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# SYNTHESIS, STRUCTURAL AND GAS SENSING PROPERTIES OF PURE ZINC OXIDE NANO THICK FILM.

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## ABSTRACT

The ZnO nanostructures have been synthesized and studied as the sensing element for the detection of$H_2S$ gas. The ZnO nanostructures were synthesized by Sol-gel method followed by sonication. By using screen printing method, thick films of synthesized ZnO nanostructure were deposited on glass substrate. Gas sensing properties of ZnO nanostructure thick films were studied for low concentration $H_2S$gas at different temperature. ZnO nanostructure synthesized by this method can be used as a promising material for semiconductor gas sensor to detect gas like $H_2S$ at above room temperature with high sensitivity and selectivity.

**Keywords:** Nanostructure, ZnO, UV, FTIR, XRD, TEM, SEM, $H_2S$ Sensor.

## 1. INTRODUCTION

Today, when the world is prevailing on the roof of technology and electronics, mostly dominated by compatible electronic equipments and thereby creating the need for materials possessing useful properties. The world now demands a material that should possess inherent properties like larger band gap, higher electron mobility as well as higher breakdown field strength. So on making investigation about such a material the name of compound comes out is “Zinc Oxide” which is a wide gap semiconductor material very well satisfying the above required properties. Zinc oxide possessed many versatile properties for UV electronics, spintronic devices and sensor applications. This ignites many research minds all over the world and creates interest to develop proper growth and processing techniques for the synthesis of Zinc oxide.

The electrical, optical, magnetic, and chemical properties can be very well tuned by making permutation and combination of the two basic structural characteristics that is cations with mixed valence states, and anions with deficiencies (vacancies). Thus, making them suitable for several application fields such as semiconductor, superconductor, ferroelectrics, magnetic and gas sensing.

Nanostructured materials such as ZnO, $SnO_2$, and $WO_3$ have shown good electrical properties [1-13]. Among these nanostructure-semiconducting materials, ZnO has been studied extensively for electrical application and gas sensing. Due to its versatility and multifunctionality creates attention in the research field related to its electrical applicationsand gas sensing. A wide number of synthesis techniques also been developed by which ZnO can be grown in different nanoscale forms. Efforts were made to synthesize ZnO nanostructure with innovative morphology by Sol-gel method. The synthesized ZnO shows good electrical conductivity. In the present work, the efforts are made to study Characterizationand gas sensing of low cost (ZnO).

$H_2S$ is a toxic gas produced from the coal, oil and natural gas industries. In order to enhance the sensitivity and selectivity of $H_2S$, many attempts were made to synthesized nanostructure ZnO with different morphologies [14-18].

## II. EXPERIMENTS

### II.1. Synthesis of ZnO Nanostructure

All the chemicals used in this study were of GR grade purchase from Sd-Fine, India (purity 99%). The chemicals are used without any further purification. Zinc acetate dehydrate $Zn(O_2CCH_3)_2(H_2O)_2$, sodium hydroxide, Methanol and deionized water was used during reaction.

In preparation Zinc Oxide (ZnO) 0.2M Zinc Acetate dehydrates was dissolved in 100 ml deionized water was ground for 15 min and then mixed with 0.02 M solution of NaOH with the help of glass rod. After the mixing the solution was kept under constant magnetic stirring for 15 min. and then again it was ground for 30 min. The white precipitate product was formed at the bottom. Then abundant liquid was discarded and the product was washed many times with the deionized water and methanol to remove by products. The final products was then filtered by using Wattman filter paper and obtain precipitate in the form of white paste, now this paste was kept in a vacuum oven at $80^oC$ for 4hrs so the moisture will removed from the final product and we will get dry product. Then this dry product was crushed into a find powder by using grinding machine and finally this fine nano-powder of ZnO was calcinated at temperature $800^oC$ for 6 hrs in the auto controlled muffle furnace *(*Gayatri Scientific, Mumbai, India.*)* so that the impurities from product will be completely removed and get a final product of ZnO nanoparticles.

### II.2 Preparation of Thick Films

Thick films of synthesized nanostructure ZnO were prepared by using screen printing technique. In present process, thixotropic paste was formulated by mixing the synthesized ZnO

powder with ethyl cellulose (a temporary binder) in a mixture of organic solvents such as butylcellulose, butyl carbitol acetate and turpineol. The ratio of ZnO to ethyl cellulose was kept at 95:05. The ratio of inorganic to organic part was kept as 75:25 in formulating the pastes. The thixotropic pastes were screen printed on a glass substrate in desired patterns. The films pre-pared were fired at 500°C for 12 hr. Prepared thick films were called as pure ZnO thick films.

## III. MATERIALS CHARACTERIZATION

### III.1. Thickness Measurement

Thickness of all ZnO thick films were measured by using technique "Marutek film Thickness Measurement System" with the help of provided equipment. The thicknesses of all films were observed in the range from 35 μm. Thick films of approximately uniform thick-nesses were used for further characterization.

### III.2. UV-visible absorption spectrum

UV-visible absorption spectroscopyis widely used toolfor checking the opticalproperties of nanosized particles.Figure 1 shows the UV-visible absorption spectrum of ZnO nanoparticlescalcined at temperature 800$^{o}$C for 6 Hrs. From the spectrum four peaks are observed at 362nm, 318nm, 344nm and 296nm, out of this at 318 nm wavelength has been found maximum absorption, if we calculate band gap for this wavelength it is 3.30eV, which is very close tothe band gap of ZnO 1s–1s electron transition (3.37eV) [19].

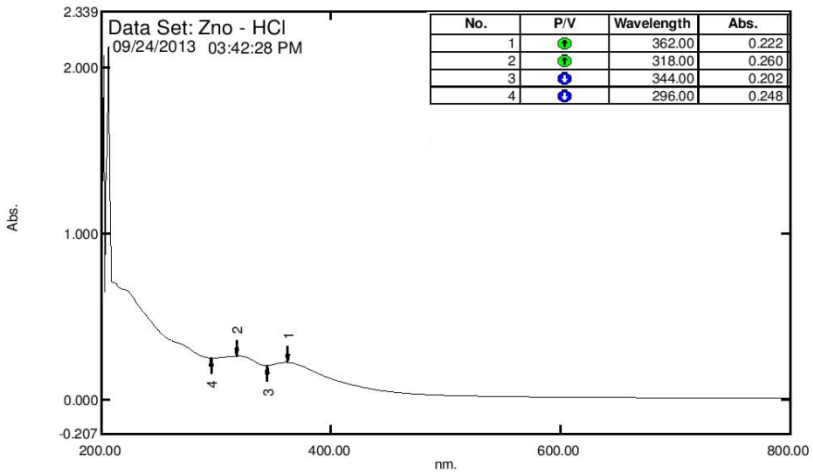


**Figure 1:** UV-visible absorption spectrumof Pure ZnO

### III.3. FTIR analysis

FTIR analysis spectrum shown in figure 2, indicating significant absorption peaks at wave numbers 4350, 4200, 3900, 3850, 1700, 1550 and 600, 510 cm$^{-1}$. The absorption band at 600 and 510 cm$^{-1}$ is obtained due existence of Zn-O bond stretching vibration [20]. The peaks at 1700 and

1550 $cm^{-1}$ shows H-O-H bending vibration due to the adsorption of moisture, when FTIR sample disks were prepared in an open air atmosphere. The remaining peaks between 4350 to 3850 $cm^{-1}$ are corresponding to O-H stretching vibrations [21].

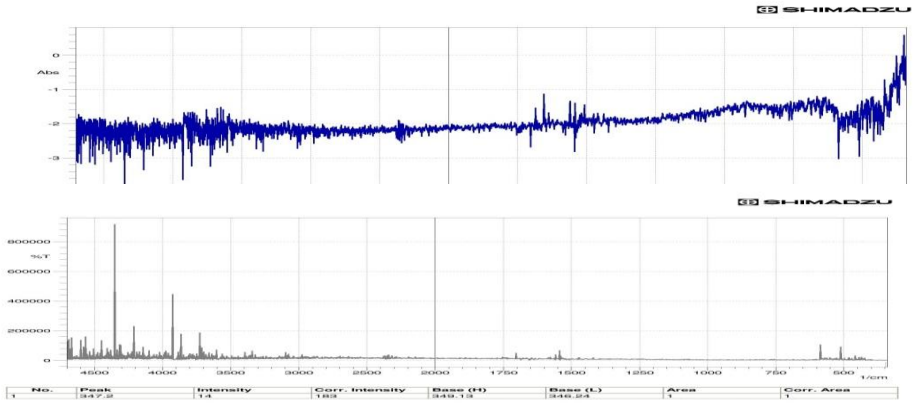


**Figure 2:** FTIR absorption/transmission spectrum of Pure ZnO

### III.4. X-Ray Diffraction Studies

The crystallographic structure of the synthesized ZnO nanostructure was characterized by powder X-ray diffraction (Philips X-ray diffractometer) with Cu-α source and 2$\theta$ range of 10° - 70°. Fig 3shows the XRD pattern of the ZnO nanostructure. The recorded XRD pattern confirmed that synthesized ZnO are highly crystalline in nature. The corresponding X-ray diffraction peak for (100), (002), (101), (102) (110), (103) and (112) planes confirm the formation of hexagonal wurtzite structure of ZnO (JCPDS card no.-01-080-0075). The domain size of the crystal can be estimated from the full width at half maximum (FWHM) of the peaks by means of the Scherrer formula $D = k\lambda/\beta\sin\theta$ , where $\lambda$ is the wavelength of incident beam (1.5406 Å), $\beta$ is the FWHM of the peak in radians, $\theta$ is the diffraction angle and $K$ is Scherrer constant. The average particle size was calculated from (101) peak ZnO is found to be 78 nm.

Using X'pert High Score Plus software it is confirm that synthesized zinc oxide powder contains Zn and O elements only, not any impurity and another element.

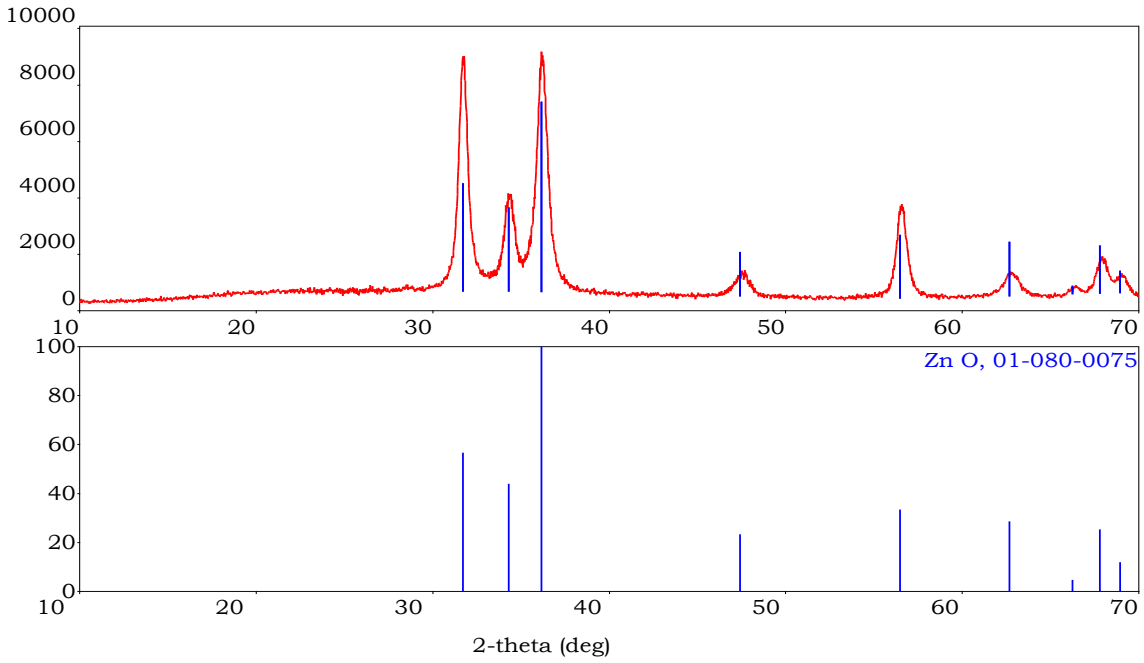


**Figure 3:** X- Ray diffraction Pattern of Pure Zinc Oxide (ZnO)

### III.5. Transmission electron microscope

Figure 4(a, b):shows transmission electron microscope image of ZnO nanostructure synthesized by liquid-phase co-precipitation method. It is clearly seen from the TEM image that the ZnO powders consist of large number of nanosphere which were cumulated to form superior size crystal.

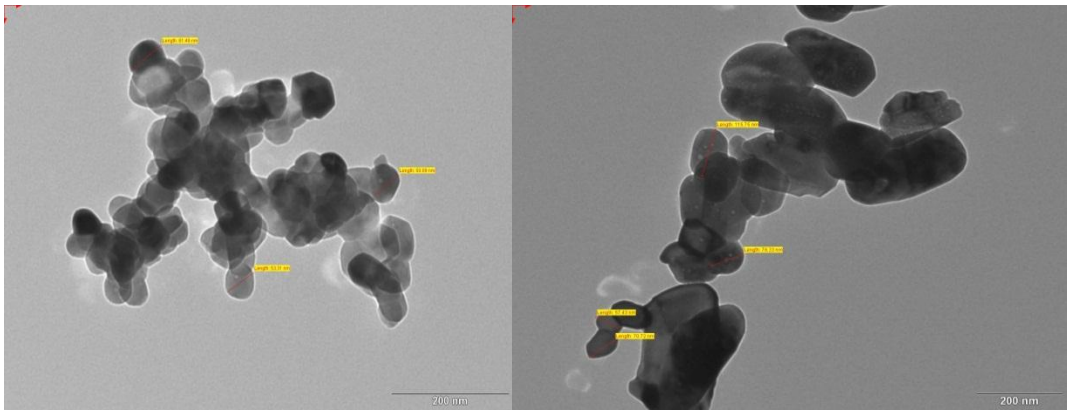

**Fig 4 (a)** **Fig 4 (b)**

**Figure 4:** Transmission Electron Microscope Pattern

### III.6. Scanning Electron Microscopic Study

Figure 5 shows typical SEM images of the pure ZnO thick film prepared by screen printing technique. The ZnO synthesized by liquid-phase co-precipitation method consist of randomly distributed nanosphere as shown in Figure 5a and Figure 5b. Due to such a deposition of nanosphere, surface to volume ratio of the ZnO may be increased.

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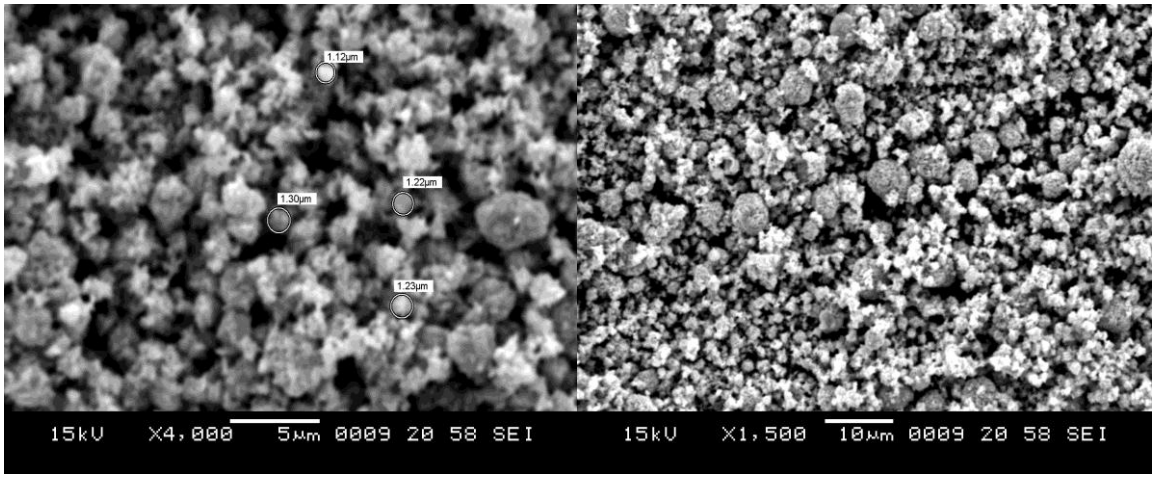


**Fig 5 (a)** **Fig 5 (b)**

**Figure 5:** Scanning Electron Microscope Pattern

## IV. GAS SENSING PROPERTIES

The gas response of the sensor was defied as the ratio of the change in conductance of a sample upon exposure to the target gas to the original conductance in air. Figure 6shows the gas responses of ZnO thick films to $H_2S$ at operating temperature. This high response of ZnO thick film to $H_2S$ may be due to the interaction of ZnO with $H_2S$, forming ZnS [22-23]. ZnS exhibits higher electronic conductivity as compared to pure ZnO.

Figure 6 also indicates the pure ZnO have maximum gas response to low concentration $H_2S$. The higher response ZnO nanostructure upon exposure to $H_2S$ may be attributed to the decrease in concentration of oxygen adsorbents ($O^{2-}$) and a resulting increase in concentration of electron.

The gas response was mainly dependent upon two factors. The first was the amount of active sites for oxygen and the reducing gases on the surface of the sensor materials. It is seen form TEM images Figure 4 (a), (b) .The surfaces pure ZnO contain more active sites .This could explain why the response of pure ZnO thick films was higher than other thick films.

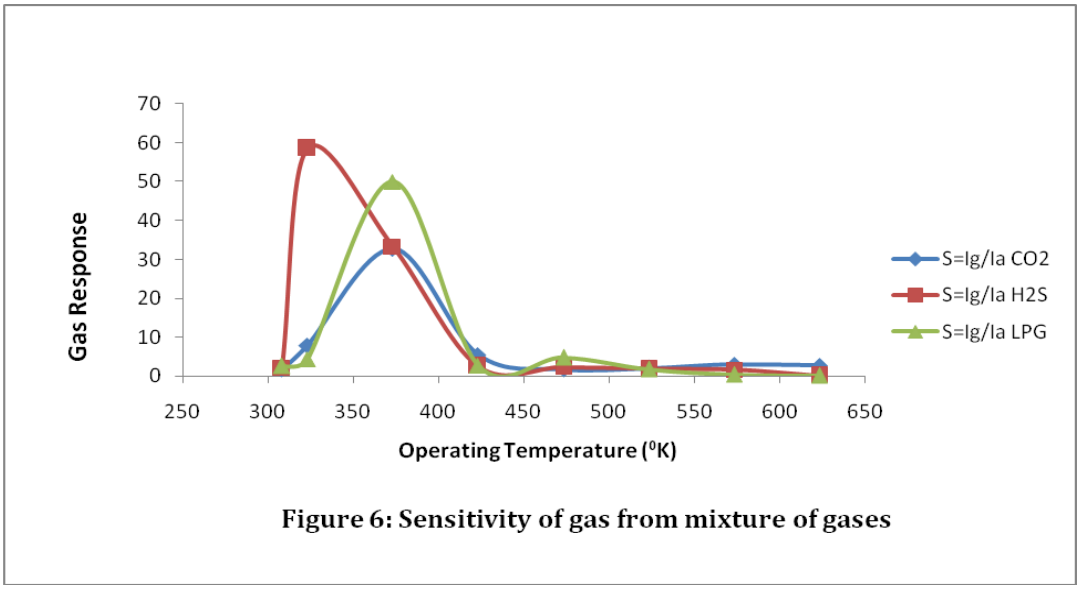


**Figure 6: Sensitivity of gas from mixture of gases**

## V. CONCLUSION

In summary, sensors were fabricated with ZnO nanostructures, which were synthesized by a liquid-phase co-precipitation method followed by sonication, and their gas sensing properties were measured. The results demonstrated that pure ZnO is very sensitive to low concentration $H_2S$. Such nanomaterials with innovative structure can be used for gas sensors to monitor hazards gas like $H_2S$.

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