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Mechanochemical synthesis, characterization and gas sensing property of nano-ZnO

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ABSTRACT

This work reports the mechanochemical synthesis of ZnO nanoparticles. ZnO thick films were deposited on glass substrate by using standard screen printing technique and fired at 450^{0}C for two hours.The Morphological, Compositional and Structural properties of the ZnO thick films were performed by Scanning electron microscopy (SEM), Energy Dispersive Spectroscopy (EDAX) and XRD technique respectively. Chemical composition of nano ZnO film samples changes with firing temperature showing non-stoichiometric behaviours. XRD study indicated the formation of polycrystalline ZnO films with hexagonal wurtzite structure. We have explored H_2S sensing properties of the nano powders ZnO thick films at 300 ^{0}C temperature.

Keywords: Nanoparticals; ZnO; SEM; XRD; gas sensitivity; H_2S.

INTRODUCTION

Zinc oxide is an attracting tremendous attention due to its interesting properties like wide direct band gap of 3.3 eV at room temperature and high excitation binding energy of 60 meV. Zinc oxide is widely used in number of application like photocatalysis [1], gas sensor [2], varistors [3], low voltage phosphor material [4] and so on. In order to realize the universal application of nanomaterials, the key is to devise simple and efficient methods for preparing nonmaterial on a large scale at low cost [5]. ZnO nanoparticles can be prepared on a large scale at low cost by simple solution-based synthesis methods, such as chemical precipitation [6], sol–gel [7] and solvothermal/ hydrothermal reaction.

Number of other methods such as photochemical, electrochemical and chemical reduction8, microwave processing [9], gamma irradiation [10], ion irradiation [11] and plasma processing, radiolysis, ultra sound processing also helps in synthesizing nanoparticles.

Zinc oxide is sensitive to many sort of gases at moderate temperature, ZnO is one of the most widely applied oxide gas sensor. ZnO gas sensing material owe to their high chemical stability, low cost and good flexibility in fabricated in various forms including single crystal [12,13,14,15], sinter pellet 16,17], thin film[18] and thick film[19,20,21].

Gas sensors have a great impact in many areas, such as environmental monitoring, domestic safety, public security, automotive applications, air conditions, air conditioning in airplanes, spacecraft and houses, sensor networks etc [22, 23].Recently, nanostructures of oxide semiconductors have received great interest due to their very large surface-to-volume ratios. Usually, the gas sensing properties of oxide semiconductors strongly depend on the surface of these materials. Thus, gas sensors based on nanostructures are expected to be able to detect sensing gas molecules at lower concentration and exhibit better sensing properties than gas sensors based on bulk material or thin films [14, 17 and 24].

In this paper, the mechanochemical method may produce single phase material; furthermore, the mechanochemical may produce single phase material at lower temperature and shorten the synthesis time. Our investigations have been focused on the preparation and characterization of ZnO nanoparticle by X-Ray diffraction (XRD) and Scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDX). We show that the gas sensors based on ZnO have rapid sensing percent response and high sensitivity to very low concentration of H2S gas at low operating temperature.

MATERIALS AND METHODS

2.1.1. Preparation of ZnO nanoparticles

ZnO Oxide was synthesized using a mechanochemical and conventional solide- state method. All the chemicals used for the preparation were of analytical grade. It includes ZnO, Poly vinyl alcohol (1%) and acetone. All the solutions were prepared in Millipore water obtained from Millipore water system for the preparation of ZnO nanoparticle. Weighted 5 g of ZnO powder and mixed thoroughly in an aceton medium using agate mortar pestle for 2 hr and dry it. The powder of ZnO has been taken in 100 ml beaker and adds 3-4 mL 1% poly vinyl alcohol. The mixture is sticky. Dry the mixture with a natural process. This mixture is added with 150 mL Millipore water. The solution was allowed to centrifuge in presence of water and acetone to remove impurities. The process of centrifuging was repeated three- four times to remove most of the impurities for the solution and allowed to dry at room temperature. The reaction was carried out at 100 ^{0}C for 2 hr in a muffle furnace. The dried powder of ZnO is used for the characterization by XRD, SEM Energy dispersive spectroscopy (EDX) and Gas sensing properties.

2.1.2.Preparation of ZnO Film

The ZnO Nanopartical powder mixing with a solution of ethyl cellulose(a temporary binder) in a mixture of organic solvent such as butyl cellulose, butyl carbitol acetate and terpineol, etc. The ratio of the inorganic to organic part was kept at 75: 25 in formulating the paste. This paste was screen printed on glass substrate in a desired pattern. The film was fired at 450^0 C for two hours. Silver contacts are made for electrical measurements

2.1.3.Details of Gas Sensing Unit

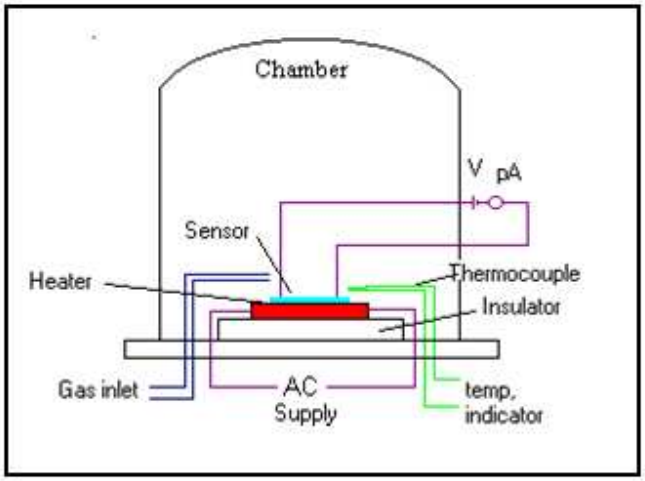

Fig.1. Block diagram of gas sensing unit

The sensing performance of the sensors was examined using a 'static gas sensing system[25]; there were electrical feeds through the base plate. The heater was fixed on the base plate to heat the sample under test up to required operating temperatures. The current passing through the heating element was monitored using a relay operated with an electronic circuit with adjustable ON-OFF time intervals. A Cr-Al thermocouple was used to sense the operating temperature of the sensor. The output of the thermocouple was connected to a digital temperature indicator. A gas inlet valve was fitted at one of the ports of the base plate. The required gas concentration inside the static system was achieved by injecting a known volume of a test gas using a gas-injecting syringe. A constant voltage was applied to the sensor, and the current was measured by a digital Pico ammeter. The air was allowed to pass into the glass chamber after every gas exposure cycle.

3. Structural and Morphological Studies

3.1.1. X-ray diffraction

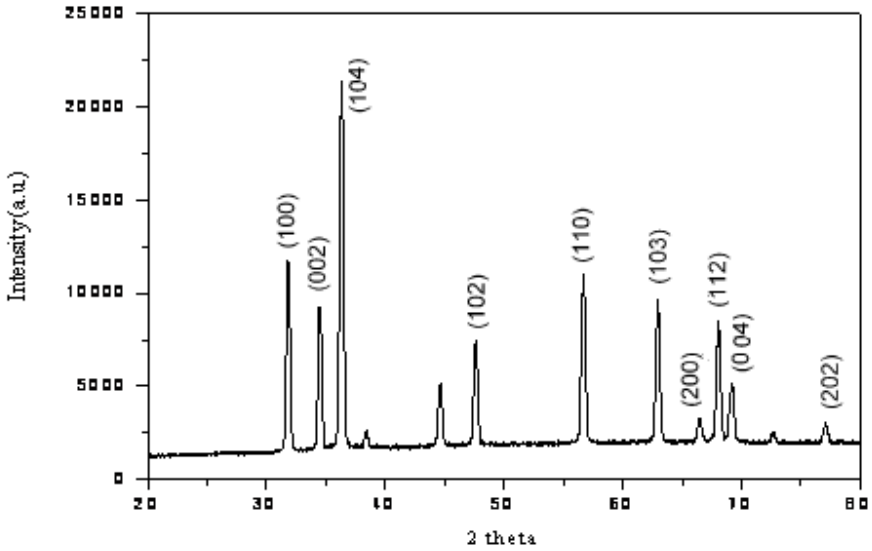

Fig.2. XRD pattern of ZnO nanoparticle

In order to understand the structural properties of ZnO sample fired at different temperature in air atmosphere, the X-ray diffraction study was undertaken. X-Ray diffraction analysis of ZnO samples was carried out in the range 20-80^0 range using CuKα radiation. Fig.2. shows an XRD pattern of ZnO sample plotted in the range 20-80^0(2Θ) versus intensity having several peaks of ZnO indicating random orientation for the hexagonal wurtzite nature and measured interplaner distance agreed with the value reported for ZnO in literature. The observed peak matches well with the reported JCPDS data of Number 21-1486 matches with calculated values, confirming the hexagonal wurtzite structre [26]. The higher peak intensities of an XRD pattern is due to the better crystallinity and bigger grain size.This clearly indicates that the structure of ZnO film is polycrystalline in nature. Besides except ZnO peaks, no other impurity peak is seen, suggesting formation of the single phasic ZnO.

The average crystallite size as per the calculations was found to be 80-100 nm (±2 nm).

3.1.2. SEM analysis

The scanning electron microscopy is useful technique to observe surface morphology of deposited films. SEM images shows that the structure like porous and wafer type. This is because of porosity of the film as deposited at room temperature. Figure-3 shows SEM images of nanostructure ZnO thick film fired at 450^{o}Cin the air. Microstructural characterization was carried out by using scanning electron microscopy. SEM indicated rod type nanostructure with porosity. However some residual, intragranular porosity was seen. The film fired at 450^{o}C has good adhesion. Therefore it is used for gas sensing.The surface morphology (SEM) of ZnO nanoparticle, which reveals the particles size was found to be about 10 nm with hexagonal shape.

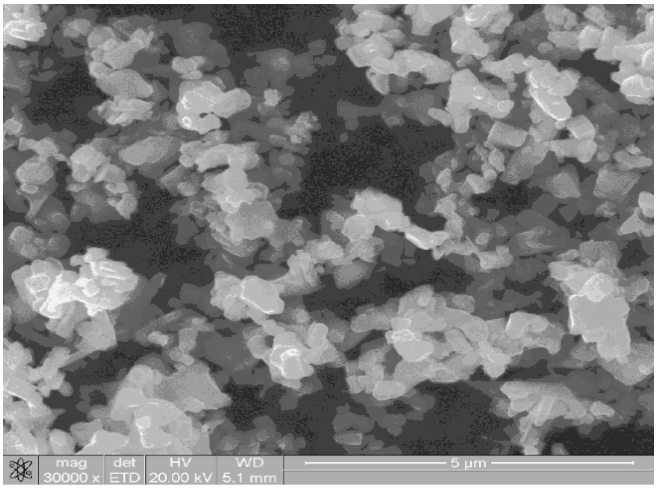

Fig.3. SEM image of ZnO nanoparticle

3.1.3. Elemental Analysis

The composition of ZnO nanoparticle fired at different temperature was analyzed by energy dispersive spectrometer (6360LA) (EDX).The EDAX was recorded in the Binding energy region between 0-20 KeV was shown in fig.4.The spectrum peak reveals the presence of Zn and O at 8.50 and 0.5 KeV respectively, which confirms the presence of Zn and O in the film.

Table1. Shows the composition of the film fired at different temperature. The EDAX spectrum showed the presence of Zn and oxygen. From the analysis it was found that the ZnO films are nonstoichiometric. The deficiency or excess of any type of atom in the crystal results in a distorted band structure, with a corresponding increase in conductivity [25]. Tin oxide looses oxygen on heating so that tin is then in excess. The oxygen, of course, evolves as an electrically neutral substance so that it is associated with each excess tin ion in the crystal; there will be **two** electrons that remain trapped in the solid material, thus leading to nonstoichiometry in the solid. This leads to the formation of the n-type semiconductor [27].

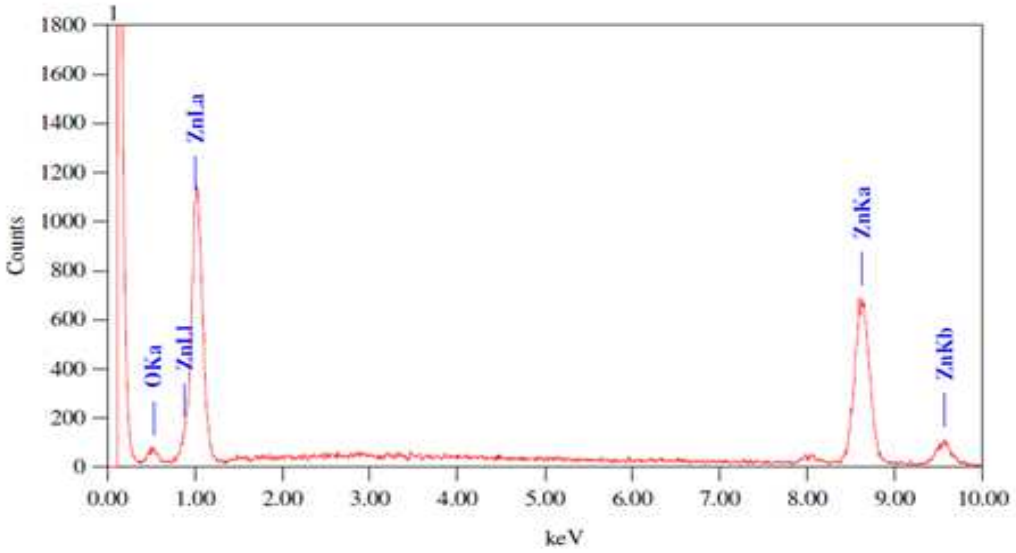

Fig.4. EDAX Spectrum of ZnO

Table1. Composition of the sample

.Element	At. Wt. %	Mass %
O	4.25	1.08
Zn	95.75	98.92
Total	100	100

4. Electrical characterization

4.1 I-V Characteristics

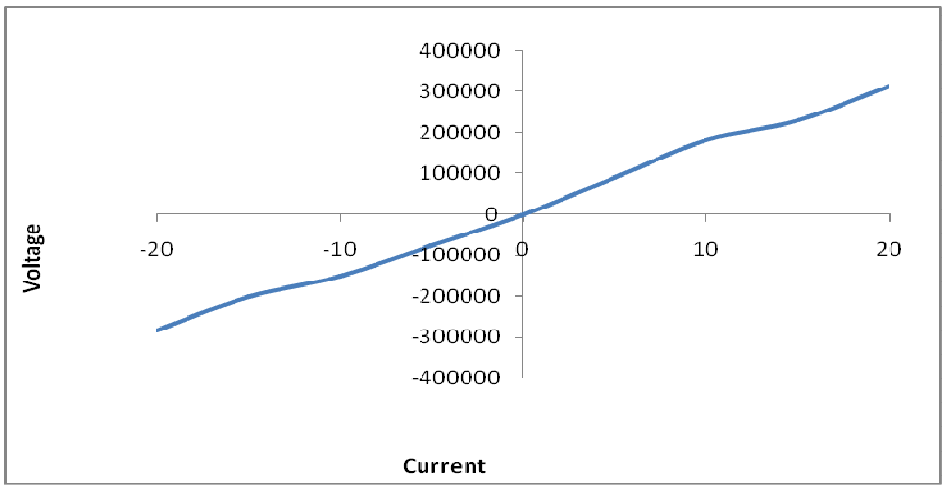

Fig.7. I-V Characteristics of the sensor

Fig.7. Shows the conductivities of ZnO nanoparticle at room temperature. I-V Characteristics of pure ZnO nanoparticle are observed to be symmetrical in nature, indicating the ohmic nature of silver contacts.

4.2 Gas Sensing characterization

Sensor response(S) is defined as the ratio of the change in conductance of the sensor in the presence and absence of target gas to the conductance in air. The relation of S is as:

$S = (G_g - G_a)/ G_a$

Where, G_a and G_g are the conductance of sensor in air and in target gas medium, respectiely. Selectivity or specificity is defined as the ability of a sensor to respond to certain gas in the presence of other gases. The time taken for the sensor to attain 90% of the maximum increase in conductance on exposure to the target gas is the response time. The time taken by the sensor to get back 90% of the original conductance is recovery time.

4.2.1. Gas response with temperature

The gas sensing performances of ZnO were tested for various gases. Fig.8. represents the variation in the gas response at different temperature for various gases at 100 ppm with temperature ranging from 350 to 50 ^{0}C. It is noted from the graph that response increases with further increase in temperature from 200 to 350 ^{0}C. It is observed from Figure-8 that the ZnO sample shows maximum response (90%) to H_2S for100 ppm at 300^{o}C. Sample showed highest selectivity for H_2S against all other tested gases. The interaction of CO_2, H_2, LPG, NH_3 and Cl_2 with ZnO is very less as compared to H_2S, hence it shows very slow response and less sensitivity.

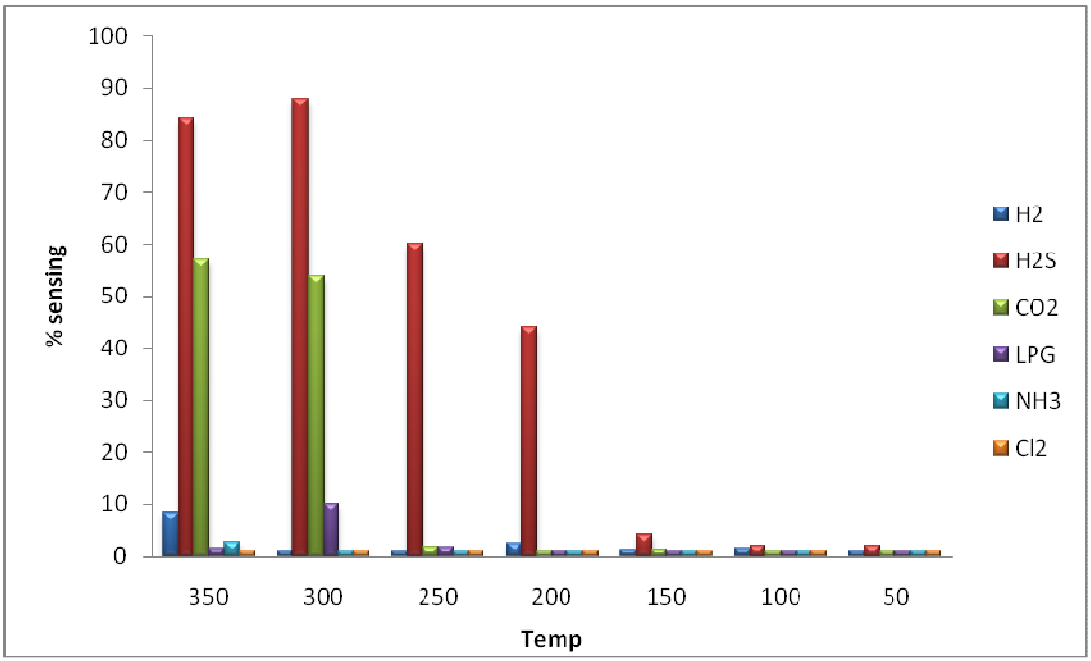

Fig.8. Selectivity of ZnO to various gases

4.2.2 Response and Recovery Time

The response and recovery times of ZnO film sample are represented in Figure-9. The response was quick (~ 28 s) to 100 ppm of H_2S while the recovery was fast (~ 35 s). The quick response may be due to faster oxidation of gas. Its high volatility explains its quick response and fast recovery to its initial chemical status.

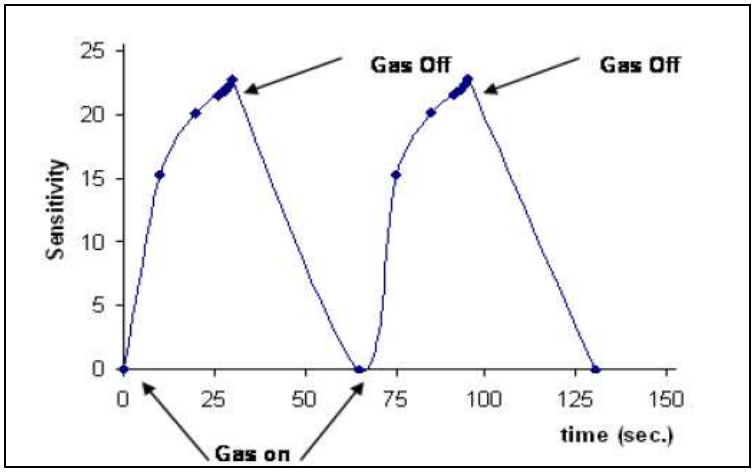

Fig. 9 Response and recovery of ZnO sample

CONCLUSION

The present study illustrates that the mechanochemical method which produce single phase material at lower temperature and shorten the synthesis time. X-Ray diffraction (XRD) result showed that the obtained ZnO nanoparticles were composed of hexagonal with very good crystallinity. Scanning electron microscopy (SEM) result showed that the average partial size was obtained 10 nm. The UV-visible spectroscopy shows absorption at the wavelength 365 nm. The ZnO nanoparticles show the highest response to the H_2S gas over the operating temperature.

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