

TiO₂ modified ZnO thick film resistors as ammonia gas sensors

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ABSTRACT

Zinc oxide nanostructures were synthesized by chemical route method. The XRD spectrum indicates that the sample is wurtzite (hexagonal) structured ZnO with lattice constants of $a = 3.249 \text{ \AA}$, $c = 5.206 \text{ \AA}$. Thick films of synthesized ZnO were prepared by screen printing technique. The TiO₂ modified ZnO were obtained by dipping them into an aqueous solution of titanium tetrachloride for different interval of time. Gas sensing properties of pure and modified ZnO thick films were investigated. The TiO₂ modified ZnO thick film dipped for 5 min were observed to be more sensitive as compared to other modified thick films at 125°C. The effect of surface microstructure and TiO₂ concentrations on the sensitivity, selectivity, response and recovery of the sensor in the presence of NH₃ and other gases were studied and discussed.

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Keywords: ZnO nanostructure; TiO₂ modified ZnO thick films; ammonia sensor; room temperature gas sensor.



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Introduction

Semiconductor metal oxide gas sensor has attracted great attention in the past few years due to its many advantages such as simple manufacture technique, low cost, rapid response and recovery. Recently zinc oxide has attracted worldwide research interest because it is considered a promising material for gas sensors [1-6]. Although ZnO is one of the earliest discovered semiconducting oxide gas

sensing materials and there are many reports concerning the sensitivity properties of ZnO, most of these works has been done on powder samples usually pressed in pellets and sintered at high temperature [7, 8]. In recent years, there appeared many publications on ZnO nanorod gas sensors [9-16]. However, most of ZnO nanorod based gas sensors operated at higher temperature. But, commercial metal oxide semiconductor gas sensor always operated at room temperature. Therefore, new approaches must be explored to make the gas sensor operated at low or room temperature.

In present study, efforts were made to prepare TiO₂ activated ZnO nanostructure thick films and studied morphological, structural and sensing properties at room temperature.

Experimental

Synthesis of ZnO nanostructure

In present work, 5.948 gm Zn(NO₃)₂·6H₂O (99.0% pure, AR grade, Sigma Aldrich) was dissolved in 100 ml distilled water and 2.0 g of NaOH (98.0% pure, AR grade, Sigma Aldrich) was dissolved in 100ml distilled water and first solution was added drop wise to the NaOH solution to form white solution. Prepared white solution was subsequently kept at 75 °C For 12 hr. The resulting precipitate were collected by centrifugation, washed with distilled water and ethanol several times and then dried at

80 °C in vacuum oven for 2hr. The synthesized ZnO nanostructure product was used for further study.

Preparation of thick films

Thick films of ZnO nanostructure were prepared by using screen printing technique. In typical process, paste was formulated by mixing the synthesized ZnO nanostructure powder with ethyl cellulose (a temporary binder) in a mixture of three organic solvents. The ratio of inorganic to organic part was kept as 75:25 in formulating the pastes. The ready pastes were screen printed on a glass substrate in desired patterns. The films prepared were fired at 500 °C for 12hr. Prepared thick films termed as pure ZnO thick films.

TiO₂ modified ZnO thick films

Surface of pure ZnO thick film were modified by dipping them into a 0.01 M aqueous solution of titanium tetrachloride (99%, AR grade, Merck) for different intervals of time (1, 3, 5 min). After dipping, thick films were dried under IR lamp for 60 min. Dried thick films were calcinated at 600°C for 2.5 hr in air ambient. The titanium tetrachloride dispersed on the film surface was oxidized in calcination process, and sensor elements with different mass% of TiO₂ on the surface of ZnO thick film were obtained. These surface activated films are termed as TiO₂ modified ZnO thick films

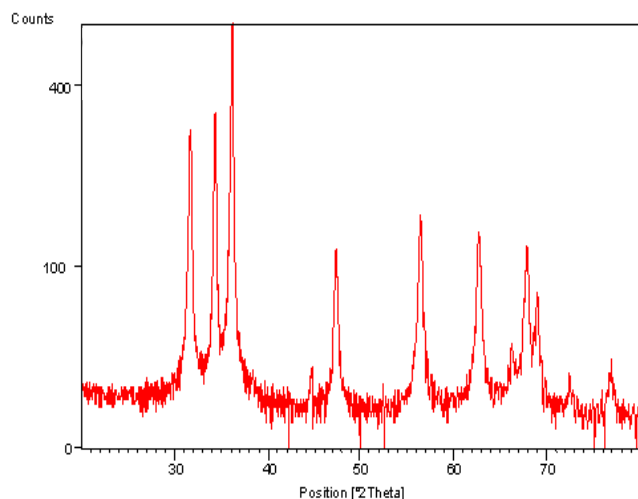


Fig. 1. XRD diffraction pattern of ZnO nanostructure synthesized by chemical route.

Results and discussion

X-ray diffraction studies

X-ray diffraction data for structural characterization ZnO nanostructure synthesized by chemical route method was collected on the Philips PW 1710 X-ray diffractometer using Cu-K α source.

Fig. 1 illustrates the x-ray diffraction pattern of the ZnO nanostructure synthesized by chemical route. This XRD pattern shows that, all the diffraction peaks in the pattern can be assigned to hexagonal ‘wurtzite’ ZnO with lattice constants $a = 0.3249$ nm and $c = 0.5206$ nm, which are in

good agreement with the literature values (JCPDS card No. 36-1451). In above XRD pattern, extra peak appear at $2\theta = 44^\circ$. This peak was identified as surface hydroxyl groups, which can be related to the formation of water on the ZnO nanostructure surface [17].

Transmission electron microscope

Fig. 2 shows transmission electron microscope image of ZnO nanostructure synthesized by chemical route method. It is clearly seen from the TEM image that the ZnO powders consist of large number of nanorods which were cumulated to form superior size crystal.

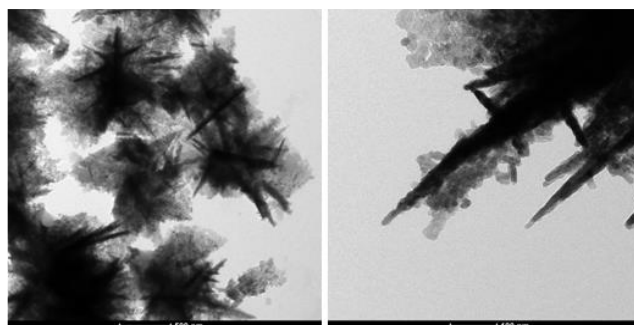


Fig. 2. TEM image of ZnO nanostructure synthesized by chemical route method with different magnification.

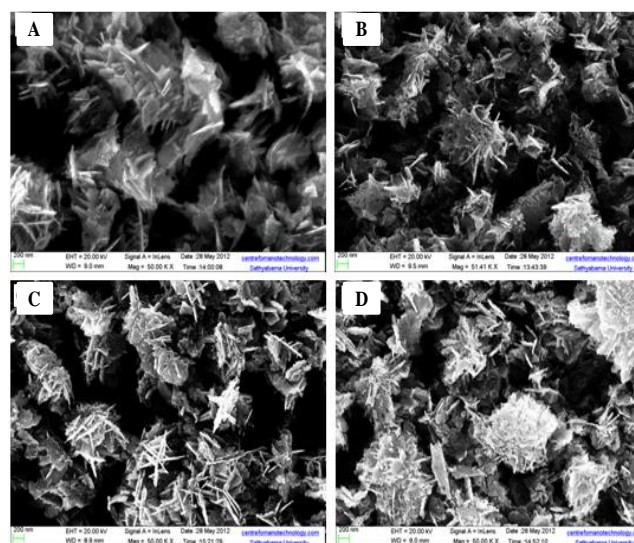


Fig. 3. FE-SEM images of (A) pure ZnO thick film, (B) TiO₂ modified ZnO thick film (1 min), (C), TiO₂ modified ZnO thick film (3 min) and (D) TiO₂ modified ZnO thick film (5 min).

Scanning electron microscopic study

Fig. 3 shows typical FE-SEM images of the pure and TiO₂ modified ZnO thick film prepared by screen printing technique. The ZnO synthesized by the chemical route method consist of randomly distributed nanosheets and nanorods as shown in **Fig. 3 (A)**. **Fig. (B)**, illustrate the FE-SEM image of TiO₂ modified ZnO thick films (1 min dipping), consist of small amount of nanowires which were randomly deposited on the surface of ZnO thick film. These nanowires could be attributed to TiO₂. Due to such a deposition of nanowires, surface to volume ratio of the

ZnO thick film may be increased. **Fig. 3 (b-d)** represents that, as the dipping time increases amount of TiO₂ nanowires on the surface of ZnO thick films increases.

Electrical measurements

Fig. 4 represents the *I-V* characteristics of the pure and TiO₂ modified ZnO thick films at temperature 100°C. Keithley 6487 picoammeter cum voltage source was used for this measurement. Current was measured while the bias voltage increased from 0 to 50 V with the step of 5V. The measurement was repeated with negative voltage. The symmetrical nature of the *I-V* characteristics for particular samples shows that the contacts are ohmic in nature.

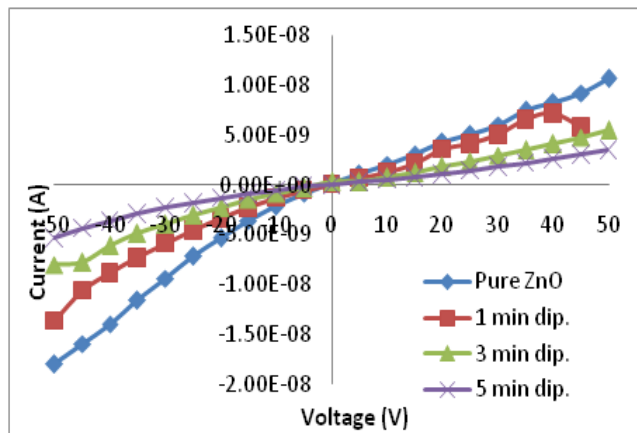


Fig. 4. *I-V* characteristics of pure and TiO₂ modified ZnO thick films.

Gas sensing properties

The gas response of pure and TiO₂ modified ZnO thick films were investigated at room temperature and 125°C. **Fig. 5** illustrates the responses to 100 ppm CO₂ LPG and NH₃ of pure and TiO₂ modified ZnO thick films at room temperature. Pure ZnO thick film gives somewhat high response to NH₃ at room temperature as compared to modified thick films. At room temperature highest response of pure ZnO thick film is found to be 6.2.

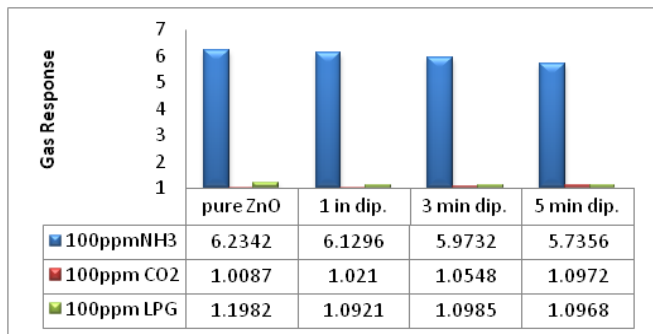


Fig. 5. Gas response of pure and TiO₂ modified thick films at room temperature.

Fig. 6 illustrates the responses to 100 ppm CO₂, LPG and NH₃ of pure and TiO₂ modified ZnO thick films at temperature 125°C. At this temperature pure ZnO thick

film gives somewhat less response to NH₃ at room temperature as compared to modified thick films. With increase in temperature of pure and modified thick films, response to NH₃ increases sharply. **Fig. 5** and **6** represent that, response of pure and modified thick films to 100 ppm CO₂ and LPG is very less or negligible at room temperature as well as at 125 °C. Therefore selectivity of these thick films to 100 ppm NH₃ is high among test gases.

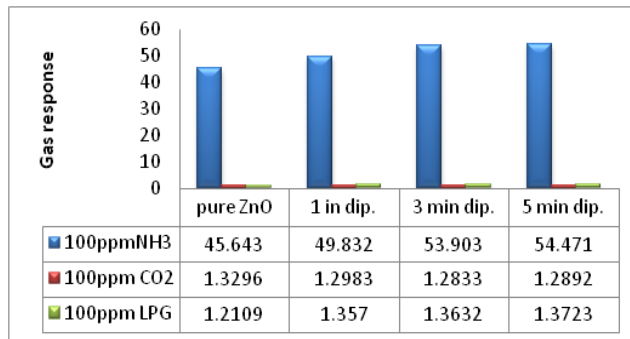


Fig. 6. Gas response of pure and TiO₂ modified thick films at temperature 125°C.

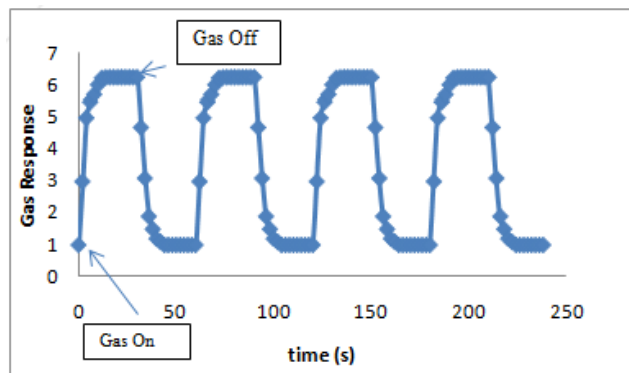


Fig. 7. Gas response & recovery of pure ZnO thick film at room temperature.

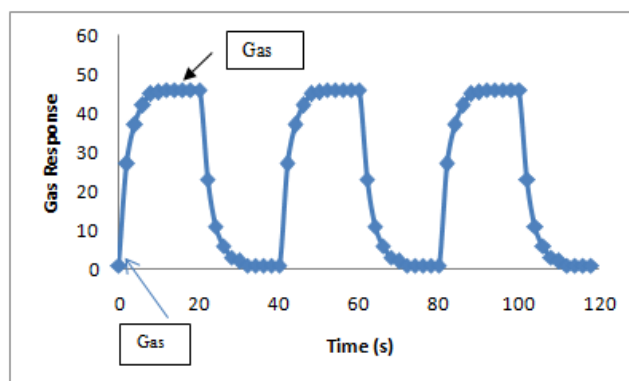


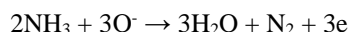
Fig. 8. Gas response & recovery of pure ZnO thick film at temperature 125°C.

Fig. 7 and **8** depict the variation of response to 100 ppm NH₃ with time for pure ZnO thick film at room temperature and 125°C respectively. The response and recovery time of pure ZnO thick film at room temperature was found 10s and 14s respectively. Whereas at 125°C, response and recovery time of pure ZnO thick film was

found to be 6s and 8s respectively. The gas sensing properties of the pure and TiO₂ modified ZnO thick films were studied. It is observed that the gas sensing properties is greatly influenced by the operating temperature.

Discussion

From **Fig. 5**, it can be seen that pure ZnO thick films are sensitive to ammonia at room temperature. Response of pure ZnO thick film to NH₃ may be attributed to adsorption and desorption of oxygen on the surface of thick film. With small grain size and large surface to volume ratio, the surfaces of ZnO nanorods have more active sites to adsorbed NH₃, which would react with the adsorbed O⁻ and release with trapped electron back to conduction band of the ZnO. This leads to an increase in conductivity of ZnO. This process could be expressed as,



Another reason in favor of response at room temperature is that, the adsorption of oxygen on the surfaces of the ZnO rods forms a surface depletion layer. The width of the depletion layers of ZnO is about several nanometers in air [18]. The depletion layer increases the width and height of the contact potential barrier between the rods. When exposed to NH₃, the surface depletion layer of single ZnO rod attenuates, leading to reduces in the width and height of the contact energy barrier between the ZnO rods, which can control electron transport [19, 20]. As a result, increase in conductivity of thick film.

Fig. 5 shows that, the response of modified thick films was slightly less than pure ZnO thick film. This could be attributed to inactiveness of TiO₂. At room temperature, titanium oxide directly does not contribute in sensing mechanism, but presence of its decrease few active sites on the surface of ZnO thick films. As a result, decrease in the sensitivity.

At higher temperature (**Fig. 6**), sensitivity to ammonia of ZnO thick film increase sharply, because the reaction between NH₃ molecule and adsorbed O⁻ is more favorable. At 125°C, response of modified thick film was higher than pure ZnO thick films. This may be attributed to participation of TiO₂ in sensing mechanism. Immediate Response and fast recovery of pure and modified ZnO thick films at room temperature and at higher temperature could be explain on the basis of rate of reaction between the NH₃ molecule and adsorbed oxygen on the surface of thick film.

Conclusion

The results of the sensing performance of pure and TiO₂ modified ZnO thick films can be summarized as

1. Zinc oxide powder synthesized by chemical route method consists of nanorods associated with nanoparticles with average crystallite size 36 nm.
2. Pure ZnO thick films are observed to be more conductive as compared to TiO₂ modified ZnO thick films.
3. Pure ZnO thick films showed high sensitivity and selectivity to 100 ppm NH₃ gas at room temperature.

4. In case of surface modified thick films, TiO₂ modified ZnO thick film (1 min dipping) shows higher conductivity.
5. All TiO₂ modified ZnO thick films shows sensitive to NH₃ at room temperature.
6. With increasing temperature sensitivity to NH₃ of pure and modified thick film increases sharply.

At higher temperature, pure and TiO₂ modified ZnO thick films shows rapid response and fast recovery as compared to room temperature.

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