Ammonia Sensing Performance of Nanostructure Cr Doped ZrO₂ Thin Film Deposited by Spray Route

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1. Introduction

Nanostructured thin films of pure ZrO₂ and Cr doped ZrO₂ have been prepared on glass substrate at 350 °C using spray pyrolysis technique. The films were deposited by spraying the solution of CrO₃ and ZrOCl₂.8H₂O having same concentration (0.05 M) in deionized water. Chronom oxide and Zirconium oxychloride were mixed at various volume ratios such as 3:97 %, 5:95 %, 7:93 % and 9:91 %. The films were annealed in air at 550 °C for an hour. These thin films were characterized by XRD, FE-SEM, TEM, SAED pattern and UV spectroscopy technique. The various gases were exposed on films in ambient air at different operating temperature. The Cr doped ZrO₂ thin films showed maximum gas response to ammonia (5-96) for 500 ppm at 300 °C. The parameters like grain size, gas response, selectivity, detection limit, stability, response and recovery time were reported and discussed.

2. Experimental Methods

2.1 Preparation of Nanostructured ZrO₂ Thin Films

As prepared precursor solution of ZrOCl₂.8H₂O (0.05 M) was sprayed, through a glass nozzle of 0.1 mm bore diameter on hot glass substrate at temperature 350 °C ± 5 °C at spray rate 5 mL/min for spray deposition time 20 min and these deposited sample was referred as C1. The horizontal movement was kept uniform and compressor air pressure controlled between 3 to 8 kg/cm², this had been done to optimized viscosity and surface tension and momentum of the droplet. Also substrate to nozzle distance played better role. The optimized spray parameters are tabulated in Table 1.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Process parameters for the nanostructured pure ZrO₂ and Cr doped ZrO₂ thin films</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spray parameters</td>
<td>Optimum Values</td>
</tr>
<tr>
<td>Nozzle</td>
<td>Glass</td>
</tr>
<tr>
<td>Nozzle to substrate distance</td>
<td>28 cm</td>
</tr>
<tr>
<td>Precursor Solution : Zirconium oxychloride octahydrate solution concentration (ZrOCl₂.8H₂O)</td>
<td>0.05 M</td>
</tr>
<tr>
<td>Doping Solution : CrO₃</td>
<td>0.05 M</td>
</tr>
<tr>
<td>Percentage Variation of dopant solution with base solution</td>
<td>3-97 %, 5-95 %, 7-93 % and 9-91 %</td>
</tr>
<tr>
<td>Solvent</td>
<td>deionized water</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>Compressed air</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>350 °C</td>
</tr>
<tr>
<td>Spray deposition time</td>
<td>20 Min</td>
</tr>
<tr>
<td>Solution Spray flow</td>
<td>5 mL/min</td>
</tr>
<tr>
<td>Carrier pressure</td>
<td>5 kg/cm²</td>
</tr>
</tbody>
</table>

2.2 Preparation of Nanostructured Cr Doped ZrO₂ of Thin Films

The glass substrate was cleaned by an ultrasonic cleaner to make surface hydrophilic. As prepared mixture of precursor solution of ZrOCl₂.8H₂O (0.05 M) and doping solution of CrO₃ (0.05 M) in mentioned percentage variation was sprayed through a glass nozzle of 0.1 mm bore diameter, on heated glass substrate at 350 °C ±10 °C temperature with constant flow spray rate 5 mL/min by means of air as a carrier gas. The process parameters of spray deposition of Cr doped ZrO₂ thin film is shown in Table 1. The pure ZrO₂ and Cr doped ZrO₂ thin films samples (C1 to C5) were annealed at 550 °C for 1 hour [11-15].
3. Results and Discussion

3.1 Determination of Film Thickness

The film thickness was measured by a weight difference method [12] using relation:

\[ t = \frac{M}{A \cdot \rho} \]  

where, \( M \) is the weight of the sample in g; \( A \) the area of the sample in cm\(^2\); \( \rho \) the material’s density in gcm\(^{-3}\).

The thickness of the films was represented in Table 3.

3.2 Structural Properties (X-Ray Diffraction Studies)

As prepared films were characterized by X-ray diffractometer (Philips PW 1730) using Cu Kα radiation (\( \lambda = 1.5418 \) Å). Fig. 1(a-e) shows the XRD pattern of pure ZrO\(_2\) and Cr doped ZrO\(_2\) thin films samples C1, C2, C3, C4 and C5 within range 20 to 80°. X-ray diffractogram of the material was confirmed the polycrystalline and nanocrystalline structures of the ZrO\(_2\). The diffraction peaks from various planes are matching well with standard JCPDS data card for ZrO\(_2\) [16]. The average crystallite size of the pure ZrO\(_2\) and Cr doped ZrO\(_2\) thin film samples were calculated by using the Scherrer’s equation and represented in Table 3.

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \] (2)

where, \( D \) = Average crystallite size; \( \lambda \) = X-ray wavelength (1.5418 Å) \( \beta \) = FWHM of the peak; \( \theta \) = Diffraction peak position.

3.3 Surface Morphology: FE-SEM Analysis

Fig. 2 (C1-C5) depicts the FE-SEM images of pure ZrO\(_2\) and Cr modified ZrO\(_2\) thin films. From these surface morphology observation, it is clear that the structure of the film is nanocrystalline. The uniform film with small spherical grains were developed. The surface morphology of this modified is different than the other dopant. The Cr doped ZrO\(_2\) thin films consists of very small spherical grains grown may be beneficial to gas sensing. Average grain size of the all the film samples (C2-C5) were observed within range 12-15 nm.

3.4 Micro Structural Analysis: TEM Images and SAED Pattern

Fig. 3(a-b) shows the TEM micrograph and SAED pattern of Cr doped ZrO\(_2\) thin film. The surface morphology of the Cr doped ZrO\(_2\) grains observed to be the same by both FE-SEM and TEM micrograph, grains are nanocrystalline and uniform resides over ZrO\(_2\) grains providing with uniform sensing layer. The d values calculated using XRD and SAED pattern for most sensitive sample C3 are tabulated in Table 2. It is well matched with standard JCPDS data card of ZrO\(_2\) [16].
From Table 2 it was concluded that as thickness of the films increases, average crystallite size and grain size goes on increases.

3.5 Elemental Compositional Analysis

The quantitative elemental compositions Zr, O and Cr of the pure and doped thin films were tabulated in Table 4. The weight percentage of Cr is different for each with oxygen deficiency. The deficiency of oxygen reduces the resistance of the film and would promote the adsorption of oxygen species for higher gas response at increase in temperature.

Pure ZrO₂ thin film sample (C1) was observed to be nonstoichiometric in nature. It is clear from Table 4 that at % of Cr goes on increasing with increasing wt % of Cr in ZrO₂ thin films (C₂-C₅).

3.6 Optical Properties: Absorption Spectra

Optical absorption spectra (Fig. 4) carried out using JASCO UV-VIS-NIR Model V-670 Spectrophotometer. Fig. 4 represents the absorption spectra of pure ZrO₂ and Cr doped ZrO₂. After modification, absorption spectra tremendously changed. It is flat above 500 nm wavelength and the absorption increases between 300 to 460 nm and thereafter it was observed to be decreased [10-15]. The band gap energies of the samples were calculated from the absorption edges of the spectra. The slope drawn from the start of an absorption edge (the onset of absorbance) and horizontal tangent had drawn on absorption minimum and intercepted each other at some point. The vertical line drawn from this point on wavelength axis gave the absorption edge wavelength [16].

The bang gap energy for the pure ZrO₂ found to be 4.46 eV and Cr doped ZrO₂ thin films were in the range of 2.4 to 2.8 eV. Large change in optical band gap energy due to the change in grain size and formation of nano-crystalline nature of the thin films.

3.7 Electrical Characterization

3.7.1 I-V Characteristics

Fig. 5 shows the I-V characteristics of pure ZrO₂ and Cr doped ZrO₂ thin film samples, it shows the semiconducting nature and good ohmic contact.
The gas response of NH$_3$ to sample C1, C2, C3, C4 and C5 have been tested at different operating temperature is shown in Fig. 7. All the samples shown response to ammonia. The maximum gas response was obtained to sample C3 (S=96) at 300 °C for 500 ppm. It is well-known that the response of the metal-oxide semiconductor sensor is mainly determined by the interactions between a target gas and the surface of the sensor [17, 18].

3.8.2 Selectivity

Selectivity of pure ZrO$_2$ and Cr doped ZrO$_2$ thin films were measured at an operating temperature of 300 °C. Fig. 8 depicts the bar diagram to indicate NH$_3$ selective ability of the sensor.

3.8.3 Calibration Curve and Detection Limit

The variation of NH$_3$ gas response with respect to gas concentration at operating temperature 300 °C is shown in Fig. 9. The gas response increased in the range 10 to 500 ppm and reached 96 in the presence of 500 ppm of NH$_3$ gas and there after it is in saturation. The detection limit is to be estimated as 10 ppm.

3.8.4 Response and Recovery Time

Fig. 10 represents the response and recovery profile of the most sensitive sample C3. The response is quick (4 s) and recovery is fast (12 s). The high oxidizing ability of adsorbed oxygen species on the surface nanoparticles and high volatility of desorbed by-products explain the quick response to H$_2$S and fast recovery [19–21].

3.8.5 Stability

Fig. 11 shows the stability of pure ZrO$_2$ and Cr doped ZrO$_2$ thin films, which were measured by repeating the target gas test many times (cycle one day per week). During the test no significant variation was recorded as shown in Fig. 11. Ammonia gas modified thin film sensor had prominent long term stability in atmosphere for around 10 weeks. The obtained change in electrical conductance during repetitive exposure of acetone is stable and reproducible.

3.8.6 Comparison of NH$_3$ Response of Reported Doped Thin Film Sensors with Sensor Prepared in the Present Paper

Table 5 presents comparison of NH$_3$ response with reported different sensor and sensor prepared in present investigation [17–20]. It is clear that response of sensor reported in the present work is extremely high as compared to previous reported sensors.

### Table 5 Comparison of NH$_3$ response with previous reported work

<table>
<thead>
<tr>
<th>Form of material/</th>
<th>Gas</th>
<th>Gas response conc. (ppm)</th>
<th>Gas response/Sensitivity</th>
<th>Operating Temperature (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>barrier Ni-ZnO</td>
<td>NH$_3$</td>
<td>500</td>
<td>96</td>
<td>300</td>
<td>Present work</td>
</tr>
<tr>
<td>(Spin- Thin film)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>17</td>
</tr>
<tr>
<td>NiO$_2$-WO$_3$</td>
<td>NH$_3$</td>
<td>200</td>
<td>13.5</td>
<td>250</td>
<td>18</td>
</tr>
<tr>
<td>(Sputter- Thin )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-ZnO</td>
<td>NH$_3$</td>
<td>1000</td>
<td>35</td>
<td>400</td>
<td>19</td>
</tr>
<tr>
<td>(SP-Thin film)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-ZnO</td>
<td>NH$_3$</td>
<td>1000</td>
<td>2.52</td>
<td>--</td>
<td>20</td>
</tr>
</tbody>
</table>

The physiorgis and chemisensorism is very important in case of gas sensing mechanism. The reaction kinetic because of adsorption occurs as a consequence of oxygen species O$_2$, O$_2^-$ may be explained by the reaction [19–21].

\[ O_2(gas) \leftrightarrow O_2(ads) \]  \hspace{1cm} (4)

The adsorbed oxygen changes to ions O$_2^-$ following the reaction

\[ O_2(ads) + e^- \leftrightarrow O_2(ads) \]  \hspace{1cm} (5)

At high temperature the ions O$_2^-$ rapidly changes to ions O$_2$:

\[ O_2(ads) + e^- \leftrightarrow 2O^- \]  \hspace{1cm} (6)

Above 150 to 175 °C, the reactivity of O$_2^-$ species is high; the formation of O$_2$ species is also possible as follows

\[ O_2(ads) + e^- \leftrightarrow O_2 \]  \hspace{1cm} (7)

The schematic of adsorption and desorption on film surface layer is shown in Fig. 12. The gas sensing performance was tested for 500 ppm concentration. The sample had shown maximum response to ammonia.
than other gases. The sample C3 had showed (Gas response = 96) than other sample. In this modified sample Cr content are optimum and surface morphology becomes nanostructure with small uniform grains. Besides over base material ZrO2. The surface to volume ratio have been increased, it results in increase in ammonia gas response. The ionic size of chromium is (0.62 Å) is less than (Zr2+) ions, also it is trivalent acceptor impurity p-type oxide forming heterojunction at grain boundaries. Effect of Cr is expressed by Eq. (8).

\[
\text{Cr}_2\text{O}_3 + \text{ZrO} \rightarrow 2\text{Cr}_2\text{Zr} + \text{V}^{*+} + 3\text{O}^\delta
\]  

(8)

where \(V^\delta\) represents oxygen vacancies and \(\text{Cr}_2\text{O}_3\) means Cr substitution in Zr. It has been observed that doping with unstable cation provides that hortest route by altering electronic and catalytic properties of gas interaction at interface. Therefore it improves the gas response. The resistance significantly reduced and the reduction in barrier height enhanced gas response [19].

\[
2\text{Cr}_2\text{S}_3 + 9\text{O}_2 \rightarrow 2\text{Cr}_2\text{O}_3 + 6\text{SO}_2
\]  

(9)

Similarly when reducing gas NH3 comes into contact the grains of Cr doped ZrO2 thin film, at elevated temperature ammonia reacts with the film surface and adsorbed oxygen on the surface of the film get oxidized ammonium hydroxide, liberating free electrons in the conduction band.

\[
\text{ZrO}_2 + 5\text{NH}_3 + 4\text{O}_2 \rightarrow \text{Zr} (\text{NH}_3)\text{OH} (\text{filmsurface}) + 2\text{NO}_2 + \text{O}_2 (\text{conduction band})
\]  

(10)

This shows n-type conduction mechanism, thus generated electron contribute to sudden increase in conductivity of the thin film, which may be due to surface reaction of ammonia with physisorbed H2O or by proton conductivity via NH+ cations, CrO3 may generate the solid acidity on the solid base ZrO2. The acidity on the sensor surface would form NH+ cations, which constitutes the proton conductivity leading to a crucial decrease of the resistance. This would decrease the barrier height among the CrO2-ZrO2 grains.

\[
\text{NH}_3 (\text{gas}) + \text{H}_2\text{O} (\text{surface}) \rightarrow \text{NH}_3\text{OH} (\text{gas})
\]  

(11)

Ammonia hydroxide NH3OH produced during the surface reaction is volatile in nature. The high volatility of NH3OH influences the quick response and fast recovery of the thin film sensor [20, 21].

![Fig. 12 Schematic of ammonia sensing on Cr doped ZrO2 thin film](image)

4. Conclusion

Nanostructured pure ZrO2 and Cr doped ZrO2 thin films prepared by simple and inexpensive spray pyrolysis technique onto the glass substrates. The average crystallite sizes were observed from XRD and it was found to be 5.8 nm. FESEM analysis revealed that, the grains were spherical in shape with grain size around 14 nm. TEM images showed the particle size ~4.8 nm. EDAX analysis confirmed that the Cr modified ZrO2 thin film was observed to be oxygen deficiency. Optical study reveals that Cr doping increases the optical band gap energy varying from 2.4 to 2.8 eV. Gas response of Cr doped ZrO2 thin film towards NH3 gas. Cr doped ZrO2 thin film helped to enhance the gas response (S=96), and selectivity towards NH3 gas. Selectivity study showed that films were most selective to NH3 gas. Speed of response (4 s) and fast recovery (12 s) is main feature of the sensor. The prepared thin films show good stability.

References


[16] JCPDS Data Card (JCPDS 36-020) and JCPDS 17-0923.


