Study on influence of Fe doping into ZnO film for ethanol sensing

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Abstract. In recent times, the importance of nanostructure of metal oxide semiconductor (MOS) as a gas sensing material is rising tremendously. Among various metal oxide semiconductors ZnO has potential to be used as a sensor for several toxic gases. In this work, we investigated the influence of Fe doping into ZnO to detect various concentrations of ethanol vapour. Pristine and Fe doped ZnO (Fe-ZnO) films were deposited on glass substrates using a spin coating technique wherein the concentration of Fe can be easily controlled. The crystallite size and surface morphology of ZnO samples were characterized by XRD, SEM and EDX techniques. The sensor performance in terms of gas response (R) of ZnO and Fe-ZnO gas sensors towards ethanol vapour were measured in the 100 to 300°C temperature range using DC electrical resistance. Fe doped ZnO samples showed enhancement in gas response due to increase in specific surface area originated from reducing grain size after doping. The 2% Fe-ZnO sample showed the good response of 40.9 for 400 ppm of ethanol vapour exposure at 260°C. This was found to be better than reported values for ZnO prepared by different methods.

Key Words: Gas sensor, Ethanol, Fe-ZnO, Sensitivity, Response time.

1. INTRODUCTION

Nano-structured metal oxide semiconductors (MOS) are promising candidates for detecting different types of flammable, hazardous and toxic gases originated at the different sites such as research laboratory, home kitchens, shopping malls, etc [1-2]. The gas sensing properties of MOS materials depend on the following factors; nanostructure and surface morphology, coupling action of gas molecules with MOS surfaces under given conditions, exposed gas quality and concentration and applied sensor geometry [3-5]. By reducing the size from bulk to nano, we improve the specific surface area of the material. This becomes one of the key impetuses in enhancing MOS sensor performance [6]. Currently, various types of MOS such as SnO₂, In₂O₃, Fe₂O₃, TiO₂, CuO, Ce₂O₃, ZnO [7-11] have been used as good sensors to detect several toxic gases. However, we still need to overcome some difficulties such as high operating temperature, low sensitivity percentage or gas response, large response and recovery times in order to advance the use of MOS gas sensors. In this regard, an in-depth and systematic investigation of metal doped ZnO prepared by different methods is an interesting problem because it can bring the changes in crystal structure and underlying electrical and electronic properties of the oxide material [12, 13]. In this work, we investigated the impact of Fe doping into the ZnO to fabricate an economic, low temperature operating, gas sensor. ZnO is an...
attractive compound semiconductor which generally exists as an n-type with wide band gap of 3.37 eV, a large exciton binding energy of 60 meV at room temperature, and piezoelectric [14-17]. Interestingly, the electrical, electronic and optical properties of ZnO can be tailored effectively in the preparation of its nano material [18-21]. ZnO, a chemically and thermally stable compound, has been extensively studied for various applications from industry to medical field. The quality of thin films of semiconductors always depends on its synthesis route. Though various sophisticated and costly methods are available to prepare thin film of ZnO, the reason for using spin coating was its simplicity and low running cost where the action of metal doping into ZnO can be effectively performed [22]. Preparation, characterization of undoped and 1-4 at.% Fe doped ZnO (Fe-ZnO) samples and its utilization to sense low concentrations of ethanol vapour were investigated herein. The changes in structure, surface topology, electrical and optical properties of films were studied using X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray (EDX) and UV-Vis spectroscopy. The impact of Fe doping into ZnO towards ethanol vapour detection were reported.

2. EXPERIMENTAL

2.1 Film Preparation
ZnO films were deposited on glass substrate using 0.35M ethanol solution of zinc acetate along with diethanolamine. Same molar ferric nitrate tetrahydrate solution was added as a dopant into the zinc acetate precursor solution. All the chemicals used here were of analytical grade. Prior to this, the glass substrates were rinsed systematically with acetone and deionised water in an ultrasonic bath and then dried in the hot air oven at 50ºC for 30 minutes to get free from foreign materials. The undoped and 1-4% Fe-doped ZnO thin films were deposited on glass substrate by using a spin coater with 3000 rpm and spin time of 30 secs which were finally annealed in air at 450ºC for 1 hr. The process is repeated few times to deposit another layer to get desire thickness [23].

2.2 Characterization of ZnO films
The structural investigation of above prepared ZnO thin films were done using X-ray diffraction (XRD) with Cu-Kα radiation (1.54056 Å) in the 2θ range from 20 to 80º. The crystallite size (D) was estimated using Debye-Scherer’s equation [24]:

\[ D = \frac{K \lambda}{\beta \cos \theta} \]  

where K (0.94), λ, β and θ are shape factor, x-ray wavelength, full width half maximum and Bragg’s angle respectively. The surface morphology, film composition and optical spectra of these films were studied using ZEISS scanning electron microscope, energy dispersive X-ray spectrum and UV-Vis spectrophotometer correspondingly.

2.3 Sensor performance
A gas sensing device consisted of air tight glass chamber having two openings, inlet and outlet, along with a heating device was used to measure change in resistance of film before and after exposing ethanol vapour in the temperature range of 100–300ºC. The operating temperature of heater was controlled by varying the current of heating coil using a variable voltage regulator. The initial temperature inside the chamber was maintained at 100ºC above the boiling point of ethanol to prevent the formation of liquid ethanol. The response (R) of the ZnO films towards ethanol was calculated by using the following formula:

\[ R = \frac{R_a}{R_g} \]  

where \( R_a \) and \( R_g \) are the resistances of the sensing element in the air and gas respectively [25]. The
corresponding response time, defined as the time required to change its response by 90% of maxima after injecting test gas from the setup.

Figure 1. X-ray diffraction pattern of ZnO films

3. RESULTS AND DISCUSSION

3.1. Structural properties

Figure 1 shows the x-ray diffraction pattern of spin coated undoped and 1-4% Fe-ZnO thin films. The pattern showed that the undoped ZnO was of polycrystalline nature with diffraction peaks orientated along (100), (002), (101), (102) (110), (103) and (112). The purity of the film deposited was checked with respect to the standard d-spacing of ZnO from JCPDS card no., 36-1451. Similar XRD patterns with major peak orientations along (100), (002), and (101) but slightly shifting towards larger angle were found for 1-4% Fe-ZnO indicating decrease of d-spacing after Fe doping. This may be due to substitution of Zn$^{2+}$ ions (0.74 Å) by smaller ionic radius Fe$^{3+}$ (0.68 Å). The sharp and intense high intensities of (002) diffraction peaks found in all the Fe-ZnO samples show preferred c-axis orientation. Table 1 below illustrates the measured average crystallite size, D values corresponding to major peaks (100), (002) and (101) of undoped and 1-4% Fe-ZnO films using Debye Scherrer’s formula (equation 1). The value of crystallite size of undoped and 1% Fe-ZnO was about 23 nm. For

| Sample   | Plane (hkl) | 2θ (degree) | d (Å)  | d (Å) JCPDS | Average D (nm) |
|----------|-------------|-------------|--------|-------------|----------------|
| Undoped  | (100)       | 31.7541     | 2.8156 | 2.8143      | 23             |
|          | (002)       | 34.4202     | 2.6034 | 2.6033      |                |
|          | (101)       | 36.2394     | 2.4732 | 2.4759      |                |
| 1%Fe-ZnO | (100)       | 32.2501     | 2.7735 | 2.8143      | 23             |
|          | (002)       | 34.9135     | 2.5677 | 2.6033      |                |
|          | (101)       | 36.7189     | 2.4456 | 2.4759      |                |
| 2%Fe-ZnO | (100)       | 32.2106     | 2.7717 | 2.8143      | 19             |
|          | (002)       | 34.8792     | 2.5659 | 2.6033      |                |
|          | (101)       | 36.6756     | 2.4444 | 2.4759      |                |
| 3%Fe-ZnO | (100)       | 32.1838     | 2.7791 | 2.8143      | 17             |
|          | (002)       | 34.8766     | 2.5704 | 2.6033      |                |
|          | (101)       | 36.6371     | 2.4508 | 2.4759      |                |
| 4%Fe-ZnO | (100)       | 32.0905     | 2.7869 | 2.8143      | 16             |
|          | (002)       | 34.7727     | 2.5779 | 2.6033      |                |
|          | (101)       | 36.5402     | 2.4571 | 2.4759      |                |
increasing Fe concentrations, the value of D continuously decreased from 23 nm for 1% Fe-ZnO to 16 nm for 4% Fe-ZnO film. This change in crystallite size produces strains in the film which leads to change in surface morphology of Fe-ZnO films [26].

3.2. Optical properties
Figure 2a shows the optical transmission spectra of undoped and Fe-doped ZnO samples captured in the wavelength range 300-1100 nm at room temperature. The transmittances of as-prepared films were more than 80%. The graph showed sharp decrease of transmittance at short wavelengths near the ultra-violet range but improved in the visible range for Fe-ZnO films. The band gap ($E_g$) of ZnO films were calculated from the tauc plot (Figure 2b) described by the equation:

$$(a \nu)^2 = A(\nu - E_g) \ldots \ldots \ldots \ldots \ldots \ldots (3)$$

where $\alpha$, $A$, $\nu$, and $E_g$ are the absorption coefficient, energy constant, photon energy and band gap respectively [27]. The results showed $E_g$ increases from 3.208 eV for undoped to 3.247 eV for 4% Fe doping sample. This increase in $E_g$ due to Fe doping was found to be consistent with the reports on similar system due to decrease in grain size of MOS film [28]. If Fe$^{3+}$ ions substitute the Zn$^{2+}$ ions from their lattice sites, the additional free charge carriers were added which were responsible for shifting the Fermi level into conduction band to increase the band gap of Fe-ZnO films.

3.3 Surface morphology
Surface morphology of as deposited ZnO films was investigated by using Scanning Electron Microscopy (SEM).
Figure 3(a) through 3(e) shows the SEM images of undoped and 1-4% Fe doped ZnO films respectively. The images clearly showed the agglomeration of ZnO grains with decreasing grain size for increasing doping concentration in the Fe-ZnO films. Compared to undoped and 1% Fe-ZnO films, the 2% Fe-doped ZnO film showed significant decreased grain size. When the grain size decreases, its specific surface area increases and more oxygen molecules are adsorbed which leads to enhance the sensing property of ZnO sensors [29].

Figure 4 shows the energy dispersive X-ray diffraction (EDX) spectra of the undoped and Fe-doped thin films. The EDX patterns reveal the presence of Zn, O and Fe elements, which confirms the purity of products and successful doping of Fe-ions into host ZnO structure. Inset of figure 4 shows the atomic % of elements content in the prepared ZnO samples.

3.4 Sensing characteristics
Since the performance or response of the MOS gas sensor at the given temperature is proportional to the reaction rate and activation energy ($E_a$), the optimization of its working temperature is required prior to measure its sensitivity. The activation energy ($E_a$) is described by Arrhenius equation [29-31]. During the process, when thermal energy approaches the limit to overcome the activation energy barrier of reaction, charge concentrations significantly increase and a high response results [30, 32]. Above this optimum value desorption of oxygen molecules occurs from the ZnO surface which can reduce response of gas sensor.
In this investigation, the sensor response is measured in terms of resistance change. The resistances of undoped and Fe doped ZnO films were measured in air and in ethanol vapour separately in the temperature range from 100 to 300ºC to optimize the working temperature and the gas response (R) is calculated using equation (2). The response of all the samples increased with temperature till it attains the saturated value after which decreases as shown in figure 5. The working temperature undoped and 1-4% Fe-ZnO samples were found to be 260, 240, 260, 240 and 240ºC correspondingly. The table 2 illustrates the measured values of R of undoped and 2% Fe doped ZnO films. Figure 6(a) illustrates the gas response of undoped and 1-4% Fe-ZnO at their respective working temperatures with various concentrations of ethanol (40-400 ppm). It clearly showed increasing response for increasing ethanol concentration. The result showed highest response of 40.91 for 2% Fe-ZnO at 260 ºC. This enhancement in R of Fe-ZnO samples with respect to undoped ZnO may be due to increase in its specific surface area (surface to volume ratio) and due to increase in carrier concentration after Fe doping in to the ZnO [33]. In Fe-ZnO samples, the substitution of Zn\textsuperscript{2+} ions by Fe ions (Fe\textsuperscript{3+}) surpluses the charge carriers that aids to enhance the reaction rates of exposed gas with adsorbed oxygen species in the measurement of gas response. This may be the primary reason to show higher gas response in Fe-ZnO samples than undoped sample. These results are consistent with the report published by Yu et al, 2011[3]. But, at very higher concentration of Fe doping such as 3 and 4% in our case more scattering atoms may available on the ZnO surface [34] that decreases the surface reaction rate and declines the oxygen capturing sites [35] and hence the response is reduced further. For clarity the graph of response of undoped ZnO and 2% Fe-ZnO along with the calculated value of response and recovery times are shown in figure 6(b). The measured values of gas response, response and recovery times of all ZnO samples are shown in table 3. The response time and recovery time were observed to be 27 sec and 288 sec in 2% Fe-ZnO sample at 400 ppm of ethanol.

![Figure 6](image_url)

**Figure 6.** (a) Gas response of undoped and 1-4% Fe-ZnO films at its operating temperatures at various concentrations of ethanol (b) Zoom in response values of undoped and 2%Fe-ZnO along with measured values of response and recovery times.

**Table 2.** Comparison of performance of ZnO based ethanol sensor in this work with reported work

| Materials | Method                  | Operating Temperature. (ºC) | Ethanol (ppm) | Response ($R_a/R_b$) | Reference |
|-----------|-------------------------|-----------------------------|---------------|----------------------|-----------|
| Fe-ZnO    | Hydrothermal            | 400                         | 500           | ~ 55                 | [3]       |
| CuO       | Micro-wave assisted hydrothermal | 210                       | 1000          | 9.8                  | [10]      |
| ZnO       | Thermal Evaporation     | 250                         | 50            | 14.4                 | [11]      |
| Sn-ZnO    | Thermal oxidation reaction method | 340                       | 1000          | 30.4                 | [12]      |
| Ti-ZnO | Furnace system with hot wire assistance | 250 | 500 | 2.76 | [13] |
|-------|----------------------------------------|-----|-----|------|------|
| ZnO   | Micro-wave assisted                    | 350 | 500 | 250  | [20] |
| Al-ZnO| Sol–gel method.                        | 500 | 2000| 92   | [25] |
| Fe-ZnO| Hydrothermal/dip coating               | 250 | 500 | 19   | [30] |
| Fe-ZnO| RF magnetron sputtering                | 300 | 300 | 2.91 | [33] |
| Ce-ZnO| Dip Coating                            | 320 | 100 | 80%  | [34] |
| Fe-ZnO| Spin Coating                           | 260 | 400 | 40.9 | 22.9 | This work |

Table 3. Gas response and response time and recovery time of ZnO and 2% Fe-ZnO at different ppm of ethanol

| Ethanol Concentration (ppm) | Undoped ZnO | 2% Fe-ZnO |
|-----------------------------|-------------|-----------|
|                             | Gas Response ($R_a/R_g$) | Recovery Time (sec) | Gas Response ($R_a/R_g$) | Recovery Time (sec) |
| 40                          | 5           | 35        | 254        | 22.9       | 21        | 288 |
| 80                          | 6           | 38        | 236        | 24.4       | 16        | 289 |
| 160                         | 7           | 44        | 268        | 30.0       | 21        | 279 |
| 200                         | 7.7         | 52        | 291        | 37.5       | 24        | 275 |
| 400                         | 12.8        | 62        | 294        | 40.9       | 27        | 288 |

4. CONCLUSIONS

In summary, the undoped and various Fe (1, 2, 3 & 4%) doped ZnO thin films were prepared using an economic and effective spin coating technique where doping percentage can be easily controlled. The XRD characterization showed polycrystalline wurtzite structure nature ZnO films along with slight disturbance in microstructure of ZnO due to Fe doping was confirmed by X-ray diffraction pattern. The purity of as-prepared films was confirmed by XRD as well as EDX spectra. The observation of increasing trend of band gap for increasing doping percentage agreed with reported value. The reduced grain size of ZnO after Fe doping shown by SEM images aided in increasing the surface to volume ratio and available more electron transport due substitution of Zn$^{2+}$ ions by Fe$^{3+}$ be the primary reasons to observe enhanced gas response in 2% Fe-ZnO film. The highest response measured with 2% Fe doped ZnO was 40.91 and corresponding response and recovery times were 27 and 288 secs respectively at 400 ppm ethanol. Finally, this work also reports that the fabrication of economic but efficient MOS based gas sensor which can be utilized to detect as small as 40 ppm of ethanol vapour.

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