Chapter III-A

Gas Sensing Properties of Zn$_2$SnO$_4$ Thin Films Prepared by Spray Pyrolysis Technique Using Alcohol as Solvent
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Gas Sensing Properties of Zn$_2$SnO$_4$ Thin Films Prepared by Spray Pyrolysis Technique using alcohol as solvent

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Gas Sensing Properties of Zn$_2$SnO$_4$ Thin Films Prepared by Spray Pyrolysis Technique Using Alcohol as Solvent

3.1 Introduction

The human activities and industries are basis to raise the level of the polluting gases. The micro, nano-structure based sensors are highly sensitive, having high spatial resolution and fast response because of the high surface-to-volume ratio [1]. Metal oxide gas sensors (WO$_3$, ZnO, SnO$_2$ etc.) are principal solid state gas sensors used in many places which includes domestic use as well as in industrial use [2]. Many advantages of MOS include low cost, easy synthesis, smaller size and durability [2]. Nevertheless, researchers are trying to enhance gas sensing performance and detection limit by means of advanced techniques and simultaneously attempts have been made to carefully synthesis novel nanostructures showing high gas sensing performance with a low sensing limit using simple chemical methods such as CBD, SILAR, spray pyrolysis [1-2]. However, during the past few years, an enormous attention has been made to develop new types of gas sensors and to test possible alternatives to binary metal oxides such as using ternary complex oxides [3], hybridizing MOS with polymers [4] and hetero-junction [5]. Among these alternatives use of ternary complex MOS systems of the form A$^{II_2}$ B$^{IV}$ O$_4$, [6] such as cadmium stannate (Cd$_2$SnO$_4$) [7], zinc stannate (Zn$_2$SnO$_4$) [8], zinc titanate (Zn$_2$TiO$_4$) [3] has received enormous interest these days. Zn$_2$SnO$_4$ is a multifunctional material [6] with higher electron mobility and conductivity, wide band gap and fascinating optical properties that makes it possible to use Zn$_2$SnO$_4$ for variety of applications, such as dye sensitized solar cells [9], gas sensors [10], negative electrode material for Li-ion battery [11] and photoelectrode for water purification [12] or as a photodetector [13]. Due to higher selectivity and sensitivity of Zn$_2$SnO$_4$ films towards oxidizing as well as reducing gases[14-17] spinel Zn$_2$SnO$_4$ has often been used to detect various gases such as i-C$_4$H$_{10}$, NO$_x$ and ethanol [18]. Sensing performance of Zn$_2$SnO$_4$ sensor towards LPG, was improved by synthesizing microcubes of Zn$_2$SnO$_4$ on the surface of ZnO nanorods.
by Sivapunniyam et al [19]. Hung et al. developed a template-free aqueous solution route combined with subsequent thermal treatment to synthesize porous ZnSnO₃ cubes for gas sensing toxic volatile organic compounds (VOCs) [20]. The phase controlled synthesis of well-defined faceted cubic ZnSnO₃ and octahedral Zn₂SnO₄ microcrystals scale by a one-step facile solution chemical route for sensor with high sensitivity, fast response, and short recovery time to H₂S and C₂H₅OH was reported [21]. The photoanodic performance of the Zn₂SnO₄ film synthesized by a simple sol-gel route was reported by Uchiyama et al. [22]. Gautam et al. [23] reported on the electronic structure of ZnₓSn₁₋ₓO₂ nanorods synthesized via a versatile solvothermal method. Microstructural evolution of spinel Zn₂SnO₄ nanofibers was manipulated by Choi et al. [24] via an in situ phase separation process of inorganic precursors and a matrix polymer during electrospinning and calcination. They reported chemiresistive gas sensors using porous Zn₂SnO₄ fibres exhibiting superior C₂H₅OH sensing response.

3.2. Experimental Procedure

The chemicals used for the synthesis of the zinc stannate (Zn₂SnO₄) thin films were zinc chloride (ZnCl₂) and stannic chloride (SnCl₄.5H₂O) as sources of zinc and tin, respectively and 2-propanol was used as a homogenizing agent for the both precursors. The chemicals were procured from S.D.Fine Chem. Ltd., Mumbai, and used as received without any further treatment. To obtain the Zn₂SnO₄ thin films, ZnCl₂, SnCl₄ of required quantity were dissolved in 50 ml of 2-propanol to form 0.1 M solution keeping Zn/Sn ratio 2:1. The solution was then stirred for half an hour till it becomes clear. The precursor solution formed is then sprayed onto the preheated glass substrates at different temperatures ranging from 325 to 400 °C. The spray solution quantity (50 ml), spray rate (5 ml/cc) and the nozzle to substrate distance (28 cm) were optimized by observing uniformity and adherence of the films.

3.3 Results and discussion

3.3.1 Reaction mechanism
Synthesis of multicomponent metal oxide thin films composed of ternary compounds using the spray pyrolysis method is a challenging job, since the probability of growth of individual oxides or formation of composite materials or formation of both phases unanimously is more [28]. Making both components to deposit simultaneously on the substrate, rigorous attempts are necessary to optimize the preparative parameters. The deposited films are highly uniform, desired thickness (~250 nm) and well adherent. The reaction involved in the synthesis of the oxide system of Zn$_2$SnO$_4$ is as follows:

$$2\text{ZnCl}_2 + \text{SnCl}_4 + 8(\text{CH}_3)_2\text{CHOH} \xrightarrow{\Delta} \text{Zn}_2\text{SnO}_4 + 8(\text{CH}_3)_2\text{CHCl} \uparrow + 4\text{H}_2\text{O} \uparrow$$

(3.1)

When the atomized precursor solution travels through the temperature gradient, precursor solution decomposes within the aggregates, due to the evaporation of the solvent. Nucleation and growth of the film start as this partially decomposed part reaches the hot substrate and the crystallization reaction of the precursors result in the Zn$_2$SnO$_4$ films after complete decomposition of the precursor.

### 3.3.2 Structural characterization of Zn$_2$SnO$_4$ thin films

The study of structural characteristics of Zn$_2$SnO$_4$ thin films include (i) Structural characterization using XRD (ii) Surface morphology using SEM and (iii) AFM

#### 3.3.2.1 X-Ray diffraction study

X-ray diffraction (XRD) studies of the Zn$_2$SnO$_4$ were carried out using Bruker D2 phaser. The patterns were recorded in the 2θ range of 20–80° with step width 0.02° using CuKα radiation of wavelength 1.54056 Å. The patterns were analyzed by matching with the JCPDS cards and indexed accordingly.

The identification of crystal structure of the as-prepared films was done by X-ray diffraction (XRD) studies. XRD patterns of Zn$_2$SnO$_4$ thin films deposited at different substrate temperatures along with the stick pattern of JCPDS card No. 24-1470 are presented in the Fig. 3.1. As observed from Fig 3.1 the XRD patterns matches well with the JCPDS card No. 24-1470 and possesses perfect cubic inverse spinel crystal structure [29-30]. The nanocrystalline nature of the films is evidenced from the observed broad peaks. The calculated lattice
parameter of the sample deposited at 375 °C about 8.6826 Å which is in good agreement with the reported value in the above mentioned JCPDS. Diffraction peaks from other phases of zinc stannate (ZnSnO₃) and other impurities were not observed [16, 31]. The diffraction peaks observed at 2θ value of 34.18, 36.53 and 51.55°, can be assigned respectively to (311), (222) and (422) planes of the cubic crystal structure of Zn₂SnO₄. Intensity of the diffraction peaks slowly increases with an increase in the substrate temperature, representing that the crystallinity of the material enhanced with increasing substrate temperature. At higher temperature (400 °C) peak intensity of (311) plane decreases. It may be due to the decrease in the film thickness. At higher temperatures, precursor solution decomposes before reaching substrate, decreasing the film thickness. Shift in the position of (311) peak is observed with increase in substrate temperature indicating change in lattice constant and structure becoming perfect cubic. Crystallite size (D) was estimated (table 3.1) from the XRD peaks using the Scherrer formula for the prominent peaks corresponding to the plane (311).
Figure 3.1 XRD patterns of the Zn$_2$SnO$_4$ thin films deposited at various substrate temperatures

Table 3.1 Crystallite size and thickness of Zn$_2$SnO$_4$ thin films deposited at various substrate temperatures.

<table>
<thead>
<tr>
<th>Substrate temperature ($^\circ$C)</th>
<th>Crystallite Size (nm)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>325</td>
<td>10.3</td>
<td>375</td>
</tr>
<tr>
<td>350</td>
<td>12.5</td>
<td>315</td>
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<tr>
<td>375</td>
<td>14.4</td>
<td>267</td>
</tr>
<tr>
<td>400</td>
<td>16.7</td>
<td>148</td>
</tr>
</tbody>
</table>
3.2.2 Scanning electron microscopy (SEM) study
Figure 3.2 SEM micrographs of Zn$_2$SnO$_4$ thin films prepared at (a) 325°C (b) 350°C (c) 375°C (d) 400°C substrate temperature.

Surface morphology of the Zn$_2$SnO$_4$ thin films was studied using scanning electron microscopy technique. A scanning electron microscopy SEM (SEM Model: JEOL JSM 6360) operating at 20 kV was employed to characterize the samples.

Figure 3.2(a, b, c and d) shows the SEM micrographs of the Zn$_2$SnO$_4$ thin films prepared at substrate temperatures 325°C, 350°C, 375°C and 400°C respectively. All the SEM images are recorded at 15000 X magnification for comparison.

Microstructures of Zn$_2$SnO$_4$ thin films were uniform having moderately packed grains with different grain sizes as shown in Fig 3.2. With increase in the substrate temperature, no considerable change in surface structure is observed but the particle size increased. For the films deposited at substrate temperature up to 375°C randomly distributed moderately packed spherical grains of various sizes are observed (Fig 3.2 a, b, c). Whereas, for the films deposited at higher substrate temperature (Fig 3.2 d) non uniform growth with larger grains is observed. When the substrate temperature increased, the small spherical grains are transformed into irregular cuboids along with spherical grains (Fig. 3.2 c). As reported by Jiang et al [32], it is known that Zn$_2$SnO$_4$ particles in quasi-cubic structure have lower surface-to-volume ratio than the ideal cubic phase Zn$_2$SnO$_4$, hence when changing grain shape from spherical to cubic gas response increases, it is also evidenced from our results. At much higher temperature (>400 °C) films is non uniform and solution boils in the nozzle itself making it difficult to deposit thin films.

3.3.2.3 Atomic force microscopy study

Atomic force microscope (Bruker, USA -INNOVA 1B3BE) was used to study the topography and to measure surface roughness of the films.

Figure 3.3 shows AFM images of the Zn$_2$SnO$_4$ thin films deposited at four different substrate temperatures viz. 325°C, 350°C, 375°C and 400°C. It can be seen that, with increasing the substrate temperature, morphology of the samples becomes rougher. At lower substrate temperatures Zn$_2$SnO$_4$ thin films show the
particulate structure. In the film deposited at substrate temperature 400 °C the overgrown particles can be seen and the same is also confirmed from the SEM images. The increase in the particle size with substrate temperature is due to the rapid formation of the grains due to the faster reaction rate at high temperature. At lower substrate temperature growth rate of the film is slow due to the less reaction rate and droplets reach substrates causing smaller grains whereas when substrate temperature growth rate of films is higher causing coalescence of residue resulting in larger grains. The surface area exposed to the analyte gas and thus the surface roughness of the films is a key factor deciding the performance of a gas sensor [33]. Due to the spherical grains on the surface, actual surface area is larger than the projected surface area of the films. The RMS (root mean square) surface roughness and actual surface area the films deposited at various temperatures were evaluated over a 3× 3 μm² area from the AFM micrographs and listed are the table 2. The surface roughness of the films increased from 9.5 to 24.4 nm with increase in the substrate temperature from 300 to 375 °C and then it reduced to 12.4 nm at 400°C. Highest roughness and thus the surface area are observed for a film deposited at 375°C. This supports an increase in the gas response with increase in substrate temperature, further at higher temperature (400°C) particles are larger and sensing sites available for gas adsorption are less, thereby decreasing gas response. Also actual surface area is decreased at highest substrate temperature resulting in decrease in gas response.
3.3.3 Optical characterization

3.3.3.1 Thickness measurement of the Zn$_2$SnO$_4$ thin films

Thickness of the film was calculated by using interferometric method comparing observed spectra with the standard spectra of known thickness of the same material on the similar substrates. Reflectance was recorded over the region of wavelength 400 to 1100 nm, wherein well developed interference patterns were observed. Thickness is calculated by fitting observed and standard reflectance pattern [34], and observed thickness is shown in table 3.1. Film thickness decreases with an increase in the substrate temperature due to the decomposition of the precursor solution prior to the film surface.
3.3.3.2 UV-Visible analysis of Zn$_2$SnO$_4$ thin films

In order to estimate the band gap energy of the films, optical transmission of Zn$_2$SnO$_4$ films is studied at room temperature in the wavelength range of 300–1100 nm. Fig. 3.4 shows the variation of transmittance with wavelength for Zn$_2$SnO$_4$ thin films deposited at various substrate temperatures. Films are highly transparent in the visible region and the average transmission in the visible region varies from 70% to 90% depending upon the substrate temperature. It is due to the fact that the reflectivity is low and there is no (or less) absorption due to transfer of electrons from valence band to conduction band owing to optical interference effects, it is possible to maximize the transmission of thin film at particular region of wavelengths. Relatively higher transmittance of about 90% at 850 nm for films deposited at 375°C has been observed. In metal oxides, stoichiometry and crystalline structure is responsible for resulting transparency. In the present case films exhibit relatively higher transparency due to resulted better crystallinity and homogeneity. Films having better crystallinity would show better gas response due to decreased scattering of the charge carriers. In the interband transition region (365–390 nm) [35], the transmittance decreased because of the onset of fundamental absorption.

Optical absorption coefficient (α) is calculated using transmittance; it varies with photon energy and has a sharp absorption edge. ‘α’ is of the order of $10^4$ cm$^{-1}$ following the direct and allowed band transition. The variation of $(\alpha h\nu)^2$ with $h\nu$ (Fig. 3.5) has a straight line portion demonstrating that transition observed is direct allowed type [36]. Extrapolating the linear portion to the energy axis to $(\alpha h\nu)^2=0$ band gap is determined; it is observed to be 3.71 eV higher than the value of $E_g = 3.6$ eV reported for single crystal Zn$_2$SnO$_4$ [36]. At higher substrate temperature (400°C) it is narrowed to 3.45 eV due to the stoichiometric differences [32]. As reported by Aviles et al the fundamental band-gap of Zn$_2$SnO$_4$ is 3.60-3.70 eV, due to the inclusion of excess Zn into the Zn$_2$SnO$_4$ network and after heat treatment, band gap is narrowed up to 3.25 eV [37]. On the other hand, based on the discussion of the Jiang et al [32] the red-shift in the fundamental band-gap for quasi-cubic Zn$_2$SnO$_4$ is attributed to differences in the crystal structure.
Thin films often show a small band gap widening and the absorption edge moves to a shorter wavelength than that of the bulk material.

![Figure 3.4 Transmittance spectra of the Zn$_2$SnO$_4$ thin films deposited at various substrate temperatures.](image1)

![Figure 3.5 Tauc plots to measure band gap energy and inset shows transmittance spectra of the Zn$_2$SnO$_4$ thin films deposited at various substrate temperatures.](image2)

3.3.4 Gas sensing study of Zn$_2$SnO$_4$ thin films

The gas sensing performance of the Zn$_2$SnO$_4$ thin films towards NO$_2$ is studied at different operating temperatures and gas concentrations.
selectivity of the films was tested using the different analyte gases at the optimized operating temperature and gas concentrations. Gas response was calculated by measuring the change in the resistance of the film as \((Ra-Rg) / Ra\) where \(Ra\) is the resistance of the film in the air and \(Rg\) is the resistance of the film in the vicinity of gas. Response time is determined by the time taken by the sensor to reach 90% of its final value when subjected to analyte gas concentration and recovery time is the time taken by the sensor to reach 10% of the value it had before exposure to the gas. To obtain the gas atmospheres for measurements of sensor resistance fresh air was passed into a glass test box at room temperature, and then a pure test gas was injected into the box to obtain a desired concentration. Gas response and selectivity for various gases viz. \(NH_3\), \(CO\), LPG (Propane: Butane, 6:4), \(SO_2\), \(H_2S\) and \(NO_2\) were tested.

### 3.3.4.1 Optimization of operating temperature and sensitivity for NO2 gas sensing

The operating temperature was optimized by comparing gas response for \(Zn_2SnO_4\) thin films deposited at various substrate temperatures at different operating temperatures for 200 ppm of \(NO_2\) The sensitivity was optimized by studying gas response for \(Zn_2SnO_4\) thin films deposited at various substrate temperatures optimized operating temperatures for different \(NO_2\) concentrations.

#### 3.3.4.1.1 Variation of gas response with operating temperature

It is well studied that the operating temperature plays an important role not only in determining the gas response, but also response and recovery times of the sensors [1, 33]. To determine the operating temperature of the sensors, we measured gas response, response and recovery times of the sensors at various operating temperatures ranging from 100 to 250°C. Variation in the gas response at various operating temperatures is shown in Figure 3.6. The sensor response towards \(NO_2\) has been studied for all the films and a maximum \(NO_2\) sensitivity has been recognized at 200°C. It can be observed that gas response increases up to 200°C and decreases at higher operating temperature. Thermal energy assists the reactions involved in sensing mechanism and overcome the corresponding activation energy barriers. [38]. At higher operating temperature
(>200 °C), the pre-adsorbed oxygen species and NO$_2$ molecules on the surface of the film are decreased and therefore limiting gas response at higher operating temperatures. Moreover, at lower operating temperatures (<200°C) NO$_2$ gas molecules do not have sufficient thermal energy to dissociate and adsorb on the surface and thus the low response is observed at lower operating temperatures. Maximum gas response 2.66 is observed for the film deposited at 375°C substrate temperature. On either side of this substrate temperature gas response is less for all the films. Taking into account the response to gas, the effect of ambient temperature, stability and repeatability, operating temperature 200 °C is believed to be the optimum and use for all further investigations. The operating temperature is moderately low as compared with the few earlier reports [16-17, 27]. NO$_2$ is known to be highly oxidizing gas, having a higher electron affinity (2.27 eV) in comparison with preadsorbed oxygen (0.44 eV) [39]. Interaction of NO$_2$ with the surface of the sensor is of two types. The monomolecular adsorption of NO$_2$ is observed for well oxidized samples, whereas; dissociation of NO$_2$ takes place at the oxygen deficient centers [40]. Thus, partially reduced cations i.e. Sn$^{4+}$ and Zn$^{2+}$ play the role of NO$_2$ chemisorption centres at comparatively low temperature 200°C. Availability of the cations in turn depends on the degree of stoichiometry of the metal oxide surface.

Monomolecular adsorption of NO$_2$ occurs on cations of the outermost surface layers as

$$Zn_2SnO_4 + NO_2^{gas} + 2e^- \rightarrow Zn_2SnO_{4n} + 2NO^-$$

(3.2)

A dissociative adsorption of NO$_2$ on the sensor surface takes place on the oxygen vacancies and forms adsorbed oxygen species:

$$Zn_{2n}SnO_{4n-1} + V^{\ast}_o + e^- + NO_2^{gas} \rightarrow Zn_2SnO_{4n} + NO^{gas}$$

(3.3)

where $V^{\ast}_o$ is the oxygen vacancy.
Figure 3.6 Variation in gas response for Zn$_2$SnO$_4$ thin films deposited at various substrate temperatures at different operating temperatures for 200 ppm of NO$_2$.

3.3.4.1.2 Variation of gas response with NO$_2$ concentration

The variation of gas response of films for various NO$_2$ concentrations at 200°C operating temperatures deposited at various substrate temperatures is shown in the Fig 3.7. It can be seen that the concentration of the analyte gas was varied and the gas response was significant even for the concentration as low as 50 ppm. As expected, the gas response increases noticeably with increase in gas concentration, at higher concentrations >200 ppm it saturates and remains nearly constant. At low NO$_2$ gas concentrations due to the enough availability of the adsorption sites gas response is directly proportional to the NO$_2$ concentration. However, at a higher NO$_2$ concentration due to the limited availability of the adsorption sites only fixed NO$_2$ molecules adsorbs and a saturation of gas response is observed. As a result, the gas response is determined by the surface reaction rate, till certain value of gas concentration after which it saturates [41]. The highest response was noted for the films deposited at substrate temperature 375°C for all the three concentrations.
Figure 3.7 Variation in gas response for Zn$_2$SnO$_4$ thin films deposited at various substrate temperatures at 200 °C operating temperatures for different NO$_2$ concentrations.

3.3.4.2 Response and Recovery time

Figure 3.8 (a, b, c and d) shows transient response of Zn$_2$SnO$_4$ film deposited at four different substrate temperatures viz. 325 °C, 350 °C, 375 °C and 400°C for 50-200 ppm NO$_2$ gas concentration at 200 °C operating temperature. From Figure 3.8 (a, b, c and d) it is observed that gas response increases with NO$_2$ concentration and response and recovery times also increases simultaneously. For the film deposited at 375 °C [Fig 3.8(d)], as the film is switched between the gas on and gas off states, gas response of the film changes almost by 20 times in tens of seconds and recovers within a few minutes for the NO$_2$ gas.

From Figure 3.9, the trend in the response and recovery times of the films deposited at various substrate temperatures for different gas concentration can be seen. The response time and recovery time values of the films deposited at 375°C for 200 ppm NO$_2$ gas read as 25 and 282 s respectively.
Figure 3.8(a) Gas responses vs. time for Zn$_2$SnO$_4$ thin film deposited at 325°C for 50, 100, 200 ppm NO$_2$ at 200°C operating temperature.

Figure 3.8(b) Gas responses vs. time for Zn$_2$SnO$_4$ thin film deposited at 350°C for 50, 100, 200 ppm NO$_2$ at 200°C operating temperature.
Figure 3.8(c) Gas responses vs. time for Zn$_2$SnO$_4$ thin film deposited at 375°C for 50, 100, 200 ppm NO$_2$ at 200°C operating temperature.

Figure 3.8(d) Gas responses vs. time for Zn$_2$SnO$_4$ thin film deposited at 400°C for 50, 100, 200 ppm NO$_2$ at 200°C operating temperature.
3.3.4.3 Selectivity of Zn$_2$SnO$_4$ thin film sensor

Response times vary for test gases viz. NH$_3$, CO, LPG, SO$_2$, H$_2$S and NO$_2$ which were used in the determination of selectivity of the films. The films deposited at 375°C were exposed to 200 ppm concentration of above listed gases at 200 °C operating temperature. Gas response and selectivity for various gases viz. NH$_3$, CO, LPG (Propane: Butane, 6:4), SO$_2$, H$_2$S and NO$_2$ were tested. Fig 3.10 shows gas response for various gases viz. NH$_3$, CO, LPG (Propane: Butane, 6:4), SO$_2$, H$_2$S and NO$_2$ gases at 200 °C for 200 ppm gas concentration.

The maximum response of around 25 times the response of other gases was noticed for the NO$_2$ gas as seen in the bar graph in Fig 3.10. The selectivity of Zn$_2$SnO$_4$ thin films towards the gases varied as NH$_3$ < CO < LPG < SO$_2$ < H$_2$S < NO$_2$. Therefore, the sensor based on Zn$_2$SnO$_4$ thin film can be used for the selective detection of NO$_2$ when there is a mixture of NO$_2$ and other gases. Further, it is observed that for repeated (10 times) on and off responses there is no major change in the signal.
**Figure 3.10** Selectivity studies of typical Zn$_2$SnO$_4$ thin film sensor for various gases at 200°C for 200 ppm gas concentration.

### 3.3.4.4 Stability of Zn$_2$SnO$_4$ thin film sensor

In order to check durability and ruggedness of the sensor, NO$_2$ response of the films deposited at 375 °C was tested after every month and it is found that gas response decreases fast initially and remains nearly constant after 240 days (Figure 3.11). This decrease in the gas response with the number of days can be attributed to the formation of layer oxides/moisture. To check the deterioration in the films causing the decrease in gas response film deposited at 375°C were annealed at 400 °C for 6 hours. After annealing film, gas response increased and restored to a value observed after one month. The gas response of annealed film is presented in the Figure 3.12.
Figure 3.11 NO₂ response as a function of time for the Zn₂SnO₄ thin film deposited at 375 °C (Operating temperature =200 °C, NO₂ concentration = 200 ppm).
3.3.4.5 Gas sensing of Pd sensitized Zn$_2$SnO$_4$ thin films

The gas sensor with high response, high selectivity, low response and recovery times are considered to be a good sensor. In order to improve the response and recovery times, the Zn$_2$SnO$_4$ films were sensitized with Pd and the gas response measurements were carried out keeping the sensing parameters same as in previous measurements. Gas response with respect to time for the Pd sensitized Zn$_2$SnO$_4$ thin film deposited at 375 °C is shown in Fig (3.13). Pd sensitization causes fast spillover of the gas resulting in enhancement in the response and recovery times. There is an overall reduction in both response and recovery times and particularly for 200 ppm NO$_2$ concentration, the response time was dropped from 25 s to 6 s while the recovery time reduced from 282 s to 221 s. The gas response was enhanced from 2.66 to 3.31. The table 3.3 presents comparison of the gas response, response and recovery times of the Zn$_2$SnO$_4$ films deposited at 375 °C and the Pd sensitized Zn$_2$SnO$_4$ films. The gas sensing results achieved are comparable to the previous reports [42-44]. Further attempts will be made to reduce the lower detection limit and improve the recovery time of the sensor as the recovery time is much higher (37 times) than the response time even after Pd sensitization.

Table 3.3 Comparison of gas response, response and recovery times of Pd sensitized and Zn$_2$SnO$_4$ thin film deposited at 375 °C for 200 ppm gas concentration at 200 °C operating temperature.

<table>
<thead>
<tr>
<th>Gas concentration (ppm)</th>
<th>Zn$_2$SnO$_4$</th>
<th>Pd Sensitized Zn$_2$SnO$_4$</th>
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<tr>
<td></td>
<td>Response time (s)</td>
<td>Recovery time (s)</td>
</tr>
<tr>
<td>50</td>
<td>17</td>
<td>290</td>
</tr>
<tr>
<td>100</td>
<td>20</td>
<td>325</td>
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</table>
Figure 3.13 Gas response vs. time of Pd sensitized Zn$_2$SnO$_4$ thin film deposited at 375°C towards 200 ppm NO$_2$ at 200°C operating temperature.

3.4 Conclusions

The ternary oxide Zn$_2$SnO$_4$ films based NO$_2$ sensors were successfully deposited by spray pyrolysis method. The formation of the Zn$_2$SnO$_4$ was confirmed by the XRD measurements. The films were very highly sensitive and selective towards NO$_2$ gas. The operating temperature of the sensor was moderately low (200°C) showing highest gas response of 2.66 for 200 ppm of NO$_2$. The films deposited at 375°C substrate temperature consisting of microstructured granules are highly active towards the sensing of the NO$_2$ gas among the mixture of gases viz. NH$_3$, CO, LPG, SO$_2$, H$_2$S and NO$_2$. The response time for the films varies from 4 to 25 s while recovery time is relatively higher than the response time. The films showed acceptably good gas response up to 240 days. This is indicative of appropriate sensitivity, fast response, stability and durability of the spray deposited Zn$_2$SnO$_4$ films. Pd sensitization further improved the gas response, response and recovery times of the sensor.
References


Chapter III-B

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Gas Sensing Properties of Zn$_2$SnO$_4$ Thin Films Prepared by Spray Pyrolysis Technique using alcohol as solvent

3B.1 Introduction

Improvement in the selectivity of the MOS can be achieved by different techniques and ideas which include synthesis of nano structured films, use of Metal oxides semiconductors (MOS) have been proved as the most suitable materials for solid state gas sensors for the past few decades [1]. This is due to their inherent properties such as ease of fabrication, fast and high response, and excellent recovery [2]. MOS can be used for detection of different oxidizing and reducing gases and with the advancement of technology it is possible now to detect ppm to ppb level gas concentration when operating at room temperature even while operating under harsh environments [3, 4]. The major drawback in MOS gas sensor is the selectivity of the sensor MOS based sensors are less selective and show significant response towards variety of gases [5]. Various dopants, using different substrates and even interdigitated electrodes of gold and platinum [6, 7]. One of the best alternatives to improve performance of the sensor is to use composite materials or to use ternary or even quaternary MOS consisting or two or more metal elements [8]. It is also reported that, desired sensing properties can be achieved by altering the polymorphic phase of a single oxide material by using another suitable transition metal [9]. It has been reported that SnO is the most suitable and widely studied material used for gas sensing and it is followed by ZnO, In$_2$O$_3$ and mixed metal oxides [1]. Large number of reports is available [1] on these materials used as film gas sensors in various fields for the detection of toxic and polluting gases. Thus it is worth to use Zn and Sn in a ternary system forming Zn$_2$SnO$_4$ for the possible selective gas detection.

Ma et al. [10] synthesized cubic ZnSnO$_3$ and octahedral Zn$_2$SnO$_4$ microcrystals by using one-step chemical solution route and studied their utility towards H$_2$S, C$_2$H$_5$OH and HCHO. Different faceted structures of zinc stannate (ZnSnO$_3$ and Zn$_2$SnO$_4$) have been synthesized by changing the stannic precursors. Polycrystalline Zn$_2$SnO$_4$ thin films were synthesized by Young et al.
using rf magnetron sputtering and their structural properties were investigated. The multiple networked Zn$_2$SnO$_4$-core/ZnO-shell nanorod sensors were synthesized by Park et al. [12] and results showed a response of 173–498% towards 1-5 ppm NO$_2$ concentrations operating at 300 °C. Thermal evaporation followed by atomic layer deposition at 1000 °C was employed for the synthesis of Zn$_2$SnO$_4$-core/ZnO-shell nanorod structure. Using hydrothermal method Ai et al. [13] synthesized Zn$_2$SnO$_4$ microcubes for the removal of NO and HCHO from the indoor air to maintain air quality. They have shown that air having concentration less than 400 ppb of NO and 2 ppm HCHO can be maintained using Zn$_2$SnO$_4$ microcubes. NO$_2$ response of 5 ($R_g/R_a$) is reported by Stambolova et al. for spray deposited Zn$_2$SnO$_4$ films at 420 °C operating temperature [14].

Even though various methods have been reported for the synthesis of Zn$_2$SnO$_4$ films [15], hydrothermal method is widely used. Herewith we report use of spray pyrolysis method for the synthesis of the Zn$_2$SnO$_4$ films. To best of our knowledge and available reports synthesis of Zn$_2$SnO$_4$ films by spray pyrolysis are not available [14, 16, 17]. Here we report synthesis of Zn$_2$SnO$_4$ films using spray pyrolysis system and effect of substrate temperatures on the physical and NO$_2$ sensing properties of Zn$_2$SnO$_4$ films. Enhanced NO$_2$ response along with selectivity is observed even at moderate operating temperature of 200 °C.

### 3B.2 Experimental Procedure

Zn$_2$SnO$_4$ thin films have been synthesized using, zinc chloride (ZnCl$_2$) and stannic chloride (SnCl$_4$·5H$_2$O) as cationic precursors of zinc and tin, respectively and double distilled water is used as solvent. The chemicals were procured from S. D. Fine Chemicals Limited, Mumbai, and used as received without any further treatment. To obtain the Zn$_2$SnO$_4$ thin films, ZnCl$_2$, SnCl$_4$ were taken in the ratio of 2:1 and dissolved in required amount of distilled water. Thus respective concentrations of ZnCl$_2$, SnCl$_4$ in the precursor solutions were 0.2 M and 0.1 M respectively. The precursor solution formed was then sprayed onto the preheated glass substrates at different temperatures. The deposition temperature was varied as 300, 350 and 400 °C respectively. To achieve optimum thickness of the films solution quantity was fixed to 200 ml.
Other spray parameters such as spray rate (10 ml/min) and the nozzle to substrate distance (28 cm) were optimized by observing uniformity and adherence of the films.

Gas sensing performance was studied using locally fabricated testing chamber equipped with Rigol digital multimeter (DM3000). Sensor of size 1 cm × 1 cm was fabricated and silver contacts were drawn for good electrical contacts. Thin film sensor was mounted in 250 ml airtight container where it is preheated at required temperature using temperature controller. Sensor was heated until its resistance stabilized and the time required for this was around two hours. Thin film sensors were then exposed to the analyte gas of desired concentration in the gas sensor unit and change in the resistance was monitored using digital multimeter. After each successive measurement, fresh air was passed in to the test box and then required amount of analyte gas was injected into the box to obtain a desired concentration. Selectivity studies were carried out by monitoring change in resistance of the film by purging various gases of desired concentration. Various canisters of H₂S, CO, CO₂, NH₃, SO₂, NO₂ and LPG, and gases having 1,000 ppm gas concentration were used as analyte gases procured from Shreya Enterprises Pvt. Ltd. Mumbai, Maharashtra, India.

Figure 3B.1 shows XRD patterns of Zn₂SnO₄ films deposited at different substrate temperatures. Phase change of the synthesized films can be clearly observed in the Figure 1. The film prepared at 300 and 350 oC exhibits mixed phases of ZnO, SnO₂ and Zn₂SnO₄ with major contribution of Zn₂SnO₄. Contribution to the XRD phase from SnO₂ phase at 300 oC is higher than ZnO. It can also be notified that with increase in substrate temperature (350 oC) contribution of SnO₂ peak decreases and that of ZnO phase is almost disappeared. XRD pattern of the film deposited at 400 oC matches well with the JCPDS card No. 73-1725 confirming cubic face centered crystal structure. It is observed that with change in substrate temperature of the film crystal orientation changes due to the different growth rate of the films at different substrate temperatures.
3B.3 Results and discussion

3B.3.1 Structural characterization of Zn$_2$SnO$_4$ thin films

The structural characteristics of Zn$_2$SnO$_4$ thin films was carried out by XRD, SEM and AFM.

3B.3.1.1 X-ray diffraction study

![XRD patterns of Zn$_2$SnO$_4$ films deposited at different substrate temperatures.](image)

Initially at 300 °C films are polycrystalline while with increase in temperature, its preferentially orientated along (3 1 1) plane. The existence of well defined reflection along (3 1 1) plane at angle 34.3° and well matching of 2θ and ‘d’ values with JCPDS card No. 73-1725 depicts the formation of phase pure Zn$_2$SnO$_4$ thin film with cubic face centered crystal structure at 400 °C. As compared with our earlier results [16] increased thickness and change in solvent enhanced crystallinity of the films and increased preferential orientation along (3 1 1) plane [18]. Peaks belonging to different mixed oxide phases ZnO and SnO$_2$
are identified in Figure 3B.1 separately using corresponding JCPDS cards. Crystallite size is calculated using Scherer’s formula [19] for the (3 1 1) plane. Crystallite size increases with increase in substrate temperature as 20, 41 and 84 nm for 300, 350 and 400 °C substrate temperatures, respectively. Crystallite size increases with increase in the substrate temperature due to annealing effect and agglomeration of smaller crystallites into larger crystallites.

3B.3.1.2 Scanning electron microscopy study

Figure 3B.2 shows SEM images of Zn$_2$SnO$_4$ films deposited at different substrate temperatures and inset of Figure 3B.2 shows enlarged images. SEM images depict that the surface morphology is characterized by the presence of cubical micro-flakes. It can easily be observed that films start to grow with increase in substrate temperatures and randomly orientated flakes, which are strongly faceted, can be observed in the inset of the film deposited at 400 °C. Agglomeration of the randomly oriented flakelike grains makes the surface considerably rough and also numerous hollow voids are formed due to overlapping of the flakes increasing the effective surface area. Film deposited at 300 °C shows that growth of the film just started and that at 350 °C shows randomly oriented flakes branched in some direction. Increase in substrate temperature increases flakes size and flakes are well distributed at 400 °C than that at 350 °C due to agglomeration of the smaller crystallites. The characteristic feature of cubical flakelike is clearly evident in the Figure 3B.2 (c). The average size of these cubical flakelike is 1 µm. These flakes provide a porous structure which increases effective surface area and thus is very helpful for adsorption of the NO$_2$. It is important to note that effective surface area increases linearly for the samples deposited at 300, 350, and 400 °C. The cubical flakelike geometry observed from the SEM images supports the findings from XRD analysis.
Figure 3B.2 SEM images of Zn$_2$SnO$_4$ thin films deposited at different substrate temperatures (a) 300 (b) 350 and (c) 400 °C, respectively.

3B.3.1.3 Atomic force microscopy study
An atomic force microscopy (AFM) was used to study topography and measure the surface roughness of the films in tapping mode. For each sample, images were scanned for different areas to check for uniformity of the thin films. Figure 3B.3 shows AFM images of Zn$_2$SnO$_4$ films deposited at various substrate temperatures. Increase in the surface roughness is observed with increase in substrate temperature. Roughness of the films is 8, 28 and 35 nm for films deposited at 300, 350 and 400 °C, respectively. It is maximum for the film deposited at 400 °C supporting the observations in the SEM studies.
Figure 3B.3  AFM images of Zn$_2$SnO$_4$ thin films deposited at different substrate temperatures (a) 300 (b) 350 and (c) 400 °C, respectively.

3B.3.2 Optical characterization of Zn$_2$SnO$_4$ thin films

3B.3.2.1 UV-Visible analysis of Zn$_2$SnO$_4$ thin films

Figure 3B.4 shows graph of $(\alpha h\nu)^2$ versus $h\nu$ calculated using optical absorption confirming direct band gap of the Zn$_2$SnO$_4$ to be 3.49 eV which is less than reported band gap of Zn$_2$SnO$_4$ (3.7 eV). Band gap was calculated by measuring absorbance of the films in transmission mode and using Tauc equation [21] for direct allowed transitions. As reported by Aviles et al the fundamental band-gap of Zn$_2$SnO$_4$ is 3.60-3.70 eV, due to the incorporation of excess Zn into Zn$_2$SnO$_4$ matrix and after heat treatment, band gap is narrowed up to 3.25 eV [18]. On the other hand, based on the discussion of the Jiang et al [22] the red-shift in the fundamental band-gap for quasi-cubic Zn$_2$SnO$_4$ is attributed to differences in the crystal structure. Absorbance of the film decreases with increase in the substrate temperature of the films due to the decrease in the film thickness. At higher substrate temperature film thickness decreases due to the increase in the thermophoretic force which causes evaporation of droplets prior to the surface of substrates [23]. Band gap increases linearly with increase in substrate temperature due to the formation of Zn$_2$SnO$_4$. For higher film thickness
plane orientation changes and hence there is increase in the band gap of film. It is also reported that oxygen content influences the absorption across the band gap and shift in absorption edge is due to the change in the lattice oxygen [24]. Decrease in the lattice oxygen is due to the high growth rate at higher substrate temperatures. Blue shift in the band gap confirms the increase in the optical band gap, which is useful for gas sensors [25].

![Figure 3B.4 (αhv)^2 versus hv curves of spray deposited Zn2SnO4 films deposited at different substrate temperatures.](image-url)
3B.3.3 Gas sensing study of Zn$_2$SnO$_4$ thin films

Gas sensing measurements of the Zn$_2$SnO$_4$ thin films deposited at different substrate temperatures were done towards various gases, gas concentrations and different operating temperatures. Gas response is calculated using formula (3B.1)

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

(3B.1)

where \( R_a \) is the resistance of the sensor in air and \( R_g \) is the resistance of the sensor in presence of gas. Response time is measured as time taken by the sensor to reach 90% of its maximum gas response upon purging analyte gas in the test chamber and recovery time is the time taken by the sensor to reach 10% of the maximum gas response value upon removal of gas.

3B.3.3.1 Selectivity of Zn$_2$SnO$_4$ thin film sensor

![Selectivity study of Zn$_2$SnO$_4$ film towards NO$_2$ operating at 200 °C temperature.](image)

Figure 3B.5 Selectivity study of Zn$_2$SnO$_4$ film towards NO$_2$ operating at 200 °C temperature.
Initially selectivity of the fabricated sensor is measured towards various oxidizing and reducing gases and corresponding bar graph is plotted in Figure 3B.5. It is observed that gas response is higher towards NO\textsubscript{2} and it is less for all other gases confirming Zn\textsubscript{2}SnO\textsubscript{4} films are exclusively selective towards NO\textsubscript{2}. Underlying origin of this exclusive selectivity towards NO\textsubscript{2} is the highly oxidizing nature and higher electron affinity (2.27 eV) of NO\textsubscript{2} in comparison with electron affinity of the preadsorbed oxygen species (0.44 eV) and other gases [26]. This results in higher gas response of Zn\textsubscript{2}SnO\textsubscript{4} films towards NO\textsubscript{2} as compared with other gases. The highest gas response towards NO\textsubscript{2} is estimated to be 29 which is much higher than that towards other studied gases (less than 2). Noting these facts further measurements were carried out towards NO\textsubscript{2} at different operating temperatures and at different NO\textsubscript{2} concentrations.

In order to quantify the selectivity, the selectivity coefficient of the sensor is calculated using equation 2 and the values are tabularized in Table 3B.1.

\[
K = \left| \frac{S_t}{S_i} \right|
\]

(3B.2)

where \(S_t\) is the gas response of the target gas and \(S_i\) is the gas response of interfering gas. Selectivity coefficient varies from 19.3 to 24.2 for optimal sensor operating at 200 °C towards 40 ppm gas concentrations. Pronounced selectivity towards NO\textsubscript{2} in presence of SO\textsubscript{2} is observed, which is another major representative coexisting air pollutant.
Table 3B.1 Selectivity coefficient of Zn$_2$SnO$_4$ films deposited at 400 °C towards various gases.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Selectivity Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$S</td>
<td>24.2</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>19.3</td>
</tr>
<tr>
<td>CO</td>
<td>18.1</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>22.3</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>20.7</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>1.00</td>
</tr>
<tr>
<td>LPG</td>
<td>24.2</td>
</tr>
</tbody>
</table>

Many reports have been published describing NO$_2$ sensing mechanism by a MOS sensor of transition metal [27-28]. The NO$_2$ adsorption takes place in two different ways depending on the type of site it is being adsorbed. Monomolecular adsorption (NO$_2^-$) and adsorption by dissociation in to NO$^-$ as discussed elsewhere [29]. Reactions involved in the adsorption and reaction are as follows.

$$Zn_{2n}SnO_{4n} + 2e^- + NO_2^{(gas)} \rightarrow Zn_{2n}SnO_{4n} + NO_2^{(ads)}$$  \hspace{1cm} (3B.3)

$$Zn_{2n}SnO_{4n+1} + V_0^* + e^- + NO_2^{gas} \rightarrow Zn_{2n}SnO_{4n} + NO^-^{(ads)}$$  \hspace{1cm} (3B.4)

where $V_0^*$ is the oxygen vacancy. This reactions shows that variation in the gas response is depend on the adsorption and charge transfer reaction which involves oxygen vacancies free charge carriers in the film.

3B.3.3.2 Variation of gas response with operating temperature

Figure 3B.6 shows variation in gas response of different Zn$_2$SnO$_4$ films operating at different operating temperatures towards 40 ppm NO$_2$ concentration. It is worth to note that gas response increases with increase in substrate temperature which in result causes change in phase of films. It is
maximum for the film deposited at 400 °C having pure Zn$_2$SnO$_4$ phase and it decreases for other films containing ZnO and SnO$_2$ mixed oxide phase. Increase in the gas response with change in phase is attributed to the increase in the adsorption sites. At higher substrate temperatures gas response increases due to the change in orientation of the film. It is observed from the XRD patterns that film deposited at 400 °C shows maximum gas response having preferred orientation along (311) plane. Change in preferred orientation changes adsorption energy of the analyte gas molecules and activation energy of the point defects in the crystallites [30].

**Figure 3B.6 Effect of operating temperature on Zn$_2$SnO$_4$ films films deposited at different substrate temperatures towards 40 ppm NO$_2$.**

This changes the chemisorption characteristics of the crystallites from one crystal orientation to another [30, 31, 32]. It can also be noted that gas response is higher for pure phase film orientated along (3 1 1) plane and it decreases for the mixed oxide phase having no preferred orientation. Similar results were reported by Kim et al. [33], they report SnO$_2$ film oriented along...
different planes showed the different gas response and different temperature dependence of gas response. Moon et al. reported that response time is closely related to the surface roughness but there was little association with the orientation of planes [34].

Thermal energy assists the adsorption of NO₂ as NO₂⁻ or 2NO⁻ by charge transfer from electrons or through the pre-adsorbed oxygen species, respectively. A dynamic equilibrium state between the adsorption and the subsequent desorption of oxygen and NO₂ occurs and it changes as the operating temperature is changed changing response values. Knowing this, in order to optimize operating temperature gas sensing is carried out at varied temperature range of 50-300 °C towards 40 ppm NO₂ (Figure 3B.6). It is observed that, gas response increases with increase in the operating temperature and maximum is observed at 200 °C and gas response decreases with further increase in temperature. Initially at 50 °C gas response is zero since gas could not adsorb and react with the film surface [35] due to low temperature. Gradual increase in gas response at 100 °C is observed and with further increase in operating temperature significant rise in the response value is seen. It is observed that, gas response increases with increase in the operating temperature and maximum is observed at 200 °C and gas response decreases with further increase in temperature. Initially at 50 °C gas response is zero since gas could not adsorb and react with the film surface [35] due to low temperature. Gradual increase in gas response at 100 °C is observed and with further increase in operating temperature significant rise in the response value is seen.

This increases the respective activation energy barriers by increasing length of depletion layers and highest response value is noted at 200 °C. With further increase in the operating temperature above 200 °C response is reduced. At higher operating temperature (>200 °C), the adsorbed analyte gas species decrease on the film surface due to the higher desorption rate than adsorption rate of the analyte gas. Decrease in the depletion length is observed thereby owing to decrease in the gas response at higher operating temperatures [36]. Film deposited AT 400 °C has higher gas response for all operating temperatures as compared with other films. Enhanced gas response can be attributed to the higher crystallinity, porosity, and surface roughness of the film compared with
other films. This shows that substrate temperature has noteworthy effect on the gas sensing properties of Zn$_2$SnO$_4$ films. Since all the films shows highest gas response at 200 °C operating temperature further measurements were carried out at 200 °C.

3B.3.3.3 Variation of gas response with NO$_2$ concentration

![Graph showing transient response curves of Zn$_2$SnO$_4$ films towards various concentrations of NO$_2$ operating at 200 °C temperature.](image)

Figure 3B.7 Transient response curves of Zn$_2$SnO$_4$ films towards various concentrations of NO$_2$ operating at 200 °C temperature.

Apart from this, we have also examined gas response of Zn$_2$SnO$_4$ films as a function of NO$_2$ concentration. Figure 3B.7 shows transient response curves of
Zn$_2$SnO$_4$ films towards various concentrations of NO$_2$ operating at 200 °C temperature. As expected, response of the sensor increases quickly as soon as gas is in and returns to its initial value when gas is evacuated out of the test chamber. It shows purely reversible gas response for all the sensors operated at different operating temperatures. Gas response increases with increase in NO$_2$ concentration from 1.32 to 29.27 for 8 to 80 ppm NO$_2$ concentration.

![Figure 3B.8](image_url)

Figure 3B.8 Effect of NO$_2$ concentration on gas response of Zn$_2$SnO$_4$ films deposited at different substrate temperatures at 200 °C operating temperature.

Clearly, the response increases sharply as the NO$_2$ concentration increases from 8 to 40 ppm but saturates when the concentration increases further to 80 ppm. It is worth noting that a response corresponding to concentration of 24 ppm is as high as 18.56 above the value 15, a criterion required for practical application of the sensor [37]. The major difference
between three curves is that the response for the film deposited at 400 °C is substantially larger than that for the films deposited at 300 and 350 °C.

3B.3.3.4 Response and Recovery time

Table 3B.2 Response and recovery times of Zn$_2$SnO$_4$ films deposited at different substrate temperatures.

<table>
<thead>
<tr>
<th>Gas concentration (ppm)</th>
<th>300 °C</th>
<th>350 °C</th>
<th>400 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Response time</td>
<td>Recovery time</td>
<td>Response time</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>35</td>
<td>1</td>
</tr>
<tr>
<td>16</td>
<td>5</td>
<td>35</td>
<td>3</td>
</tr>
<tr>
<td>24</td>
<td>6</td>
<td>45</td>
<td>4</td>
</tr>
<tr>
<td>32</td>
<td>6</td>
<td>50</td>
<td>4</td>
</tr>
<tr>
<td>40</td>
<td>8</td>
<td>55</td>
<td>5</td>
</tr>
<tr>
<td>60</td>
<td>8</td>
<td>71</td>
<td>8</td>
</tr>
<tr>
<td>80</td>
<td>8</td>
<td>34</td>
<td>8</td>
</tr>
</tbody>
</table>

The response and recovery times are two key parameters of a sensor as far as gas sensors are concerned. Table 3B.2 shows response and recovery kinetics of Zn$_2$SnO$_4$ sensors. It is important to note that response of the sensor is faster than recovery for all the NO$_2$ concentrations. Response and recovery times are measured in light of the definitions and optimal values are 8 and 58 s, respectively, for the highest response value. The response and recovery times also meet the basic demands for an industrial application of the sensor [37]. It is worth noting that the response observed for the Zn$_2$SnO$_4$ sensor is higher than several earlier reports based on NO$_2$ sensors [12, 16, 27, 38, 39]. Along with this response and recovery times of Zn$_2$SnO$_4$ sensor are fast, films are highly selective towards NO$_2$ and operating at moderately lower operating temperature. Pristine films show excellent gas-sensing characteristics without use of any noble metal.
or surfactant. These high responses, short times, together with the higher selectivity, suggest that the Zn$_2$SnO$_4$ sensors may hold the potential for developing a NO$_2$ gas sensor.

### 3B.3.3.5 sensitivity of Zn$_2$SnO$_4$ thin film sensor

Sensitivity of the sensor is calculated using slope of the graph of gas response versus gas concentration as shown in Figure 3B.8. Sensitivities of the Zn$_2$SnO$_4$ sensors synthesised at different temperatures are mentioned Table 3B.3.

<table>
<thead>
<tr>
<th>Substrate temperature (°C)</th>
<th>Sensitivity (ppm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.056</td>
</tr>
<tr>
<td>350</td>
<td>0.306</td>
</tr>
<tr>
<td>400</td>
<td>0.746</td>
</tr>
</tbody>
</table>

Sensitivity increases with increase in substrate temperature and film deposited at 400 °C shows higher sensitivity.

### 3B.4 Conclusions

The ternary oxide Zn$_2$SnO$_4$ films were successfully deposited by spray pyrolysis method using DI water as solvent. XRD analysis was used to confirm formation of Zn$_2$SnO$_4$. The sensitivity and selectivity of Zn$_2$SnO$_4$ thin films towards NO$_2$ gas was tested. Both parameters were found to be high at moderately low (200°C) operating temperature of the sensor for the films deposited at substrate temperature 400°C. Gas response varies from 1.32 to 29.27 for 8 to 80 ppm NO$_2$ concentration. The response time for the films varies from 3 to 8 s while recovery time is relatively higher than the response time.
References


