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Synthesis of ZnO-TiO_2 Nanocomposite Via Mechanochemical Method

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Abstract

This work reports the mechanochemical synthesis of ZnO- TiO_2 nanoparticles. ZnO-TiO_2 thick films were deposited on glass substrate by using standard screen printing technique and fired at 450^0C for two hours.The Morphological, Compositional and Structural properties of the ZnO-TiO_2 thick films were studied by Scanning electron microscopy (SEM), Energy Dispersive Spectroscopy (EDAX) and XRD technique respectively. Chemical composition of nanoZnO-TiO_2 film samples changes with firing temperature showing non-stoichiometric behaviours. XRD study indicated the formation of ZnO-TiO_2 films with Rutile nature. We have explored H_2S sensing properties of the nano powders ZnO-TiO_2 thick films at 250 ^{0}C temperature.
Keywords: Nanoparticals; ZnO-TiO_2; SEM; XRD; gas sensitivity; H_2S.

1. Introduction

Nano-size particles of less than 100 nm in diameter are currently attracting increasing attention for the wide range of new applications in various fields of industry[1]. Such powders can exhibit properties that differ substantially from those of bulk materials, as a result of small particle dimension, high surface area, quantum confinement, and other effects. Most of the unique properties of nanoparticles require not only the particles to be of nano-sized, but also the particles be dispersed without agglomeration. Many methods have been developed for the synthesis of nanoparticles, including vapour phase condensation, sputtering, wet chemical precipitation, sol-gel techniques and hydrothermal synthesis. Since many existing methods involve the nucleation of nanoparticles in either vacuum, gas or liquid, the separation of nanoparticles during synthesis is not guaranteed: Particles encounter one after another in the growth stage, resulting in the formation of agglomeration and relatively poor control of the overall particle size distribution. The synthesis of nanocrystalline materials by mechanical milling, mechanical alloying[2] and mechanochemical processing [3]has been widely studied. Mechanochemical processing is characterised by the repeated welding, deformation and fracture of the mixture of reactants. Chemical reactions occur at the interfaces of the nanometer-sized grains that are continuously re-generated during milling [4]. As a consequence, chemical reactions, which would normally require high temperatures to occur due to separation of the reacting phases by the product phases, can occur at low temperatures in a ball mill without any need for external heating [5]. The reactions may occur either in a steadystate manner or self-propagating combustive manner [6, 7]. By selecting suitable conditions such as chemical reaction paths, stoichiometry of starting materials and milling conditions, mechanochemical processing can be used to synthesis nanocrystalline particles dispersed within a soluble salt matrix. Selective removal of the matrix phase by washing the resulting powder with appropriate solvents

can yield nanoparticles of the desired phase as small as 5 nm [8].

Basic studies regarding the phase diagram and the physical properties of ZnO–TiO_2 system have been published since 1960s[9, 10]. Dulin and Rase [9]showed that three compounds exist in the ZnO–TiO_2 system, including Zn_2TiO_4 (cubic), $ZnTiO_3$ (hexagonal), and $Zn_2Ti_3O_8$ (cubic). Zn_2TiO_4 phase can easily be prepared by conventional solid-state reaction. The applications for zinctitanates were at that time mostly paints pigments and fusion cast thermistors. Zinc-titanate's first application was as a sorbent for removing sulfur from coal gasification products [11-13]. Nowadays, due to the development of microwave dielectrics, zinc-titanates can be used as dielectric resonators and filters in microwave devices [14, 15]. Orthotitanate with a spinel structure and cubic lattice is considered the most stabile form of three compounds that coexist in the phase diagram of the ZnO-TiO_2 system and as a high temperature titanate form, it was widely investigated [13].

The aim of the present paper was to investigate the synthesis route and characterization of ZnO-TiO_2 at room temperature by mechanochemical method.

2. Experimental details

2.1 Preparation of ZnO -TiO_2 nanoparticles

ZnO-TiO_2 nanopartical were synthesized using a mechanochemical and conventional solide- state method. All the chemicals used for the preparation were of analytical grade. It includes ZnO (A.R Grade),TiO_2(A.R.Grade), and Ethnol. Weighted 2.5 g of ZnO powder and 2.5 g of TiO_2 mixed thoroughly in an Ethanol medium using agate mortor pestel for 3 hr. Make it dry. The powder of ZnO –TiO_2 has been taken in 500 mL beaker and add 150 mL water. The mixture is kept in microwave at about 30 min. 900W power. The powder becomes dry. The products were carried out at 100^0 C for 2 hr in a muffle furnace. The dried powder of ZnO-TiO_2 is used for the characterization of XRD, SEM at 500^0 C, 700^0 C and 900^0C and Gas sensing Performance tested for various gases.

2.2 Preparation of ZnO-TiO_2 Film

The ZnO-TiO2 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 to 150^0 C. Silver contacts are made for electrical measurements.

3. Gas Sensing Unit

The sensing performance of the sensors was examined using a 'static gas sensing system'; 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.

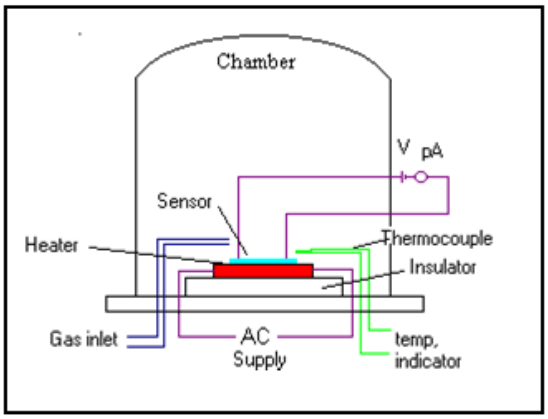


Fig.1. Block diagram of gas sensing unit

4. Structural Characterization

4.1 X-Ray Diffraction

In order to understand the structural properties of ZnO-TiO_2 sample fired at temperature 700^0C in air atmosphere, the X-ray diffraction study was undertaken. X-Ray diffraction analysis of ZnO-TiO_2 samples were carried out in the range 20-80^0 range using CuKα radiation. Fig.2. shows an XRD pattern of ZnO-TiO_2 sample plotted in the range 20-80^0(2Ɵ) verses intensity having several peak of ZnO-TiO_2 indicating random orientation for the Rutile nature and measured interplaner distance agreed with the value reported for ZnO-TiO_2 in literature. The observed peak match well with the reported JCPDS data of Number 89-0555 matches with calculated values, confirming the rutile nature[17]. The higher peak intensities of an XRD pattern is due to the better crystallinity and bigger grain size.

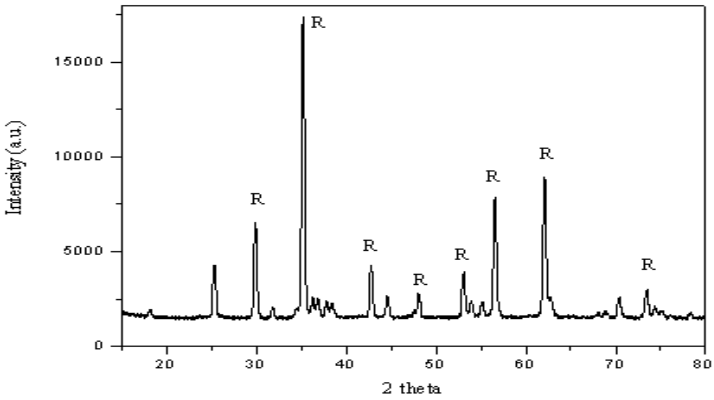
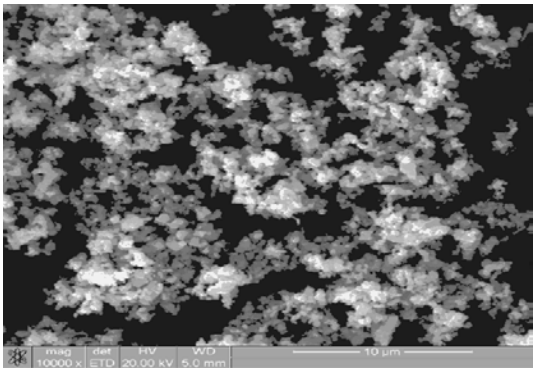
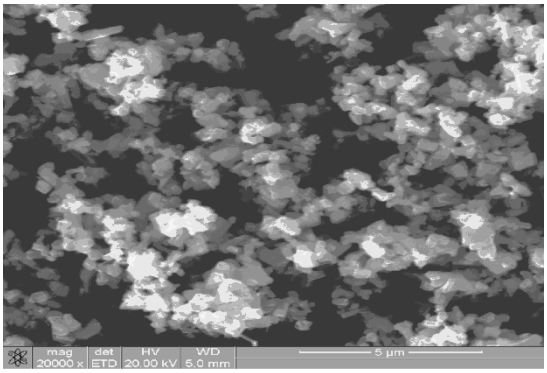


Fig.2. XRD pattern of ZnO-TiO_2 at 700^0 C

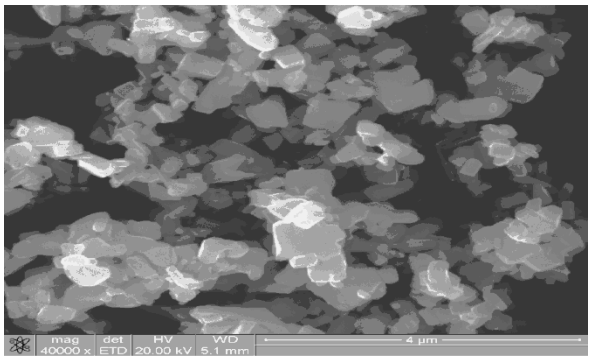
4.2 Micro structural scanning Electron Microscopy (SEM)



(a)



(b)



(c)

Fig.3. SEM Image of ZnO-TiO_2 Nanoparticle at 500^0C b) 700^0C and c) 900^0C

Micro structural characterization was carried out by using scanning electron microscopy. Fig. 3 (a, b, c) shows SEM images of ZnO-TiO_2 thick film fired at 500 ^{0}C, 700^0 C and 900^0C respectively. The micrographs consists of large number of grain sizes ranging from 0.1 µm to 1 µm, leading to high porosity and large effective surface area available for the adsorption of oxygen species.

The comparison of these micrographs shows the interesting changes in morphology. It is found that the grain size and the crystalline quality increased with increase in firing temperature. The firing temperature increases the atomic mobility; the atoms can be moved to more energetically favored sites such as voids, grain boundaries and interstitial positions. An increase in temperature improves the crystallinity and thus increases the mobility of atoms at the surface of films.

4.3 Elemental Analysis

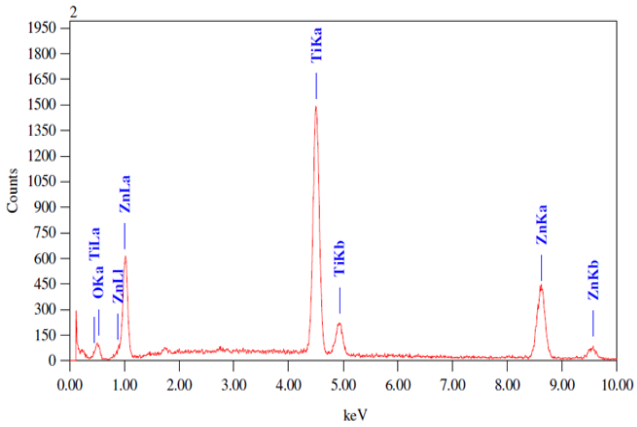


Fig.4. EDAX Spectrum of ZnO-TiO_2

The composition of ZnO-TiO_2 film 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 Ti and O at 8.7, 4.5 and 0.5 KeV respectively, which confirms the presence of Zn and O in the film.

Table 1. Shows the composition of the film fired at different temperature. The EDAX spectrum showed the presence of Zn, Ti and oxygen.

Table1. Composition of the sample

Element	At. Wt. %	Mass %
O	**11.31**	**3.46**
Zn	**45.68**	**57.12**
Ti	**43.01**	**39.41**
Total	**100**	**100**

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5. Electrical Properties of the Sensor

5.1 I-V Characteristics

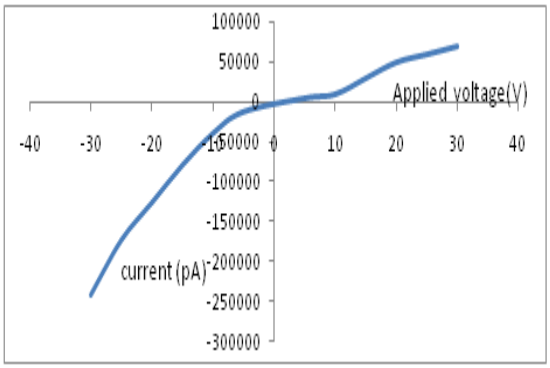

Fig.5. I-V Characteristics of the sensor

Fig.5. Shows the I-V Characteristics of pure ZnO-TiO_2 nanoparticle at room temperature in air atmosphere. The linearity in the graph indicates the ohmic nature of contact.

5.2. Electrical conductivity

Fig .6.represent the variation of conductivity with temperature for ZnO-TiO_2 film in air ambience for different temperatures. The conductivity of these films goes on increasing with increase in temperature

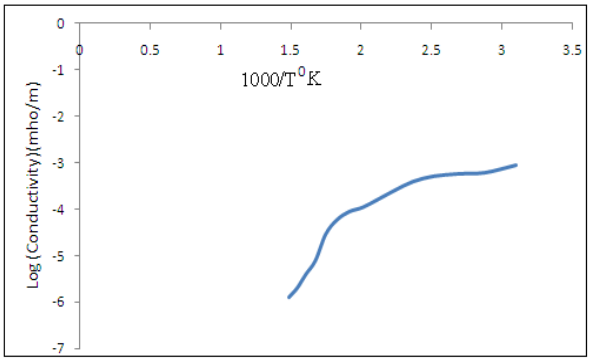

Fig.6. Variation of log (conductivity) with 1000/T ^{0}K

6 Gas Sensing performance of ZnO-TiO_2

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, respectively. 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.

6.1 Gas response with temperature

The gas sensing performances of ZnO – TiO_2 were tested for various gases. Fig.7. represents the variation in the gas response at different temperature. For various gases at 100 ppm with temperature ranging from 450^0 to150^0 C. It is noted from the graph that response increases with further increase in temperature from 200^0 to 250^0C. It is observed that ZnO- TiO_2 can sense H_2S with higher sensitivity for H_2S indicates that the ZnO -TiO_2 are selective for this gas. The interaction of CO_2, H_2, NH_3 and Cl_2 with ZnO TiO_2-is very less as compared to H_2S, hence it shows very slow response and less sensitivity.

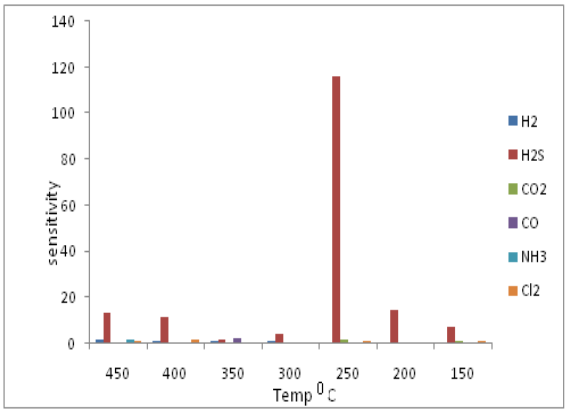

Fig.7.Response of ZnO-TiO_2 to various gases

6.2 Variation of response ZnO-TiO_2 film with H_2S Gas Concentration

Fig.8. is the variation of response with H_2S gas concentration with the gas response at 250^0C shows that the sensor response increases linearly with the gas concentration from 20 to100 ppm

This may be due to less availability of surface area with possible reaction sites on surface of the film.

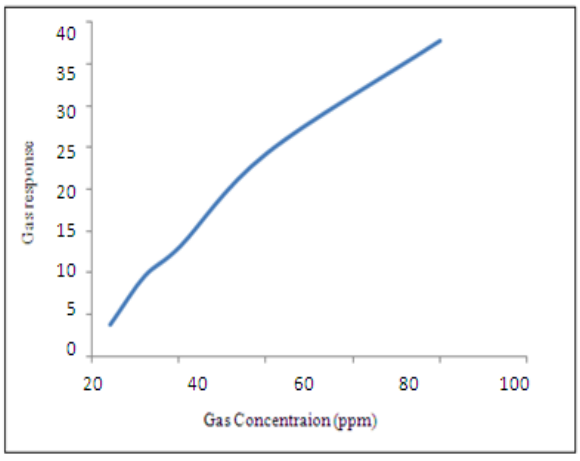

Fig.8. Variation of response with H_2S gas concentration

6.3 Response and Recovery Time of pure Film

The time taken for the sensor to attain 90 % of maximum change in resistance on exposure to gas is the response time. The time taken by the sensor to get back 90 % of the original resistance is the recovery time[16]. The response and recovery time of pure ZnO-TiO_2 film was 10 s and 20 s respectively. The large recovery time would be due to lower operating temperature

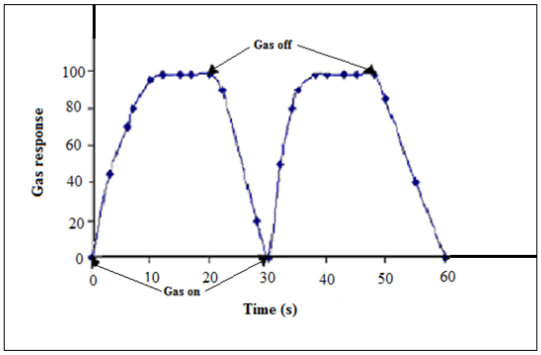

Fig. 9 Response and recovery of ZnO-TiO_2 sample

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-TiO_2 nanoparticles were composed of Rutile nature with very good crystallinity. Scanning electron microscopy (SEM) result showed that the average partial size was obtained 10 nm. The ZnO nanoparticles show the highest response to the H_2S gas over the operating temperature.

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