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A STUDY OF GAS SENSING DETECTION FOR THE SYNTHESIS OF ZnO NANORODS

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ABSTRACT
The aim of this study is to nanostructured ZnO powder and thin films by chemical routes, hydrothermal method and spray pyrolysis technique. The prepared powder and thin films were characterized by using different techniques such as XRD, SEM, TEM and UV-visible spectroscopy to correlate with their gas sensing performance towards hazardous and toxic conventional gases such as H2S, NH3, LPG, CO, CO2, O2, H2, ethanol and Cl2. In this work we tried to prepare Nano crystalline materials and thin films by using chemical routes, hydrothermal method and SPT. These films and materials were analyzed and tested to various gases. The unique data and results have been published in referred journals. But to achieve monodispersed Nano crystalline materials and thin films remains a challenge for us. There are reports to prepare monodispersed nanocrystalline materials and thin films by using ultrasonic atomization technique and ultrasonic spray pyrolysis (USP) technique. Moreover, nowadays due to increased threat of international terrorism and their use of toxic chemical attack, societies need to pay more attention on protecting their citizens from attack of toxic chemicals, either by accident or terrorist act. Therefore fast detection and identification of toxic chemicals is crucial for efficient protection of citizens. Therefore, it is our future aim to produce nanocrystalline materials/ films by using ultrasonic atomization technique and USP; and plan to test the chemical warfare agents.

KEYWORDS:- Gas Sensing Detection, ZnO Nanorods, monodispersed, Nano crystalline materials

INTRODUCTION
An immense research is going on to detect and control various harmful and toxic gases/vapors such as H2S, CO, SO2, NO2, alcohol and hydrocarbons. Semiconductors such as ZnO, In2O3, and SnO2 are immensely used as a gas sensors based on change in their electrical conductivity on exposure to the test gases. Appropriate donors can create the electronic defects that enhance the influence of oxygen partial pressure on the conductivity of semiconductor. Various dopants such as Sn, Al, In, Cu, Fe, Ru, Ga have been added in ZnO to explore their applications as gas sensors, piezoelectric devices and in the optoelectrical appliances. Detection of combustible and/or toxic gases is one of the rapidly developing fields of sensor technology. The hydrogen sulfide is a toxic and malodorous gas often produced in coal, coal oil or natural gas manufacturing, gasoline, natural gases and sewage. Human exposures to H2S gas at the level higher than 250 ppm are likely to result in neurobehavioral toxicity and may even cause death. Hence, monitor and control over traces of such hazardous gas

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has become extremely important. Therefore, it is an ongoing need to have H2S sensors with high sensitivity, selectivity, reproducibility, low cost and ease of operation. Different semiconductor oxide based materials such as SnO2, ZnO, In2O3, ZrO2, CeO2, WO3, Fe2O3, have been reported as a H2S sensor in the literature. In general, response towards H2S is reported at the higher temperatures; however, there are a few references wherein response at room temperature is also reported. Zinc oxide, the n-type semiconductor having Wurtzite structure with direct energy wide-band gaps of about ~3.4 eV holds an important status in the field of gas sensor. It is studied in the form of nanostructured, bulk, as well as thin films, of which their thin film form have found wide applications such as transparent electrode for photovoltaic devices, acoustic wave device and solar cells, etc. Various techniques such as spray pyrolysis, sputtering, vacuum arc deposition, sol–gel process, pulse laser deposition, plasma enhanced chemical vapor deposition, spin coating and dip coating have been implemented for the deposition of undoped and doped ZnO thin films. Among these, spray pyrolysis is a simple and inexpensive technique having ease to incorporate various materials, reproducibility, high growth rate and mass production capability for uniform coatings. Many studies have been done over about three decades on chemical spray pyrolysis (SP) processing and preparation of thin films, since the pioneering work by Chamberlin and Skarman in 1966 on cadmium sulphide (CdS) films for solar cells. Thereafter, due to the simplicity of the apparatus and good productivity of this technique on a large scale it offered a most attractive way for the formation of thin films of noble metals, metal oxides, spinel oxides, chalcogenides and superconducting compounds. Despite its simplicity, SP have a number of advantages. (a) It offers an extremely easy way to dope films with virtually any element in any proportion by merely adding it in some form to the spray solution. (b) Unlike closed vapor deposition methods, SP does not require high quality targets and/or substrates nor does it require vacuum at any stage, which is a great advantage if the technique is to be scaled up for industrial applications. (c) The deposition rate and the thickness of the films can be easily controlled over a wide range by changing the spray parameters, thus eliminating the major drawbacks of chemical methods such as sol-gel which produces films of limited thickness. (d) Operating at moderate temperatures (100- 500oC), SP can produce films on less robust materials. (e) Unlike high-power methods such as radio frequency magnetron sputtering (RFMS), it does not because of local over-heating that can be detrimental for materials to be deposited. There are virtually no restrictions on substrate material, dimension or its surface profile. (f) By changing composition of the spray solution during the spray process, it can be used to make layered films and films having composition gradients throughout the thickness. (g) It is believed that reliable fundamental kinetic data are more likely to be obtained on particularly well characterized film surfaces, provided the films are quiet compact, uniform and that no side effects from the substrate occur. SP offers such an opportunity. In the past

decade, one-dimensional (1D) nanostructures, such as carbon nanotube, ZnO, In2O3, and SnO2 have attracted much interest because of their potential applications in many fields and theoretical importance. Until now, the main efforts have been made on the preparation of 1D nanostructure materials. Recently, gas sensors based on single carbon nanotube, SnO2 nanowire and In2O3 nanowire were reported. These sensors have better sensing performance, but it is difficult to obtain single nanowire and to fabricate this kind of device in large quantities. Thick film sensors based on ZnO nanowires were reported to have good gas-sensing properties by Wan et al, but it is not easy to fabricate ZnO nanowires by an evaporation method. As per knowledge, there are very few reports about the H2S sensing properties of ZnO nanorods up to now. In this work, we fabricated thin film sensors based on ZnO nanorods, which were prepared by a spray pyrolysis method and investigated their gas-sensing properties. The thin film sensors showed a large response to H2S when operated at different temperatures.

Preparation of spraying solutions

All the chemicals used in the work were of analytical grade. The chemicals such as zinc acetate dihydrate, methanol (A.R.) were used without further purification. Zinc acetate dihydrate was dissolved in the mixture of methanol (10 ml) and double distilled water (5 ml) to obtain 0.1 M zinc acetate solution. Such solution was used as precursor solution for synthesis of ZnO thin films.

Substrate Cleaning

The substrate cleaning is very important in the deposition of thin films. Commercially available alumina slides with a size of 25mm×25mm×1mm were washed using soap solution and subsequently kept in hot chromic acid and then cleaned with deionized water followed by rinsing in acetone. Finally, the substrates were ultrasonically cleaned with deionized water for 20 min and wiped with acetone and stored in a hot oven.

Details of spray pyrolysis system

The schematic experimental set up of the spray pyrolysis system which is built in the laboratory as shown in Fig. 1 (a, b). It consists of spray gun with nozzle, substrate heater, automatic temperature control unit, air compressor, pressure regulator, thermocouple, stepper motor with controller and power supply. The heater is a stainless steel block furnace electrically controlled by an automatic temperature controller unit to attain the required substrate temperature to an accuracy of + 2oC. The resulting temperature on the surface of the substrate is measured with a chromelalumel thermocouple. Hazardous fumes evolved during the thermal decomposition of the precursor are given out an exhaust system attached to the spray pyrolysis unit. The spray nozzle is made up of borosil glass having a different bore diameter (viz. 0.1mm, 0.3mm, 0.5mm). Due to the air pressure of the carrier gas, a vacuum is created at the tip of the nozzle to suck the solution from the tube after which the spray starts. The spray nozzle is fixed at an appropriate distance from the substrate. The precursor solution was sprayed on to the substrate in the air as small drops and around a high temperature zone, where thermal decomposition and possible reaction between solutions occur, through

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compressed air, which is used as carrier gas with a flow rate controlled through the air compressor regulator. To achieve uniform deposition the moving arrangement has been used. For this substrate is kept stationary, while the nozzle is free for to and fro motion with mechanical moving arrangement as stepper motor has been advantageous, so we do not have to spend energy moving the table with the hot plate and all electrical connections. The nozzle system is very lightweight with easy slider trolley attached. The spraying system and heater are kept inside a metallic chamber of size 60×60×60 cm3. The inner surface of the box is painted by epoxy liquid, to reduce the heat loss through the surface.

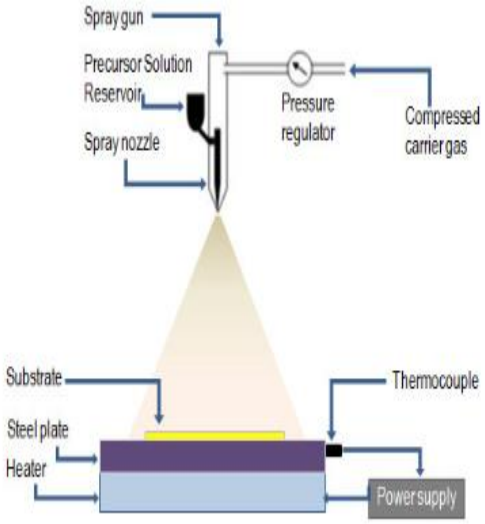

Fig. 1 (a): Schematic representation of the spray system

Fig. 1 (b): Photograph of the spray pyrolysis unit

Kinetics in thin film deposition

The deposition process needs fine droplets to react on the heated substrate, owing to the pyrolytic decomposition of the solution. The hot substrate provides the thermal energy for the thermal decomposition and subsequent recombination of the constituent species. In many cases large droplets of the solution do not vaporize before reacting to deposit on the substrate. They hit the surface and form a powdery deposit. If it strikes at a high enough velocity, the droplet will splatter and form a dispersed powdery layer. As mentioned above, the droplet cannot be completely vaporized before it hits the surface and for this reason, film growth cannot occur. The influence of forces which determine both the trajectory of the droplets and evaporation were examined and a film growth model was proposed. Fig. 2 shows

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the types of trajectories that are expected to occur in the spraying of a solution on hot glass substrate. It is reported that the behavior of precursor drops that undergo three major steps during the course of spray pyrolysis: (a) drop size shrinkage due to evaporation, (b) conversion of precursor into oxides, and (c) solid particle formation. The particle formation may involve two mechanisms: intraparticle reaction (conventional one- particle-per-drop mechanism) and gas-to-particle conversion. In the one particleper-drop mechanism, each droplet is regarded as a micro reactor and converts into one solid particle when it travels towards substrate. In contrast, gas-to-particle conversion occurs when the precursor is volatile and is transported across the particle-gas interface.

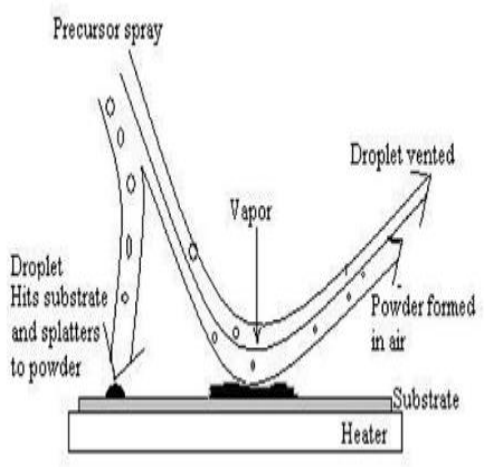

Fig. 2: Kinetics in thin film deposition

CHARACTERIZATIONS OF ZNO THIN FILMS

The optical absorbance of the films was measured using spectrophotometer (UV-visible-2450 spectrophotometer, Shimadzu) in the wavelength range 300-700 nm. The crystalline structure of the thin films was confirmed by using X-ray powder diffraction (BRUKER D8 Advance) with CuKα = 0.15418 nm radiation in the range of 20^o –80^o, and field emission scanning electron microscopy (FESEM). The transmission electron microscopy (TEM, PHILIPS EM 200 Make) and selected-area electron diffraction (SAED) were obtained. The gas sensing properties were measured by the static gas sensing measurement system explained elsewhere.

1 Structural properties of ZnO the films

1.1 X-ray diffraction analysis (XRD)

The XRD spectra of the synthesized ZnO nanorods thin film is shown in Fig. 3 and the results indicate that the ZnO material has a nanocrystalline structure and it grows with hexagonal Wurtzite- type. The main significant peaks for ZnO were found to be (100), (002), (101), (102) and (110). The crystallite size of the ZnO was determined from (101) diffraction peak using Scherrer formula and the average crystallite size was found to be 22.11 nm.

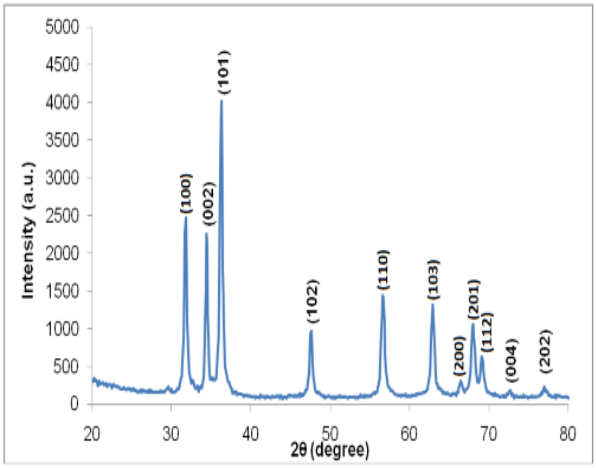

Fig. 3: XRD pattern of ZnO thin film

GAS SENSING PERFORMANCE OF THE ZNO THIN FILMS

1. Gas response of ZnO nanorod thin films with operating temperature

Gas response of a sensor is defined as the ratio of the conductance change upon exposure to a test gas to the conductance in air. The as prepared ZnO films were tested

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to various gases such as LPG, CO, CO_2, Ethanol, O_2, NH_3, H_2S, H_2 and Cl_2 at various temperatures ranging from 30o to 450^{o}C. It shows maximum response to H2S gas at 50^{o}C for 100 ppm gas concentrations. The variation of H2S gas response with operating temperature ranging from 30 to 450^{o}C. The response goes on increasing with the temperature, attains its maximum (50^{o}C) and then decreases with further increase in temperature. It is clear from graph that the optimum operating temperature is 50^{o}C.

2. Selectivity of ZnO thin films for various gases

The ability of a sensor to respond to a certain gas in the presence of other gases is known as selectivity. The sensor showed maximum selectivity to H2S gas against other gases. The figures indicated on the histogram shows the response values of concern gases.

3. Response and recovery time

The time taken for the sensor to attain 90% of the maximum change in resistance upon exposure to the gas is the response time. The time taken by the sensor to get back 90% to the original resistance is the recovery time. The response and recovery profile of the ZnO film to H2S gas. The response time is 4 s and recovery time is 60 s respectively. The faster response time of ZnO thin film would be due to fast mass transfer of gas molecules to and from the interaction regions of the film.

4. Variation in gas response with H2S gas concentration

The variation of gas response of ZnO thin film with H2S gas concentration is 50^{o}C. Each film was exposed to varying concentrations of H2S gas (10–140 ppm). At lower gas concentrations, a monolayer of the gas molecules would be expected to be formed on the surface, which could interact with the surface more actively, giving larger responses. There would be multilayer of gas molecules on the sensor surface at the higher gas concentrations, resulting in saturation in response. The active region of ZnO thin film is from 10 to 100 ppm H2S gas concentrations.

CONCLUSION

Chemical, hydrothermal, and spray pyrolysis methods have been used to synthesise nanostructured ZnO powder and thin films in this thesis. XRD, SEM, TEM, and UV-visible spectroscopy were used to characterise the produced powders and thin films in relation to their gas sensing ability towards hazardous and poisonous conventional gases such as H2S, NH3, LPG, CO, CO2, O2, H2, ethanol, and Cl2. Chemical, hydrothermal, and SPT methods were all explored in this study in an attempt to create nanocrystalline materials and thin films. Analyses and tests were conducted on these films and materials in the presence of various gases. Refereed journals have published the original data and findings. Achieving monodispersed nanocrystalline materials and films is still a challenge for us. Several studies have shown that ultrasonic spray pyrolysis (USP) and ultrasonic atomization can produce monodispersed nanocrystalline materials and thin films. Society must now give greater attention to safeguarding its inhabitants from toxic chemical attacks, whether they are accidental or the result of international terrorism utilising toxic chemical weapons. In order to ensure the safety of individuals, rapid identification and detection of harmful compounds is essential. Thus, we propose to make Nano

crystalline materials/films utilising the ultrasonic atomization process and USP; and we intend to conduct chemical warfare agent tests. Chemical warfare (CW) refers to the use of chemical weapons that have hazardous qualities. It is separate from nuclear and biological warfare, which together form the acronym NBC, which stands for Nuclear, Biological and Chemical (warfare or weapons). As a result, none falls under the umbrella phrase "conventional" weaponry. Explosive force is not required in chemical warfare to achieve a goal.

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