SYNTHESIS AND PROCESSING OF ZnO NANO-SIZED PARTICLES FOR GAS SENSING USING ULTRASONICATION

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ABSTRACT

In nanotechnology to produce and process nano size particles of various materials, the most frequently used method is ultrasonication. Ultrasonic processors are now a days widely used and have become important equipment for dispersion and deagglomeration of nanoparticles. ZnO is most important material for gas sensing applications. ZnO nanoparticles have been prepared by ultrasonic technique. The structural characterizations of the material were analyzed by means of X-ray Diffraction (XRD) and Transmission Electron Microscope (TEMs). The gas sensing properties of ZnO for different gases was investigated at room temperature. The experimental result shows that nanostructured ZnO is a promising material as ethanol gas sensor. Results were found reproducible. XRD shows the crystalline nature of the synthesized material. The minimum crystalline size was found around 13nm and average crystallite size was found around 18nm which is a significant factor for sensor fabrication purpose.

Key Words : Gas sensor, Ultrasonication, Crystallite size, Nano size particle, Zinc oxide

INTRODUCTION

Zinc oxide (ZnO) is one of the most important semiconductor materials belonging to II-VI group. It is a direct wide band gap semiconductor (3.37eV) and it has high excitation binding energy of 60meV, due to the wide range of electrical and optical properties, ZnO films are of technological importance1. ZnO films have many advantages like high chemical and mechanical stability, nontoxic in nature, high abundance and transparency over other oxide thin films like ITO, CdO, SnO2 etc. A major driving force of research in ZnO films is its perspective use of Transparent Conductive Oxide (TCO) films, mainly in solar cells2, heat mirrors and organic light emitting diodes.3 It can also be used as piezo electric devices and gas sensors.4 Different methods have been employed to prepare the ZnO films, such as sputtering, thermal evaporation5, sol-gel method6, electron beam evaporation method, pulsed laser evaporation7 and spray pyrolysis8 technique. One of the most important and serious problem around the world is air pollution. Environment pollution has greatly increased during the last few decades due to the advancement in industrial technology and overall technological advancement and is becoming one of the global hot issues as it adversely affects on living being. These pollutants are not only undesirable and dangerous but also detrimental to the environment. Their presence in huge concentration leads to global warming, acid rain, smog and adversely affect leaving organisms. Therefore it is extremely necessary and essential to have sensors capable of detecting hazardous pollutants. In order to safe guard public health, private property, environmental and strict regulations governing pollution sensors has received great attention.9 For the implementation of regulations to identify and to control the amount of pollutants, there is a need to develop cost effective, innovative, environment friendly sensors capable of working under adverse conditions. Alcohols and hazardous gases are one of the pollutants which affect the environment and are the main cause of sick house syndrome due

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to poor indoor air quality. Presence of alcohol and hazardous gases may lead to all allergies, asthma, cancer and emphysema.\textsuperscript{10} Ethanol is one of the most extensively used and wide spread alcohols and thus there is a demand to develop sensors for its detection. Gas monitoring devices are in demand for a rapidly growing range of applications. Metal oxide based chemical gas sensors have been widely used in environmental monitoring and industrial applications for the detection of toxic pollutant gases, combustible gases and organic vapors. The main advantages of these sensors are small size, low cost, high sensitivity, low power consumption and convenient operation. Alcoholic fermentation occurs in the production of alcoholic beverages and ethanol fuel and in the rising of bread dough. Ethanol can be made by the fermentation of sugars and it is the alcohol of all alcoholic beverages. The synthesis of ethanol in the form of wine by the fermentation of sugars of fruit juices was probably our first accomplishment in the field of organic synthesis. Sugars from a wide variety of sources can be used in the preparation of alcoholic beverages. Often these sugars are from grains. So, ethanol is referred as grain alcohol. Fermentation alone does not produce beverages with ethanol content greater than 12 to15\% because the enzymes of the yeast are deactivated at higher concentrations. To produce beverages of higher alcohol content the aqueous solutions must be distilled. Brandy, whisky and vodka are produced in this way. The proof of an alcoholic beverage is simply twice the \% of ethanol (by volume). One hundred proof whisky is 50\% ethanol. Ethanol is explosively utilized for beverages, industrial and scientific sectors. Ethanol is a hypnotic (sleep producer) gas. It depresses activity in the upper brain even though it gives the illusion of being a stimulant, it is having toxic nature. Abuse of ethanol is a major drug problem in most countries. Having exposure and/or consumption of alcoholic beverages particularly by smokers, increase the risk of cancer of the upper respiratory and digestive tracks. Amongst the women, the chances of breast cancer increase with alcoholic consumption or exposure. Workers working for the ethanol synthesis have great chances of being victim of respiratory and digestive track cancer. So there is a great demand and emerged challenges for monitoring ethanol gas at trace level.

\textbf{AIMS AND OBJECTIVES}

To develop the sensor using ZnO thick films, which could be able to detect the C\textsubscript{2}H\textsubscript{5}OH gas. It was observed that ZnO is very good material in promoting the sensing properties to ethanol in air.

\textbf{MATERIAL AND METHODS}

\textbf{Preparation (synthesis) of ZnO nano-sized particles(powder), paste and thick films}

Nanostructured ZnO powder was synthesized by microwave irradiation followed by ultrasonication and centrifugation process. Ultrasonicator is developed in our laboratory which uses disc type probe is as shown in Fig. 1. The ultrasonicator is operated at 20KHz. Time selection switch is used to select the ON-OFF time period automatically. First zinc chloride was taken in suitable proportion which was added to distill water. The arrangement was made to add drop wise aqueous ammonia (approx.0.1ml/min) to the solution to get pH of 8. The solution was heated up to 90\(^{\circ}\)C with constant stirring until that formation of precipitation occurs. After complete precipitation the powder in a glass beaker was placed in a microwave oven for 15 minutes with switching ON-OFF cycle. The dried precipitate was ultrasonicated for 30 minutes to get nanoparticles. The dried precipitate was ultrasonicated for 30 minutes to get nanoparticles. The dried precipitate was annealed in a muffle furnace at around 1200\(^{\circ}\)C for 6 to 7 hours. The phase purity and degree of crystallinity of the resulting ZnO samples were monitored by XRD analysis. The thixotropic paste was formed by mixing the synthesized nanostructured ZnO fine powder with a solution of ethyl cellulose (a temporary binder) in a mixture of organic solvents such as butyl cellulose. To form a paste the ratio of inorganic to organic part was kept as 75 \(:\) 25. The thixotropic paste was then screen printed on a pre cleaned glass substrate in desired pattern to form thick films.
Materials characterization

The crystalline structure of the films was analyzed with XRD (Make: Philips, model X’pert MPD) using CuKα radiation with a wavelength 1.542 Å. The microstructure and chemical composition of the material were analyzed using TEM (Make: Philips, Model: Technai 20) and EDAX (Make: Philips, Model: XL 30ESEM).

The gas sensing characteristics were measured using a static gas sensing setup as shown in Fig. 2.

Fig. 1: Laboratory developed ultrasonicator

Fig. 2: Gas sensing set-up

The static gas sensing set up is used to measure the sensing performance of the sensor. Electrical feed throughs are used in base plate. On the base plate heater is used to heat up the sample to required operating temperature. A thermocouple (Cr-Al) was used to measure the operating temperature of the sensor. The output of the thermocouple was connected to the temperature indicator/meter. A gas inlet valve was fitted at one of the ports of the base plate. Gas injecting syringe was used to inject a known volume of test gas to pass the required gas concentration inside the system. A constant voltage was applied to the sensor and current was measured using digital pico ammeter. After every C₂H₅OH gas exposure cycle air was allowed to pass into the glass dome.
RESULTS AND DISCUSSION

Structural and elemental analysis (XRD, TEM, EDAX)

Fig. 3 shows the XRD pattern of synthesized material and Fig. 4 shows TEM of nano ZnO. The average particle size nano particles was calculated using Scherer’s formula as \( t = \frac{0.94 \lambda}{\beta \cos \theta} \) where \( \lambda \) is wavelength of X-ray in Å, \( \beta \) is full width at half maximum (in radian). The average particle size of ZnO nanoparticles was found to be 18 nm.

![Fig. 3: XRD pattern of nano structure ZnO](image1)

![Fig. 4: TEM of nano structure ZnO](image2)

Quantitative elemental analysis

The quantitative elemental composition was analyzed using an energy dispersive analysis of X-ray technique and mass % of Zn and O are represented in Table 1.

Sensing performance of the sensor:

Measurement of gas response and selectivity

Gas response (sometimes called as gas sensitivity (s) is defined as the ratio of change in conductance of the sensor on exposure of the target gas to the original conductance in air medium.

Mathematically is written as,

\[ S = \frac{(G_g - G_a)}{G_a} \]

Where, \( G_a \) is the conductance of sensor in air medium and \( G_g \) is the conductance of sensor.

<table>
<thead>
<tr>
<th>Element</th>
<th>EDAX ZAF quantification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt %</td>
<td>At %</td>
</tr>
<tr>
<td>ZnK</td>
<td>64.59</td>
</tr>
<tr>
<td>O K</td>
<td>35.41</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
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</tbody>
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in gaseous medium. Specificity or selectivity is defined as the ability of a sensor to respond to certain gas in the presence of more gases. Percentage selectivity factor of one gas over other is defined as the ratio of maximum response of the other gas to the maximum response of the target gas at optimum temperature.

\[
\text{Selectivity in } \% = \left( \frac{S_{\text{gas}}}{S_{\text{target gas}}} \right) \times 100 \%
\]

**Effect of operating temperature**

The gas response is determined and is plotted as a function of temperature to determine an optimum operating temperature. Fig. 5 shows the variation of gas response with operating temperature of ZnO thick film for 50 ppm and 100 ppm ethanol gas.

![Gas Response vs Operating Temperature](image)

**Fig. 5** : Variation of response with operating temperature

The response to ethanol gas goes on increasing with operating temperature, reaches to maximum at 325°C (8 for 50 ppm and 14 for 100 ppm) and decreases with the further increase of operating temperature. Response to a gas is related generally to number of oxygen ions absorbed on the surface of the film. If film surface chemistry was favourable for adsorption response and selectivity would be enhanced. In case of pure ZnO, oxygen adsorption seems to be poor which is the cause of poor response. Also ZnO films requires relatively larger operating temperature to absorb the oxygen ions and therefore it would have responded at higher operating temperature. So to improve the sensing performance of ZnO, it is essential to modify its surface.

**Selectivity for ethanol gas of nano ZnO**

Fig. 6 shows the selectivity of nanostructured ZnO films to 50 and 100 ppm ethanol gas against various gases at 325°C. It was observed that the zinc oxide sample showed enhanced response towards ethanol (for 100 ppm compared to 50 ppm) and very high selectivity.

![Selectivity Graph](image)

**Fig. 6** : Gas response among various gases
CONCLUSION

The ZnO nanoparticles were developed using a novel technique known as probe type ultrasonication. The characteristics of XRD pattern confirms the crystalline nature of the material. The average crystallize size was calculated. The gas response was measured for fabricated sensor. Results shows that it is more sensitive to ethanol gas as compared to other gases.

REFERENCES


7. H. Xiong, Growth and properties of ZnO film grown on AIN buffer layer by PLD, International photonics and opto electronics meetings, OSA Technical Digest (online) optical society of America, paper ITh4A.10, (2012).


