

Orientation and Purpose of the problem

Currently, the environmental pollution has become a global issue. The gases from auto and industrial exhausts are contaminating the atmosphere and monitoring the air quality, particularly, in urban areas has become precedence due to the large amounts of pollutants liberated in the atmosphere, which have a harmful effect on the human and animal's health and also on the vegetation. The need to detect, measure and control a variety of harmful and toxic gases/vapors like NH_3 , CO , H_2S , SO_x , NO_x , alcohol and hydrocarbons has led to the research and development of a large variety of sensors using archetypal materials and techniques.

The hydrogen sulfide, sometimes termed as hydrosulfuric acid, stink gas, or sewer gas, is a colorless, highly toxic, flammable gas. This reducing gas is produced naturally and as a result of human activity. Natural sources comprise about 90% of the total hydrogen sulfide in the atmosphere. In nature, it is found in volcanoes or cold/hot springs. In the absence of oxygen, H_2S often results from the bacterial breakdown of organic matter, such as in swamps and sewers (anaerobic digestion). It is released largely as a gas and is formed in coal, petroleum refineries or natural gas manufacturing, gasoline, natural gases and sewage. Other anthropogenic sources of hydrogen sulfide include coke ovens, paper mills, and tanneries. H_2S is a intoxicating chemical asphyxiant that combines with haemoglobin in red blood cells and with intracellular cytochromes and rapidly obstructs oxygen from access to cellular metabolism just like gases such as carbon monoxide and hydrogen cyanide. In fact H_2S is conceivably as toxic as Hydrogen Cyanide HCN . Although, this foul-smelling gas can be detected in the air by smell at concentrations as low as 0.5 parts per billion; concentrations at 100 parts per million (ppm) or above in air cannot be detected by smell. At such higher concentrations the gas paralyses the ability of the human olfactory nerve to detect the gas. This makes the higher concentrations of H_2S even more dangerous to human exposure, especially in confined spaces. Indeed, the human exposures to H_2S gas at the level higher than 250ppm can result in neurobehavioral toxicity and may even cause death. Consequently, smell cannot be relied upon to provide warnings of this

treacherous gas. In reference to the safety standards ascertained by American Conference of Government Industrial Hygienists, the threshold limit value (TLV) defined for H_2S is 10 ppm. Meanwhile, the type of oil or natural gas is comparative with the concentration of H_2S . The oil or natural gases mines can be found depending on the H_2S concentration. So, the detection and monitoring of H_2S are of high importance for both resource exploitation and human health.

As a result, monitor and control over traces of such noxious gas has turn out to be very imperative. Hence, it is a constant call for to have H_2S sensors with high sensitivity, selectivity, reproducibility, low cost and ease of operation. Recent years have witnessed great interests to improve the H_2S sensing characteristics with semiconducting oxides such as SnO_2 , ZnO , WO_3 and In_2O_3 etc. However, still there is a need to improve the H_2S sensing properties toward low concentrations especially at lower temperatures through structural and/or chemical modification of metal oxides. For this intent, metal oxide nanocrystals in thin film form attract an increasing interest due to the larger surface-to-volume ratio as well as crystal (grain) size effect.

The wurtzite structured zinc oxide (ZnO), an n-type metal oxide semiconductor sensing material with a wide band gap ($E_g = 3.37 \text{ eV}$ at 300 K), has been under extensive research owing to its low cost, bio-safe characteristics, high chemical/thermal stability, good flexibility in fabrication and high sensitivity to toxic and combustible gases. The ZnO shows a high chemical stability in reducing environments, as is the case of hydrogen plasma. It has high mobility of conduction electrons ($200 \text{ cm}^2/\text{V-s}$, which is higher than SnO_2 and In_2O_3) with a wide range electrical resistivity which can extend from 10^{-4} to $10^{12} \Omega\text{-cm}$ according to the deposition conditions. Further, the large conductivity changes in response to the adsorbed gases make it an ideal sensor candidate. Indeed, as a gas sensing materials, ZnO is one of the earliest discovered and the most widely applied oxide gas sensing material. ZnO gas sensor elements have been fabricated in various forms, such as single crystals, wintered pellets, thick films, thin films and hetero junctions. However, the nanocrystalline ZnO thin films are the most promising metal oxide for solid state chemical sensors, due to

small dimensions, low cost, low power consumption and high compatibility with microelectronic processing.

Therefore, it is not astonishing that ZnO thin films have been under intensive investigation for gas sensing application and several techniques have been employed for synthesis of such a significant material. Physical methods are comparatively expensive than chemical methods due to some disadvantages viz. small area deposition, high working cost, necessity of sophisticated instruments, and relentless hygiene of system. The chemical methods are economical processes and the films are found to be of as good as quality to those deposited by sophisticated and expensive physical methods. One of the useful chemical methods of formation of metal oxides is a chemical spray pyrolysis technique. Besides its cost effectiveness, this technique offers easy control over deposition parameters as well as reproducibility. Especially, doping in spray pyrolysis technique is simple than the other methods. However, the high substrate temperature ($\sim 673\text{K}$) required for the formation of the metal oxide films such as ZnO. Such high substrate temperature limits the use of variety of substrates in device fabrication. Moreover, the ZnO films obtained at such a high growth temperatures are highly compact and the crystallite /grain sizes are mostly larger than the 'Debye length' for the undoped ZnO. i. e. $\sim 30\text{nm}$. As a result, only the atoms in the space-charge region can participate in surface reactions during the gas exposure; whereas the atoms in the core of ZnO crystals are not involved in the sensing response. However, very few efforts have been devoted to modify the conventional spray system.

Plan of work

The objective of this work is to modify the conventional spray pyrolysis system, by retaining all its advantages, to deposit the metal oxide semiconductor thin films such as ZnO at much lower temperature, probably half of that used in case of conventional spray technique. In the present setup, it is planned to complete the reaction in the reaction chamber and the final product will be deposited on the substrates, which are kept at a low temperature. Thus, the lower substrate temperature used herein is supposed to change the micro structural properties of the deposits, especially the morphology, porosity and the

crystallite/grain size. Decreasing the size of a ZnO crystallite will likely thus result in a much larger portion of the ZnO which interacts with an analyte gas, which should increase the sensitivity of the sensor.

At the outset, subsequent to the optimization of the process parameters viz. the substrate temperature, reaction (core) temperature, solution quantity, air pressure, nozzle to substrate separation etc., the nanocrystalline zinc oxide thin films will be deposited onto glass substrates process at various substrate temperatures, core temperatures, film thickness, etc. to study their effect on the structural, morphological, optical, electrical and gas sensing properties of the film. The X-ray diffraction (XRD) technique will be used for the structure identification and crystallite size determination. The surface morphology of the films will be studied using field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM). The optical properties will be studied in the visible range of spectrum using spectrophotometer. The electrical properties will be studied by dc two-point probe method. Further, the doping effect of copper (Cu) and tin (Sn) on the ZnO thin film properties will be evaluated.

The sensing performance of undoped and doped ZnO thin films at different concentrations of H₂S will be studied at different operating temperature by measuring the change in resistance of the sheet resistance. Lastly, the performance of H₂S sensors will be evaluated in terms of their sensitivity, and stability. The H₂S sensor performance of optimized ZnO sample will be demonstrated for the real time detection.