Enhanced Ammonia Sensing By Cost-Effective ZnO Thin Films Through Yttrium Doping

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Enhanced ammonia sensing by cost-effective ZnO thin films through Yttrium doping

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Nebulizer spray coated yttrium doped ZnO thin film for ammonia vapour sensing
Highlights

- Yttrium doped ZnO thin films have been fabricated for room temperature ammonia sensor
- Surface roughness and oxygen vacancies are created by yttrium doping
- Morphology and defect based gas sensing performance are explained
- The maximum sensitivity observed for 5% yttrium doped ZnO film
- The gas sensing mechanism yttrium doped ZnO film was proposed
Enhanced ammonia sensing by cost-effective ZnO thin films through Yttrium doping

Abstract

Yttrium (Y) doped (doping concentration - 0, 1, 3 and 5 wt%) ZnO thin films were deposited using spray pyrolysis technique. The structural, surface morphological, optical and compositional properties were analysed using X-Ray diffraction (XRD), Atomic Force Microscopy (AFM), UV-vis NIR spectrophotometry (UV), photoluminescence study (PL) and elemental composition analysis. Ammonia vapour sensing properties such as response/recovery, stability and repeatability were studied at room temperature. XRD results confirmed that the prepared samples have hexagonal wurtzite structure. ZnO:Y thin film with 5 wt% yttrium doping exhibits excellent sensing response of 99, fast response/recovery times of 29 s/7 s which may be due to the existence of oxygen vacancies in the case of ZnO:Y (5 wt%) film sample confirmed by photoluminescence (PL) study. These oxygen vacancies attract more electrons and thus enhance the gas sensing. In addition, increase in the number of active sites caused by the substitution of $Y^{3+}$ (trivalent) ions into the $Zn^{2+}$ (divalent) regular sites as confirmed by the observed M-B (Moss-Burstein) effect also causes an enhancement in the gas sensing. Surface roughness, another reason for the enhanced sensitivity, has been confirmed by AFM.

Key words: Thin films, Yttrium doped ZnO, Nebulizer Spray Pyrolysis, NH$_3$ sensor
1. Introduction

Recent days, ammonia gas sensors play an important role in the industries of explosives, fertilizers, textiles and plastics [1]. The acceptable limit of ammonia for human body is 25 ppm, beyond which it can affect the various parts of the body causing damage to skin, eyes and respiratory tract [2]. Hence, researchers pay attention on making cost-effective ammonia sensors with improved ‘3S’ parameters viz. sensitivity, stability and selectivity [3].

Plenty of metal oxide semiconductors like V$_2$O$_5$, SnO$_2$, TiO$_2$, NiO, BaTiO$_3$ and ZnO are widely used to detect ammonia vapours [4-10]. Of these, ZnO is one of the promising materials due to its attracting properties which include high thermal and chemical stability, non-toxicity, wide band gap, availability, environmentally benign nature, low-cost and ease of doping [11].

Moreover, literature survey shows that the gas sensing ability of ZnO can be improved through the addition of suitable dopants. Select dopants desirably alter the energy gap and surface morphology of the host material. In addition, doping causes an increase in defects and carrier concentration and thereby favouring the sensing phenomena [12]. Various rare earth metals like lanthanum, cerium, erbium, terbium, gadolinium and yttrium [13-18] have been used as dopants owing to their unique properties. Among the various rare earth elements, yttrium is used as dopant because of its peculiar properties arising from the 4f shell such as changes in energy band structure, morphology, surface to volume ratio and ability for creating more active centres at the grain boundaries [19, 20]. Thus, the gas sensing response of ZnO can be improved by the addition of suitable proportion of yttrium.

Li and co-workers reported that yttrium doped ZnO nanofibers exhibit good sensing to acetic acid [21] due to the large specific surface area and small grain size of ZnO:Y nanofibers. Nithya et al. reported that yttrium doped titania nanoparticles prepared towards ethanol sensing exhibit short response/recovery times and long-term stability that may be due to the small crystal size
and increase in oxygen vacancies [22]. Shruthi et al. reported that $\text{Y}_2\text{O}_3$-$\text{In}_2\text{O}_3$ nanocomposites exhibit sharp response/recovery times for methanol detection. It may be attributed to the formation of hetero junction between host and dopant materials [23]. However, to the best of our knowledge yttrium doped ZnO thin films towards ammonia sensing is scarcely available in the literature.

Undoped and doped ZnO films can be prepared by different techniques like magnetron sputtering, hydrothermal, sol gel, wet chemical route, SILAR and nebulizer spray Pyrolysis method [24-29]. Among these methods, nebulizer spray pyrolysis offers many advantages: economic, simple and safe, facilitate large surface area coating, flexible process parameters and uniform thickness [30].

In this work, undoped and yttrium doped ZnO film sensors have been developed using cost effective nebulizer spray pyrolysis method. The sensing ability, response and recovery times and stability of the sensor towards the reducing vapour ($\text{NH}_3$) at room temperature were studied and reported.

2. **Experimental details**

2.1 **Chemicals used**

Zinc acetate dihydrate ($\text{Zn(CH}_3\text{COO)}_2\cdot\text{2H}_2\text{O}$), yttrium nitrate hexahydrate($\text{Y(NO}_3\text{)}_3\cdot\text{6H}_2\text{O}$) were purchased from Sigma Aldrich and used without any further purification.

2.2 **Film deposition**

$\text{Zn(CH}_3\text{COO)}_2\cdot\text{2H}_2\text{O}$ and $\text{Y(NO}_3\text{)}_3\cdot\text{6H}_2\text{O}$ were used as host and dopant precursors, respectively and methanol (10 mL) was used as solvent. Four sets of stock solutions (0.2 M) were prepared with dopant concentrations 0, 1, 3 and 5wt%. The solution was stirred for 15 minutes at 35°C. Substrates (glass) were cleaned well with usual cleaning procedure and then
placed on the substrate holder (hot plate) maintained at 450°C. The solution was sprayed on the hot substrates over the area of 2.5 x 7.5 cm². The distance between the spray nozzle and substrate was optimized as 30 mm. Nebulizer was mounted with the help of a stand and slowly moved in horizontal direction to cover large surface area. After the deposition, the hot plate was allowed to cool to room temperature.

2.3 Characterization techniques

The structural characterization of the prepared thin films was made using X-ray diffraction (Panalytical X’Pert PRO) using Cu-Kα radiation (λ=0.1540nm). Stylus profilometer was used to measure the thickness of the prepared films. Atomic Force Microscope was used to analyse the surface topography of the samples. A UV-vis-near-IR spectrophotometer (Perkin Elmer Lamda-35) was used to study the transmittance. Fluorescence spectrophotometer (Perkin Elmer LS55) was used to record the photoluminescence spectra at room temperature (λexc= 325 nm). Keithley Meter model-2450 was used to study the room temperature (32°C) ammonia sensing.

2.4 Sensing study

The gas sensing setup consists of a cylindrical chamber and a computer assisted Keithley electrometer (model- 2450). The prepared thin film was placed inside the chamber and to attain a baseline, the sample’s resistance was measured under dry air. The ammonia taken in solution form was injected into the chamber with the help of microliter syringe. The introduction of NH₃ vapour produces a marked change in the resistance of the sensor. The reduction in resistance confirms the n-type behaviour of the sensor towards reducing vapours like NH₃. The change in resistance was observed using Keithley meter. The chamber is opened to air ambience when the resistance attained the saturation level. The resistance values were measured with respect to baseline and recorded for different ammonia concentrations.
3. Results and discussion

3.1 XRD study

Figure 1 shows the X-Ray diffraction patterns of pure and doped ZnO thin films with yttrium doping concentrations 1, 3 and 5 wt%. From the figure, we observed that all the peaks at different 2θ values match well with the JCPDS card no 36-1451 which confirms the wurtzite (hexagonal) structure of the ZnO. The diffraction peaks are at the angles 31.82°, 34.53°, 36.25°, 47.66°, 57.12°, 63.20° and 68.32° correspond to the Miller indices (100), (002), (101), (102), (110), (103) and (112), respectively. No secondary peaks related to yttrium as well as no shift in XRD peaks were observed which may be due to the low doping concentration of yttrium. From Fig.1, it is clearly observed that the preferential growth of ZnO:Y is along (002) plane. The intensity of this preferential orientation decreases as the yttrium doping level increases which may be due to the deterioration of crystallinity [31]. This reduction in intensity may be due to the possible movement of zinc atoms into interstitial sites from the regular zinc locations caused by the substitution of yttrium ions [32]. Scherrer’s formula was applied for calculating the crystallite size (D),

\[ D = \frac{0.94 \lambda}{\beta \cos \theta} \]  \hspace{1cm} (1)

Dislocation density and lattice parameters can be calculated using the formula,

\[ \frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + k^2 + hk}{a^2} \right) + \frac{l^2}{c^2} \] \hspace{1cm} (2)

\[ \delta = \frac{1}{D^2} \] \hspace{1cm} (3)

The calculated values of crystallite size are presented in Table 1. We noticed that the crystallite size gradually decreases with the increase of yttrium doping level. This may be due to the incorporation of Y^{3+}(0.89 Å) into Zn^{2+} (0.74 Å) site which causes deformation in the lattice system. This deformation in turn can lead to the restriction of growth of crystallite boundaries.
called Zener pinning effect [33]. Rietveld refinement analysis was performed using Bruker Topas version 6 to study the lattice parameters. From Table 1, it can be seen that there is a slight change in the lattice parameter values after doping which may be attributed to the difference in the ionic radii of zinc and yttrium ions. The observed increase in the value of dislocation density with the increase in doping concentration of yttrium shows the formation of defects on the surface of the film [34]. Reduction in the size of the crystallites and the increase in the defects will help for adsorbing more ammonia molecules [35].

### 3.2 Surface morphological study

Figure 2 shows the AFM images of the pure and yttrium (1, 3 and 5 wt%) doped ZnO films. From the figure, we can observe clear edges of the grains which are generally highly reactive when exposed to target gases. This is one of the main advantages in gas sensing applications [36]. The undoped ZnO thin film exhibits relatively low surface roughness, whereas, considerably higher roughness is observed when yttrium is incorporated into ZnO lattice. The roughness value for pure ZnO increases from 26 to 46 nm due to the influence of yttrium doping. This increase in roughness results in more active centres for gas adsorption favouring better sensing as explained by Wenzel’s effect [37, 38]. EDX was used to identify the presence of elements in the prepared films. Figure 3a and b shows the EDX spectra which confirms the existence of zinc, oxygen and yttrium in the samples.

### 3.3 Photoluminescence study

In order to analyse the surface defects, photoluminescence (PL) study was used. Fig. 4 shows the PL spectra and its Lorentz fitting of pure and yttrium doped ZnO films. The emission band observed at 384 nm is related to the transition between the CB and VB [39]. This peak is found to shift to lower wavelength side due to the influence of yttrium doping. The blue-green emission peaks observed at 435 nm (2.84 eV) and 488 nm (2.53 eV) correspond to Zn$_i$ (zinc
interstitials) and singly ionized V\textsubscript{o} (oxygen vacancies) as reported by Kumar \textit{et al.} [40] and Radhidevi \textit{et al.} [34]. Thus, the PL study confirms that the electron donor defect concentration increases when yttrium doping concentration is increased, which is favourable for gas sensing as it can be able to attract more number of gas molecules. In our case, the peaks shifted slightly towards the higher wavelength may be attributed to the bond length of Y-O (2.3 Å) is relatively higher than Zn-O (1.89 Å). Therefore, the origin of the emission defects could be varied with respect to metal doping.

3.4 Optical study

Figure 5 shows the extrapolation of the leading edges of the plot to the x-axis giving the energy band gap as per the Tauc’s relation,

\[
(\alpha h\nu)^2 = A(h\nu - E_g)
\]

From the figure, we can observe a slight increase in the energy gap as the yttrium doping concentration increases. This increase in the band gap may be due to the uplift in electron number caused by the Y\textsuperscript{3+} (trivalent) ions incorporation into the ZnO lattice. When, we dope yttrium with ZnO, the Fermi level moves towards the conduction band of ZnO resulting in band gap widening as explained by Moss-Burstein effect [41].

3.5 Sensing characteristics

3.5.1 Selectivity

The sensing response of the prepared sample (ZnO:Y-5wt%) tested towards six reducing vapours under room temperature is shown in Fig. 6. The selectivity study was carried out by keeping the concentration at 100 ppm and the response was calculated using the formula,

\[
S = \frac{R_a}{R_g}
\]
The response values of the films are 4, 7, 10, 16, 22 and 99 for toluene, acetone, isopropanol, ethanol, methanol and ammonia. From the results, we observed that the film shows poor response to toluene, acetone, isopropanol, ethanol, methanol compared to ammonia. The reason for the best response to ammonia may be the electron donating ability of ammonia compared to other tested vapours due to the presence of lone pair of electrons [42].

3.5.2 Sensing characteristics

Figure 7 shows the response and recovery curves of pure and yttrium doped ZnO films exposed to NH$_3$ vapours (100 ppm) at 32°C. When yttrium doped ZnO thin films were exposed to NH$_3$ vapour, a rapid change in resistance was observed indicating the response at room temperature. The response values of the films are 22, 39, 52 and 99 for undoped and yttrium (1, 3 and 5 wt%) doped ZnO films, respectively. The corresponding response and recovery times are 52s/11s, 39s/9s, 30s/11s and 29s/7s. Response and recovery times are the time to reach 90% decrease from the base line upon exposure of target gas and the time taken to return back to the base line, respectively. The results show that 5 wt% yttrium doped ZnO film exhibits quick response and recovery times compared to other films. To study further, transient resistance response curves for 5 wt% yttrium doped ZnO films towards different concentrations of NH$_3$ vapours (from 100-200 ppm) were recorded (Fig.8). From the figure, we found the same fashion of reduction in resistance during the application of NH$_3$ and increase in resistance as the consequence of removal of NH$_3$ vapour for all the five cases. This decreasing and increasing nature of the resistance of n-type material shows the stability of the sensor.

Results of recent research works on NH$_3$ sensing at room temperature are presented in Table 2. Pandeeswari et al. reported that β-Ga$_2$O$_3$ film exhibits excellent sensing towards NH$_3$ and fast response/recovery times of 40 s/18 s. This rapid response may be due to the catalytic action of β-Ga$_2$O$_3$ [42]. Niu et al. reported that P$_2$O$_5$ catalyzed covalent triazine frameworks
exhibit short response/recovery times of 54 s/200 s. It may be attributed to the transfer of electrons between triazine ring and NH$_3$ molecules [43]. According to Yan et al., Ag$_3$PO$_4$ nanoparticles exhibit superior sensing activity towards NH$_3$. The reason may be the lone pair of NH$_3$ molecules that coordinate with the atoms of Ag$_3$PO$_4$, resulting in a large adsorption of energy and electron transferring [44]. Kathwate et al. reported that Al doped ZnO thin films exhibit fast response/recovery times of 29 s/ 19 s that might be attributed to the structural and morphological changes occurred due to Al doping [45]. In the present work, yttrium doped ZnO thin films exhibit short response/recovery times of 29 s/ 7 s towards NH$_3$ vapours.

3.5.3 Repeatability and stability

Repeatability, one of the important factors in sensing, was tested for 5 wt% yttrium doped ZnO film sensor for five cycles of NH$_3$ (100 ppm). We found that the response of the sensor remains the same for all the five cycles as shown in Fig. (9a) indicating that the prepared ZnO:Y film (with 5wt% doping) is a good sensing material for sensing NH$_3$ vapours.

The stability of the sensor is another essential parameter in vapour sensing. To determine the stability, 5 wt% yttrium doped ZnO sensor was tested after 50 days of its preparation with NH$_3$ vapours (100 ppm) at 32°C. Figure 9b shows that the response of the sensor is nearly the same even after 50 days.

3.5.5 Sensing mechanism

Gas sensing is a surface controlled reaction in which change in resistance of the sensor might be attributed to the adsorption and desorption of target vapours (Fig.10). The adsorbed oxygen molecules can form three types of ions (O$_2^-$-below 100°C(equation 6), O$^-$-between 100°C to 300°C and O$_2^-$-above 300°C). Previous reports showed the formation of O$_2$ ions on the film surface at room temperature [40]. In the present study, we believe that these oxygen ions
form a depletion layer over the surface of ZnO:Y films and thus resulting in a high electrical resistance.

\[ \text{O}_2 + \text{e}^- = \text{O}_2^{\text{ads}} \]  \hspace{1cm} (6)

Upon exposure to NH\textsubscript{3} vapours, desorption takes place and concomitantly electrons already trapped are released back to the film which results in reduction in resistance as per the equation (7). As ZnO is an n-type material having a wide band gap, large number of oxygen ions are adsorbed on the ZnO:Y film surface. Oxygen vacancies and zinc interstitials are donor defects favouring the adsorption of oxygen ions and consequently increase the interaction of NH\textsubscript{3} molecules with the sensing surface. The higher the donor defects the higher is the adsorption of oxygen molecules which leads to an increase in the sensing response as evidenced from the PL results.

\[ 4\text{NH}_3 + \text{O}_2^{\text{ads}} = 2\text{N}_2 + 6\text{H}_2\text{O} + 3\text{e}^- \]  \hspace{1cm} (7)

4. Conclusion

Yttrium doped ZnO films prepared using cost-effective spray pyrolysis technique exhibit good ammonia vapour sensing. The ZnO sensor with 5 wt% yttrium doping shows superior sensing response (99) and quick response/recovery times of 29 s/7 s for 100 ppm of ammonia at 32°C. ZnO:Y (5 wt%) film has more oxygen vacancies and zinc interstitials, which can adsorb more ammonia molecules during sensing. The enhanced sensing response may also be due to the excessive electrons donated by the trivalent (yttrium) ion into the divalent (zinc) lattice. The resultant band gap widening is evidenced by the Moss-Burstein effect. Increase in roughness plays a crucial role in sensing. From the above results, we have concluded that yttrium doped ZnO thin films can be considered as promising candidates for NH\textsubscript{3} sensing.

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**Conflict of interests**

The authors declare that they have no conflict of interest.

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**Figure Captions**

**Fig.1** X-ray diffraction patterns of ZnO and ZnO:Y thin films

**Fig.2** AFM images of ZnO:Y thin films with different Y loading levels a) 0 b) 1 c) 3 and d) 5wt%

**Fig.3 (a,b)** EDX spectra of ZnO and ZnO:Tb (5wt%) thin films

**Fig.4** Photoluminescence spectra of ZnO and Y doped ZnO thin films

**Fig.5** Tauc’s plot of ZnO and ZnO:Y (1, 3 and 5 wt%) thin films to measure the bandgap

**Fig.6** Selectivity of ZnO:Y-5wt% thin film towards various test vapours

**Fig.7** Response and recovery curves of ZnO:Y (0, 1, 3 and 5 wt%) thin films towards 100 ppm of NH₃ at room temperature

**Fig.8** Response and recovery curves of 5 wt% yttrium doped ZnO thin film towards various concentrations of NH₃

**Fig.9.a)** Repeatability curve of 5 wt% yttrium doped ZnO thin films **b)** Stability curve of ZnO:Y (0, 1, 3 and 5 wt%) thin films over 50 days

**Fig.10** Sensing mechanism of ZnO:Y thin film

**Table Captions**

**Table 1** Crystallite size, Lattice parameters and dislocation density of ZnO:Y (0, 1, 3 and 5 wt%) thin films

**Table 2** Response/recovery times and sensitivity of various materials towards NH₃ sensing
Fig. 1
Fig. 2
Fig. 5
Fig. 6

The bar chart shows the response of different chemicals: Tolune, Acetone, Isopropanol, Ethanol, Methanol, and Ammonia. The y-axis represents the response, ranging from 0 to 100, with each chemical having a distinct response value.
Fig. 7
Fig. 8
Fig. 9 a and b
O₂ Molecule  
NH₃ (Reducing gas)  
O₂⁻ Adsorbed oxygen  
e⁻ Conduction band electrons  
CB- Conduction band  
VB- Valence band  
E_F- Fermi energy  

Fig. 10
| Samples          | Lattice parameters | Crystallite size | Dislocation density $\delta \times 10^{15}$ lines/m$^2$ | Film thickness (nm) |
|------------------|--------------------|------------------|--------------------------------------------------------|---------------------|
|                  | a (Å)              | c (Å)            | D (nm)                                                 |                     |
| ZnO              | 3.222 (5)          | 5.231 (9)        | 32                                                     | 0.976               | 350                 |
| ZnO:Y (1%)       | 3.185 (2)          | 5.173 (8)        | 30                                                     | 1.111               | 340                 |
| ZnO:Y (3%)       | 3.186 (13)         | 5.155 (5)        | 29                                                     | 1.189               | 330                 |
| ZnO:Y (5%)       | 3.179 (2)          | 5.136 (9)        | 26                                                     | 1.479               | 320                 |
| Material                        | Method                  | Sensing Temperature | Concentration (ppm) | Response (S) | Response time(s) | Recovery time(s) | Ref.       |
|--------------------------------|-------------------------|---------------------|---------------------|--------------|------------------|------------------|------------|
| Sr doped ZnO                   | SILAR                   | RT                  | 100                 | -            | 22               | 6                | [34]       |
| β-Ga2O3                        | Spray pyrolysis         | RT                  | 0.5-50              | 19-33,250    | 40               | 18               | [42]       |
| P2O5 catalyzed triazine        |                         | RT                  | 50                  | 3.3%         | 54               | 200              | [43]       |
| Cds decorated PANI             | Chemical co-dispersion  | RT                  | 20-100              | 250          | 58               | 104              | [46]       |
| SnO2/MoS2                      | Hydrothermal            | RT                  | 50                  | 2080.36      | 23               | 1.6              | [47]       |
| NiO/CuO                        | Electroless deposition  | RT                  | 20                  | -            | 72.5             | 35               | [48]       |
| Pd/SnO2/RGO                    | One pot route           | RT                  | 100                 | 19.6         | 420              | 3000             | [49]       |
| Yttrium doped ZnO              | Nebulizer spray Pyrolysis | RT              | 100                 | 99           | 29               | 7                | Present work|
Figure 1

X-ray diffraction patterns of ZnO and ZnO:Y thin films
Figure 2

AFM images of ZnO:Y thin films with different Y loading levels a) 0 b) 1 c) 3 and d) 5wt%
Figure 3

(a,b) EDX spectra of ZnO and ZnO:Tb (5wt%) thin films
Figure 4

Photoluminescence spectra of ZnO and Y doped ZnO thin films
Figure 5

Tauc’s plot of ZnO and ZnO:Y (1, 3 and 5 wt%) thin films to measure the bandgap

Figure 6

Selectivity of ZnO:Y-5wt% thin film towards various test vapours
Figure 7

Response and recovery curves of ZnO:Y (0, 1, 3 and 5 wt%) thin films towards 100 ppm of NH3 at room temperature
Response and recovery curves of 5 wt% yttrium doped ZnO thin film towards various concentrations of NH3
Figure 9

a) Repeatability curve of 5 wt% yttrium doped ZnO thin films  
b) Stability curve of ZnO:Y (0, 1, 3 and 5 wt%) thin films over 50 days
Figure 10

Sensing mechanism of ZnO:Y thin film

**Supplementary Files**

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