristine, alkali and rare earth element doped tin oxide nanocrystalline materials with the objective of investigating their gas sensing properties towards various reducing gases such as acetone, ethanol, ammonia and LPG. Here, we are presenting the synthesis and various physico-chemical characterizations of nano-crystalline pristine and doped SnO$_2$ materials by several techniques such as Thermo Gravimetric/Differential Thermal Analysis (TG/DTA), X-ray Diffraction (XRD), Brunauer–Emmet–Teller (BET), X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), Field emission Gun scanning electron microscopy (FEG-SEM), Energy Dispersive Spectroscopy (EDS), Transmission Electron Microscopy (TEM), High Resolution Transmission Electron Microscopy (HR-TEM), Selected Area Electron Diffraction (SAED), Ultra Violet-Visible-Near Infra-Red (UV-Vis-NIR) Spectroscopy, Fourier Transform Infrared (FTIR) Spectroscopy, Raman Spectroscopy etc. The nano-crystalline materials are synthesized by using facile co-precipitation method. Alkali and rare earth elements are chosen for doping pristine SnO$_2$; further ternary systems are synthesized by loading palladium and Ruthenium as noble metal additive to investigate their influence on physico-chemical and gas sensing properties of pristine SnO$_2$. The detailed studies of these materials have been discussed in various chapters as described below.

**Objectives of the Thesis:**

The foremost objectives of the proposed research work are to explore the gas sensing properties of pristine and alkali and rare earth metal doped SnO$_2$ nanoparticles. To explore the gas sensing properties following aspects were considered in the present work,

1. The synthesis of nanostructured pristine and doped SnO$_2$ nanoparticles by facile co-precipitation route.
2. Fabrication of thick film sensors using screen printing technique.
3. Characterization techniques employed to study the structural, morphological, compositional properties of the nanoparticles.
4. The gas sensing properties of the nanocrystalline thick film sensors towards the various reducing gases.
5. The effects of rare earth and alkali element doping and noble metal loading on gas sensing properties of SnO$_2$ gas sensor.
6. Investigation of gas sensing properties like response, selectivity, optimum temperature, response, recovery time and stability to develop a suitable sensor.

The thesis comprises of in all nine chapters including of summary and conclusions.

Chapter-1 Introduction and Theoretical background.

Chapter-1 gives the general introduction of semiconducting metal oxides gas sensors, historical background and the relevant literature survey of the various gas sensing materials used according to the various parameters such as materials, synthesis methods used in general and alkali and rare earth doped SnO₂ in particular. This chapter also gives the Outline and objectives of present study.

Chapter-2 Experimental and Characterization Techniques

Chapter-2 is devoted to the details (Introduction, basic principles of working, instrumentations, sample preparations, applications and specifications) of techniques used for synthesis of nano-crystalline pristine and doped tin oxide, screen printing method for the deposition of the thick film sensors and various physico-chemical characterization techniques such as TGA/DTA, XRD, SEM, FESEM, EDAX, TEM, HRTEM, SAED, BET, XPS, UV, FTIR, Raman etc.

Chapter-3 Synthesis, characterization and enhanced ethanol sensing performance of Sr-doped SnO₂ nanoparticles

Chapter-3 describes the synthesis of pristine and (2, 4 and 6 mol%) Sr doped SnO₂ nanocrystalline material and their characterizations using TG-DTA, XRD, TEM (HRTEM), SAED, FEG-SEM, SEM-EDAX, XPS UV-vis and FTIR techniques. Pristine and (2, 4 and 6 mol%) Sr doped SnO₂ nanocrystalline thick film sensor are designed by using facile co-precipitation method followed by conventional screen printing technique. It is confirmed that the Sr doping significantly affects morphology, particle size, surface area and porosity of pristine SnO₂. Thick film gas sensors fabricated are further studied for their gas sensing properties using dynamic gas sensing unit towards acetone, ethanol, ammonia and LPG. A systematic comparative study on gas sensing properties of the sensors was carried out. Interestingly, It is found that Sr doping in pristine SnO₂ nanoparticles exhibits a critical role in improving ethanol sensing performances of pristine SnO₂, including lower working temperature, higher gas response, quick response–recovery time and better long term stability.
It is found that the sensor Sr$_2$(4.0 mol% Sr doped SnO$_2$) exhibits highest response of 65% towards 100 ppm of ethanol at 300 °C with a shorter response (2 s)/recovery time (7 s) and a better selectivity as compared to that of S$_0$ (pristine SnO$_2$). These results indicate that the sensor Sr$_2$(4.0 mol% Sr doped SnO$_2$) has a potential application for fabricating high performance ethanol vapor sensor.

**Chapter-4 Synthesis, characterization and enhanced ethanol sensing performance of Pd: Sr-SnO$_2$ nanoparticles**

Chapter-4 deals with the effect of palladium loaded on the gas response of 4 mol% Sr doped SnO$_2$ thick film. The (0.5, 1.5, 2.5 and 3 wt%) Pd loaded Sr doped SnO$_2$ nanocrystalline materials were synthesized by using facile co-precipitation method. The effect of Pd loading on the structural and morphological properties of Sr doped SnO$_2$ was examined by X-ray diffraction, FEG-SEM, EDAX, HR-TEM, SAED techniques. The ethanol sensors were deposited via conventional screen printing technique. Further, the gas sensing properties were carried out, the Pd-loading in 4 mol% Sr doped SnO$_2$ decreases the particle size considerably as well as increases the porous morphology of Sr doped SnO$_2$. It is found that the gas response performance of 4 mol% Sr doped SnO$_2$ is found to be affected by Pd-loading. The sensor Sr$_4$Pd$_{2.5}$ (2.5 wt% Pd loaded 4 mol% Sr doped SnO$_2$) shows higher response (83%) towards lower ethanol concentration (100 ppm) at lower operating temperature (275°C) with a rapid response/recovery and an excellent selectivity, stability and reproducibility than (Sr$_4$Pd$_{0.5}$, Sr$_4$Pd$_{1.5}$ and Sr$_4$Pd$_3$) sensors. These results reveal that 2.5 wt% Pd loaded 4 mol% Sr doped SnO$_2$ (Sr$_4$Pd$_{2.5}$) has remarkable response performance towards ethanol proving to be a promising material for ethanol detection in practical applications.

**Chapter-5 Synthesis, characterization and enhanced ethanol sensing performance of Ru: Sr-SnO$_2$ nanoparticles**

Chapter-5 describes the effect of ruthenium loading on the gas response of 4 mol% Sr doped SnO$_2$ thick film. The (2, 4, 6 and 8 wt%) Ru loaded Sr doped SnO$_2$ nano-crystalline material was synthesized by using facile co-precipitation method. The effect of Ru loading on the structural and morphological properties of Sr doped SnO$_2$ was examined by X-ray diffraction, FEG-SEM, EDAX, HR-TEM, SAED, BET, Raman spectroscopic techniques. The sensors were deposited via conventional screen printing technique. Further, the gas sensing properties were carried out. The Ru-loading in 4 mol% Sr doped SnO$_2$ decreases the particle size considerably as well as increases the porous morphology of Sr doped SnO$_2$. It is found that the gas sensing performance of thick film sensors are influenced by Ru-loading in Sr:SnO$_2$. The Sr$_4$Ru$_6$ (i.e. 6 wt% Ru: Sr-SnO$_2$) sensor exhibits superior selective response of
93% towards ethanol (100 ppm at 300 °C) as compared with Sr₄Ru₂, Sr₄Ru₄ and Sr₄Ru₈ sensors. The response and recovery times are observed to be less than 1 s and 3 s respectively which is quiet fast as compared with the other Ru:Sn sensors. The results proves that sensor Sr₄Ru₆ (i.e. 6 wt% Ru:Sn) can be used as a potential candidate for designing an effective ethanol sensor.

Chapter-6 Synthesis and Characterization of pristine and Sm₂O₃ doped SnO₂ Gas Sensing Nanomaterial.

Chapter-6 describes the synthesis of pristine and (2, 4, 6 and 8 mol%) Sm₂O₃ doped SnO₂ nanocrystalline material by simple co-precipitation route. The samples were calcined (450 °C) and sintered (700 °C). Further the calcinated samples were characterized by TG-DTA and sintered samples were characterized by XRD, FEG-SEM, Energy dispersive analysis by X-rays EDAX, TEM, HRTEM, BET, XPS and UV-Vis techniques. The structural and morphological properties confirmed that the Sm₂O₃ doping considerably increases the porous morphology and decreases the particle size of pristine SnO₂. Thick film sensors were deposited by screen printing technique. The gas sensing properties of the sensors were systematically carried out towards acetone, ethanol, ammonia and LPG. Interestingly, doping of Sm₂O₃ in pristine SnO₂ shows a critical role in refining acetone sensing performance such as lowering operating temperature, enhancing gas response, faster response and recovery time and improved stability.

The gas response performance of sensor is found to be affected by Sm₂O₃ doping. The S₃ (6.0 mol% Sm₂O₃ doped SnO₂) sensor shows maximum acetone response of 82% for 100 ppm concentration at 250 °C with a fast response/recovery time, better selectivity and stable response than S₀ (pristine SnO₂) sensor. Thus, S₃ (6.0 mol% Sm₂O₃ doped SnO₂) can be used as a potential candidate for fabricating high performance acetone thick film sensor.

Chapter-7 Synthesis, characterization and enhanced acetone sensing performance of Pd: Sm-SnO₂ nanoparticles

Chapter-7 describes the synthesis of Pd loaded Sm doped SnO₂ nanomaterials using facile co-precipitation method. The effect of Pd loading on the structural and morphological properties of Sm doped SnO₂ was examined by XRD, FEG-SEM, EDAX, HR-TEM, SAED techniques. The acetone sensors were deposited via conventional screen printing technique and further, the gas sensing properties were carried out. It is revealed that the Pd-loading in 6 mol% Sm doped SnO₂ decreases the particle size considerably as well as increases the porous morphology of Sm doped SnO₂. The gas sensing performance of 6 mol% Sm doped SnO₂ is found to be affected by Pd-loading. The sensor P₃ (2 wt% Pd loaded 6 mol% Sm doped
SnO$_2$ shows higher response (81%) towards lower acetone concentration (25 ppm) at lower operating temperature (200°C) with a rapid response/recovery and an excellent selectivity, stability and reproducibility than (P$_1$, P$_2$ and P$_4$) sensors. These results indicate that 2wt% Pd loaded 6 mol% Sm doped SnO$_2$ (P$_3$) can be used as a potential candidature for acetone sensor.

**Chapter-8 Structural and optical properties of Dy$^{3+}$ doped SnO$_2$ nanoparticles and their ethanol sensing behavior.**

**Chapter-8** describes the synthesis of pristine and Dysprosium (Dy$^{3+}$) doped SnO$_2$ nanocrystalline powder by facile co-precipitation method. The thick films of these samples were deposited by using screen printing technique. The resultant thick films were sintered at 650 °C for 2h. The structural, morphological and compositional properties were studied by using XRD, TEM, SAED, FE-SEM, EDAX, UV-Vis, FTIR and Raman spectroscopic techniques. The XRD, TEM and SAED analyses confirm the tetragonal rutile structure of SnO$_2$. FE-SEM images show the nanocrystalline porous morphology of the samples. EDAX confirms the elemental composition of the samples as per the initial precursors taken. The gas sensing characteristics have been investigated for various gases such as acetone (C$_3$H$_6$O), ethanol (C$_2$H$_5$OH), Liquefied Petroleum Gas (LPG) and Ammonia (NH$_3$) as a function of temperature and concentration. The Dy$^{3+}$ doping in SnO$_2$ sensors have exhibited significant enhancement in sensor response towards ethanol accompanied with the reduction in optimum operating temperature.

The gas response performance is found to be affected by Dy doping. The sensor D3 (3.0 mol% Dy doped SnO$_2$) exhibits highest response of 78% towards 100 ppm of ethanol at 300 °C with a shorter response (13 s)/recovery time (22 s) and a better selectivity as compared to D1, D2 and D4 sensor. These results indicate that the sensor D3 (3.0 mol% Dy doped SnO$_2$) has a potential application for fabricating high performance ethanol vapor sensor.

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