Enhanced toxic gas sensing properties with hexagonal- polyhedral 3D like ZSO chemiresistive sensor

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Abstract

An enhanced thickness modification of gas sensing device was fabricated in our lab which integrates the gas adsorbent and the electrochemical detection of toxic gas (NO\textsubscript{2}). The polyhedral perovskite ZSO nanocomposite has been synthesized by sol-gel method and report on novel, selectivity, low operating temperature NO\textsubscript{2} gas sensor based on ZSO nanocomposite. The conventional ZSO nanocomposite material has been measured the influence of width discrepancy from 230 nm to 644 nm. The ZSO nanocomposite film thickness ~ 460 nm exhibited a greatest sensor response ~ 2.1×10\textsuperscript{3} towards 20 ppm NO\textsubscript{2} at an operating temperature of 90°C. Moreover, NO\textsubscript{2} detection was observed earlier response kinetics in which response and recovery time to be 3.51 and 6.91 min, respectively. The detected reproducibility tested sensor was 97%. The sensor exhibits high selectivity to NO\textsubscript{2} (20 ppm) than other cross-sensitivity such as CO, acetone, IPA, CH\textsubscript{4}, NH\textsubscript{3} and CO\textsubscript{2} (2000 ppm) were also investigated. Finally, the investigated sensor could be used for the trace detection of NO\textsubscript{2} at industrial level.

1. Introduction

Semiconductor oxides such as SnO\textsubscript{2}, ZnO, hBN, CdS, In\textsubscript{2}O\textsubscript{3}, and WO\textsubscript{3} have worldwide explored materials for low-level detecting of many gases such as CO, CO\textsubscript{2}, SO\textsubscript{2}, NH\textsubscript{3}, CH\textsubscript{4} and NO\textsubscript{2}, with the rapid growth in globalization, industrialization is of huge significant to both personal and environmental safety [1–4]. The production of toxic gas which has a corrupt effect environment protection, occupational safety and public health [5]. At 50–110°C, a resistive electron exhaustion layer is set up close to the n-type semiconductor oxide surface by the adsorption of adversely exciting oxygen. Which has an oxidative or reductive collaboration with the objective gases that prompt a substantial change in electrical conductivity [6]. The principle preferences are the straight forward sensor structure and working calculation. In any case, these detecting materials respond with few gases instantaneously. Different methodologies have been acquainted with accomplish particular gas detecting [7]. These incorporated the operating temperature with the accumulation of a noble material or metal clusters [8], surface alteration [9–10], control of the nanostructure [11], the utilization of neural system calculation [12] and the plan of multi-compositional detecting semiconductor [13–14].

Tin oxide has been generally utilized for different catalytic applications such as gas detection, translucent conducting probes and LCD, etc. [15–19]. As we know that the wide vitally band gap shows the n-type semiconductor, tin oxide and zinc oxide (SnO\textsubscript{2} & ZnO) traverse an extensive scope of utilizations in the form of conductive anodes and straight forward coatings, to composite photovoltaic and sensors application [20–21]. SnO\textsubscript{2} and ZnO possess the excellent capability of simple trade of oxygen from the air because of its common non-stoichiometry, it is a most appropriate material for gas sensor. The conductance of SnO\textsubscript{2} and ZnO is change due to which adsorption/desorption on the surface of an oxygen molecule. The adsorbed oxygen at first glance (or grain area) of SnO\textsubscript{2} and ZnO catches the free electrons and progresses toward becoming O\textsuperscript{2–}. The significant to point of the chemisorption's oxygen on the surface is pivotal for gas detection device. Gas detection characteristic is subjected to
microstructure, contaminations and size impact of crystallites. It is outstanding that gas-detection attributes of SnO$_2$ can be drastically changed by governing the surface morphology and microstructural highlights, for example, surface to volume ratio, size distribution, structure and porosity of the material. SnO$_2$ and ZnO nanostructures have been described to be readied utilizing diverse chemical methods [22–24]. One of them, the chemical route technique has the benefit as on low working temperature handling and there is no O-H group on the surface, which influences its properties [20, 22]. SnO$_2$ nanoparticles have been observed to be capable for toxic gas detection to distinguish gases, for example, NO, NO$_2$, CO, H$_2$S, C$_2$H$_5$OH etc. [25–29] however, the sensors dependent on SnO$_2$ nanostructures request higher working temperatures. Then again, the real-world gas sensors required room temperature work sensor with improved response properties for detection of trace-level toxic gas. ZnO is an additional semiconductor material used for the production of gas detection; though their detection response is not so encouraged however, the working temperatures are low. Later, a nanocomposite thin film of SnO$_2$ with ZnO might be useful in diminishing the working temperature with improved detecting response.

Worldwide, NO$_2$ interact with water, oxygen and other chemicals to form acid rain, which are harm the constancy of ecosystem. NO$_2$ is the real reason for prearrangement of ozone bellow the stratosphere layer, acid rains and a functioning fixing to an unnatural weather change. Introduction to elevated concentrations of NO$_x$ can make living beings progressively powerless to bacterial diseases and lung malignant growth. Much the same as different poisons, nitrogen dioxide influences individuals with existing ailments more extremely than sound individuals. From now, it is essential to develop a NO$_2$ gas sensor to continuously monitor environment.

In this investigation, SnO$_2$ doped ZnO various nanocomposite thin films were dropped on the surface of an ID Electrodes substrate by spin coating of two solutions containing the precursors for composite (ZSO) solution with consequent warmth conduct. The sensing materials utilized for selective identification of toxic gas as NO$_2$ was structured from the relation in-betweens them of sensing material composition and gas detection response.

The accessible NO$_2$ detection response is very low even at high concentration of gas inserted in the chamber and high operating temperature (150–800 °C) as appeared in Table 1[30–39]. So, our efforts are going to improve the detection response of NO$_2$ gas along with a decrease in gas concentration and working temperature by doping of a few catalysts as described in Table 1. Hence in this paper, a sensor developed on SnO$_2$ doped with ZnO nanocomposite has been studied for low concentration and low working temperature of NO$_2$ gas detection identify.
Table 1
Comparative literature survey on metal oxide-based catalyst modified work as NO2 gas sensors.

<table>
<thead>
<tr>
<th>Material used</th>
<th>Catalyst/doping</th>
<th>Method</th>
<th>Temp (°C)</th>
<th>Sensor Response (gas concentration)</th>
<th>Response/Recovery time</th>
<th>Ref. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO thin film</td>
<td>Au/SnO2</td>
<td>Scalable Synthetic</td>
<td>300</td>
<td>13 (10 ppm)</td>
<td>108 sec / 127 sec</td>
<td>30</td>
</tr>
<tr>
<td>SnO2 thin film</td>
<td>Graphene</td>
<td>Chemical route</td>
<td>25</td>
<td>0.25 (10 ppm)</td>
<td>310 sec / 700 sec</td>
<td>31</td>
</tr>
<tr>
<td>WO3 thin film</td>
<td>Iron oxide</td>
<td>Sputtering</td>
<td>300</td>
<td>20 100 ppm)</td>
<td>- / -</td>
<td>32</td>
</tr>
<tr>
<td>WO3 thick film</td>
<td>TiO2, In2O3, SnO2/ Au, Pd, Pt</td>
<td>Screen Printing</td>
<td>300</td>
<td>95 (80 ppm)</td>
<td>2 min / 3 min</td>
<td>33</td>
</tr>
<tr>
<td>ZnO thin film</td>
<td>SnO2</td>
<td>Solvothermal Route</td>
<td>200</td>
<td>258 (100 ppm)</td>
<td>53 sec / 10 min</td>
<td>34</td>
</tr>
<tr>
<td>SnO2 nanowires</td>
<td>Bi2O3</td>
<td>Vapor-Liquid-Solid Growth</td>
<td>250</td>
<td>56 (2 ppm)</td>
<td>200 sec / 250 sec</td>
<td>35</td>
</tr>
<tr>
<td>SnO2 thin film</td>
<td>Fe2O3</td>
<td>Wet Chemical</td>
<td>150</td>
<td>110 (10 ppm)</td>
<td>10 min / 20 min</td>
<td>36</td>
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<tr>
<td>SnO2 thin film</td>
<td>Pt/Pd</td>
<td>Vapor-phase growth</td>
<td>300</td>
<td>880 (10 ppm)</td>
<td>13 sec / 9 sec</td>
<td>37</td>
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<tr>
<td>TeO2 branched nanowire</td>
<td>SnO2</td>
<td>Vapor-Liquid-Solid Growth</td>
<td>100</td>
<td>10 (10 ppm)</td>
<td>10 min / 15 min</td>
<td>38</td>
</tr>
<tr>
<td>TiO2 nanowire</td>
<td>ZnO</td>
<td>Hydrothermal synthesis</td>
<td>200</td>
<td>21 (40 ppm)</td>
<td>65 sec / 235 sec</td>
<td>39</td>
</tr>
</tbody>
</table>

2. Experimental

2.1 Sensor Preparation

Pure SnO2, ZnO and ZSO nanocomposite thin films were prepared through the chemical route method. The sensing materials were synthesized using chemicals like as tin(IV) chloride pentahydrate (SnCl4·5H2O), zinc acetate, lithium hydroxide (Alfa Aesar, Thermo Fisher Scientific) having analytical grade quality. Ethanol (99.5%), isopropanol (99.5%), propan-2-ol (99.9%) and n-butyl acetate (99%) were purchased from Sigma-Aldrich Chemical Co.

2.2 Preparation of SnO2 solution
Take 12.37 g of tin tetrachloride (SnCl$_4$.5H$_2$O) with 15 ml isopropanol was dissolved to prepare a homogeneous solution. An exothermic reaction was taken place and later the homogenous precursor solution was chilled at room temperature. Now further take 3.42 ml DI water and 10 ml propan-2-ol homogeneous mixture solution was added into a 100 ml Teflon-lined autoclave. The homogeneous mixed solution was the reaction in Nabertherm furnace at 180 °C for 12 h and then the formation of sol SnO$_2$ nanoparticles [40].

### 2.3 Preparation of ZnO solution

The synthesis of ZnO solution discusses our previous published paper [13]. The zinc acetate sol was refluxing for 30 min at 75°C and after permitted to cool at room temperature (RT) and find clear stable Zn precursor, then further 0.05 gm of LiOH was mixed in 50 ml of ethyl alcohol and the colloidal solution was ultrasonicated for 15 min at RT to get a transparent solution and Zn-based precursor added dropwise with magnetic steering to get transparent ZnO sol is obtained. The addition of transparent precursor LiOH to the formation of ZnO solution nanoparticles (NPs) [13].

The growth of solution ZnO NPs were incorporated into SnO$_2$ NPs a homogeneous solution in the 2:3 molar ratio. SnO$_2$ and ZnO:SnO$_2$ (ZnSnO$_3$/ZSO) homogeneous solution was used to deposit own thin films by spin coating technique on IDEs (Interdigital Electrodes) patterned on corning glass substrates. Thin films were sintering at 500 °C for 2 h in atmospheric air.

Figure 1 depict that the overview of SnO$_2$, ZnO and ZSO nanocomposite thin film was deposited on the Interdigital electrode substrate by a spin coating method. The Pt Interdigital Electrodes were prepared on the corning substrate by a using conventional photolithography technique, after that sensing layer deposited (SnO$_2$, ZnO and ZSO nanocomposite film). Now Pt metal target was deposited on the corning substrate (90 nm film) using RF sputtering technique in presence of 100% Argon gas. The Pt on a corning substrate to improve the adhesion ultrathin layer of Ti (10 nm) was deposit before to Pt sputtered.

### 2.4 Characterization

Thickness profiler (Veeco Dektak 150) meter was measured the surface roughness of thin film deposited by a spin coating method. Crystalline structure was studied of an X-ray Diffractometer analysis (Bragg-Brentano; Bruker D8 Discover) using the CuK$_{\lambda 1}$ source ($\lambda = 1.5406 \text{ Å}$), film surface roughness of the sensing sheet was deliberate on Atomic Force Microscopy (AFM; Veeco DICP2) and Transmission Electron Microscopy (TEM; TecnaiG2, at 300 kV) respectively. UV-visible spectra of the samples (Perkin Elmer) were employed to study an optical characteristic of ZnO, SnO$_2$ & ZSO thin films.

### 2.5 Gas Detection System

NO$_2$ gas detecting attributes of sensors were examined in a uniquely designed chamber “Gas Test Calibration System (GTCS)”. NO$_2$ gas was transported in dome detection chamber utilizing aligned holes through needle controllers. In the detection system, the control flow of target gas was used Pirani gauge
with a rotary. In the test chamber, \( \sim 10^{-3} \) Torr order of vacuum was first created and then, the simultaneous mixture of clean air and known concentration of target gas was introduced in the detection chamber at atmospheric pressure. The development of vacuum confirms the elimination of target gas from the detection system. In static mode, all the sensing characteristic measurement was carried out. The recovery time of sensor defined as in the test chamber target gas was flushed out (by creating a rotary pump) and the fresh air was inserted in the chamber. The sensor was put in between thermocouple and central controlled heating hunk inside the detection system. The ID Electrode (IDE: Inter Digital Electrode) contacts of sensing film determined the detection response with the temperature of function. Initially, the sensing film was stabilised in the open chamber and become a constant resistance value at a given temperature. In detection chamber, the target toxic gas (NO\(_2\)) was introduced with specific concentration and variation of sensor resistance was noted subsequently all-time via data achievement scheme involving of an electrometer (Keithley 6514) connected with our computer. The oxidising detection response value was defined as:

\[
\text{Response (S)} = \frac{R_g - R_a}{R_a}, \quad \text{for } R_g \gg R_a
\]

\[
\text{Response (S)} = \frac{R_g}{R_a} \quad (1)
\]

Where, \( R_a \) and \( R_g \) are the resistance of the sensor in uncovered air and verified gas, respectively. The response time and recovery times were demarcated as the times essential to reach 90% of whole resistance variation [41].

3. Result and Discussion

The UV-visible optical transmission spectra were used to survey the optical characteristic of the film. The transmission spectra were recorded in wavelength range 190 to 1100 nm of the film SnO\(_2\), ZnO and ZSO growth on the corning glass substrate. Figure 2 depict that the transmission spectra of SnO\(_2\), ZnO and ZSO thin-film reduce by 30% i.e. from 90–60% in the UV-visible section and found a sharp-edge absorption at 340 nm in UV region, which is same as reported in the open literature [42]. It is observed that the transmission coefficient with an increase in wavelength and a sharp cut off is observed near the absorption edge. The energy gap of SnO\(_2\), ZnO and ZSO thin films were estimated by generalizing the rectilinear part of these plots to the energy axis. Figure 3 shows the Tauc plot and the ZnO nanoparticles incorporated to SnO\(_2\) thin film was found increased the bandgap 4.15 eV. When SnO\(_2\) and ZnO confining to the formation of ZSO nanocomposite hybrid due to electronics interaction of ZSO thin film in a variation of the bandgap.

Figure 3 show that the Tauc plot of \( (\alpha h\nu)^2 \) vs photon energy \( (h\nu) \) of optical band gap SnO\(_2\) thin film was measured from the interrupt on the energy axis. The less than 5% error was resolve in the bandgap. The extrapolation of the linear portion of SnO\(_2\) thin film predictable worth of band gap was measured to be
4.07 eV which is nearby to the reported ethics for SnO$_2$ thin films (4.3 eV) grownup by numerous methods.

As the growth of ZnO, SnO$_2$ and ZSO nanostructured thin film was observed to be amorphous nature and converted nanocrystalline subsequently annealed at 500 °C for 2 h in air annealing fameness. Figure 4(a, b, c) depicts that the XRD spectra of ZnO, SnO$_2$ and ZSO thin films. The strong adhesion film was found after the post annealed treatment of thin film to be smooth and transparent. Figure 4(a) depict that the initial peak can be indexed sharp wurtzite hexagonal structure of ZnO reflection plane described in our previous report [13]. The diffraction pattern of SnO$_2$ thin film was displaying well-defined peaks with corresponding to (110), (101), (200), (111), (210), (211), (223) and (220) planes from Fig. 4(b). The SnO$_2$ thin film highest orientations were observed plane (110), (101) and (211) at an angle 26.6°, 33.8° and 51.8° respectively and these are reflecting decent agreement with rutile structure values reported [30]. The lattice parameter ‘a’ and ‘c’ can be calculated from XRD data for SnO$_2$ thin films was found 4.62 Å and 3.21 Å respectively, which are close to the reported values for bulk [43]. The slight deviation in lattice constant may be attributed to the presence of stress in the film prepared using the chemical route. The XRD pattern of orthorhombic perovskite ZSO nanocomposite crystal structures are depicted in Fig. 4(c). It may be noticed from the figure that the highest peaks observed at 2θ = 25.3°, 31.7°, 34.4° and 36.3° correlate with to the (110), (311), (002), (222) and (101) reflection planes of ZSO, where peak noticed at 2θ = 33.8° corresponds to (101) reflection plane of ZnO confirming the presence of ZnO and SnO$_2$ in ZSO nanocomposite [44–45].

The crystallite sizes were estimated as ~ 9.8 and 8.6 nm for SnO$_2$ and ZSO nanocomposite thin films respectively. Thus, the formation of SnO$_2$ and ZSO thin films having small crystallite size, which is providing a higher surface to volume ratio and helpful for gas sensing device. The smaller crystallite size contributes to a large number of grain boundaries which may provide higher to the gas molecule to interact with the sensing film.

The SEM image of SnO$_2$, ZnO and ZSO thin films are depicted in Fig. 5. SEM micrograph of SnO$_2$ thin film from Fig. 5(a & b) shows that all the grains are almost unbalanced and hexagon in shape. Figure 5(c) depicts that the energy-dispersive X-ray spectroscopy (EDX) achieved on SnO$_2$, which shows that element present (tin, oxygen and carbon). From Fig. 5(d & e) depict the SEM micrograph of ZnO thin film are agglomeration formed in smaller spherical shape morphology with particle size in the nanometer range. The energy-dispersive X-ray spectroscopy (EDX) achieved on ZnO, which show Fig. 5(f) the element present in the Zn, O and small impurity peak found. The composite sample of SEM micrograph from Fig. 5(g & h) reveal that ZSO thin film has Hexa-spherical small grain and regular grain polycrystalline nature, and are pronounced with nano-size Hexa-spherical grain boundaries. The chemical composition of the thin film was observed by energy-dispersive X-ray spectroscopy (EDX) achieved on ZSO, which show Fig. 5(i) the element presents of Zn and Sn and O in the thin film. We noted that there are no other impurities in this film, which is displays a high degree of purity of film and good accordance with the XRD pattern.
The structure and surface morphologies of the as-grown SnO$_2$, ZnO nanostructures and ZSO nanocomposites were studied by TEM and shown in Fig. 6 (A, B and C). First formulating sample for TEM observation, as per synthesis of products were added into an ethanol solution (molar ratio of product and solvent, 1:99) and 1 hour ultrasonic to form a homogeneous solution; afterwards, a drop of solution containing SnO$_2$, ZnO nanostructure and ZSO nanocomposite was dipped on a copper grid used for TEM analysis. It is displayed from Fig. 6A(a-e) that the hexagonal prearrangement shape of SnO$_2$ nanostructure having size 40 to 200 nm. SAED pattern indicates the crystalline nature of SnO$_2$ displays in Fig. 6A(f). Figure 6B(a-b) is the TEM image of ZnO nanostructures which exhibits the tetrapod structure of top and side view of prepared ZnO nanoparticles. It is confirming that the tetrapod has an approximate uniform width and shapes over the whole lengths. In a large view of Fig. 6B(b), it can be displaying that ZnO is composed of nano-triangles with a length array from 120 to 150 nm. So, we can say that some nano-tetrapod structure ZnO is also formed in addition to nano-triangles. The formation of the tetrapod structure may be attributed to the presence of strain arise after the lattice discrepancy or deformation [43, 45–46]. SAED pattern indicates the crystalline nature of ZnO displays in Fig. 6B(f). The TEM images of ZSO nanostructures are illustrated in Fig. 6C(a-e). Different polyhedral shaped crystals may be observed in TEM images. The regular crystal structure was observed like hexagonal shape in the range of 10–60 nm as calculated from TEM images. Therefore, the formation of cap type tetrahedron and pyramidal-shaped structure is observed. The formation of possible hexagonal-like particles shows the ZnSnO$_3$ phase which is also reported by Found et al. and Dong et al. [43, 47] Fig. 6C(f) shows the SAED pattern to study the structural properties of the prepared ZSO nanocomposites.

AFM images of the SnO$_2$, ZnO and ZSO nanocomposite thin film-based sensor structures are depicted in Fig. 7. The gray worth of respectively pixel position of AFM image can be transformed to elevation value by the height-gray ruler demonstrations in Fig. 7. The surface roughness $\sigma$ and grain size $R_0$ are usually defined as [48];

$$\sigma = \left[ \sum \frac{(h_{ij} - \bar{h})^2}{(N-1)} \right]^{\frac{1}{2}}$$ (2)

where $h_{ij}$ is the height of the site $(i,j)$ and $h$ is the average height of the entire film and $R_0$ defined as;

$$R_0 = \left( \frac{S_0}{N_0\pi} \right)^{\frac{1}{2}}$$

Where $S_0$ is the whole film area of the AFM and $N_0$ is the grain number. The planer image demonstrates the grain size and surface roughness of the sample. Figure 7(a-c) reveals that the AFM image of pure SnO$_2$ thin film has got uniformly distributed spherical grain structure with rough surface morphology. The forthcoming image represents the release of the granular structure same as reported by Hassun et al. [49]. The average surface roughness of SnO$_2$ thin film was discovered to be $\sim$ 42 nm. The AFM image
ZnO reveals that the change in surface morphology such as grain size and line profiling with particle distribution is shown in Fig. 7(d-f). The average surface roughness of ZnO thin film was calculated to be 40 nm and similar polyhedral shape reported by Sun et al. [48]. From Fig. 7(g-i) shows that the ZSO film has a very rough surface due to the degenerated shape surface morphology caused by increased surface roughness. However, with the incorporation of SnO\textsubscript{2} into ZnO, the surface roughness increases to \( \sim 70 \) nm along with the reduction in grain size (Fig. 7). The elongated channels are observed in ZSO nanocomposite thin film which provides more grain boundaries to target gas for interaction leading to enhancement in gas sensing response [50].

Figure 8 (a) and (b) shows the topographical 2D and 3D image of ZSO thin film surface over an area 50 x 45 \( \mu \text{m}^2 \) using a surface profiler. It can be observed that the average surface roughness of ZSO film having 460 nm thickness, was found to be about 70.66 nm which shows the deposited ZSO thin film is having absorbent and irregular surface morphology. The availability of rough surface morphology of the sensing portion is beneficial for gas detection because due to the large accessibility of surface area for target gas interaction.

### 3.1 Sensing Measurement

Figure 9, 10 and 11 shows that the transform sensing response, response time and recovery time respectively for pure SnO\textsubscript{2}, ZnO and ZSO composite thin films of different thickness as a function of temperature when exposed to NO\textsubscript{2} gas toward 20 ppm. I can be fulfilled the sensing response from Fig. 9 (a) for all prepared sensor response first increases with increasing in temperature till 90°C and on a further increase of the temperature, sensing response reduces. The result indicates that the SnO\textsubscript{2} thin film maximum sensing response \( \sim 280 \) towards operating temperature 90°C, whereas, ZnO based sensor exhibited a poor sensing response of \( \sim 20 \) at towards the same working temperature (90°C). The improvement in gas sensing response was obtained with the formation of thin-film by the incorporation of ZnO nanoparticles into SnO\textsubscript{2} colloidal solution. However, the thickness of the ZSO nanocomposite thin film tells a crucial characteristic in enhancing the detection response. The sensing response was increased from \( \sim 300 \) to 2100 with increases in thickness from 230 to 460 nm ZSO. Through, the further rise in thickness to 644 nm, the sensing response reduces. Chen et al. have also prepared ZnO:SnO\textsubscript{2} nanocomposite thin film using microemulsion technique and reported the detection response \( \sim 34 \) at a working temperature 250°C [51]. The present study is observed that the higher sensing response, which ascribed toward the development of nanostructure ZSO composite thin films taking nanoporous microstructure (Fig. 5). The large surface area of nanocrystalline ZSO films provides higher detection response due to the adsorption on the surface of toxic (NO\textsubscript{2}) gas. The impact of relative humidity on the reaction has been considered ZSO (460 nm) film towards 20 ppm of NO\textsubscript{2} gas at a working as room temperature which are represented as in Fig. 9 (b). The sensor responses were obtained to be decreasing from 2100 to 532 for ZSO (460 nm) thin film at higher humidity. In Fig. 9(b) curve (I) represent the transient resistant variation of ZSO (460 nm) film with the increasing relative humidity (%RH) when NO\textsubscript{2} gas is not exposed, whereas curve (II) represents the same after the exposure of NO\textsubscript{2} gas.
The characteristic response (gas sensing response, response/recovery time) curve obtained at 90°C working temperature for the deposited thin film sensor structures taking SnO$_2$ and ZSO composite thin films are summarised in Table 2. It may be observed from Figs. 10 and 11 depict that the response/recovery times are found to be decreased through an increase in the working temperature due to an increased rate of adsorption and desorption at a higher temperature. The pristine SnO$_2$ thin film was detected to give slow sensing response/recovery time of about ~ 12 min / ~10 min whereas, the pure ZnO thin film was found to give comparatively faster-sensing response/recovery time ~ 6.6 and 3.5 min. The incorporation of ZnO into SnO$_2$ film to form a hybrid nanocomposite yielded enhanced response and recovery time (Figs. 9 and 10). ZSO thin film of thickness 230 nm shows faster response time ~ 5.3 min, whereas on increasing the thickness of nanocomposite ZSO thin film, the response time becomes slower about 5 min till 550 nm thick whereas on further increasing the thickness to 644 nm. The slower response time with increasing the thickness may be attributed to the increased area of the sensing surface whereas huge interactions of nitrogen dioxide gas molecules are increases. Similarly, ZSO sensor thickness film is increasing then increasing in the recovery time of the sensor. The recovery time was observed to be decreased with the incorporation of ZnO into SnO$_2$ through a rise in the width of ZSO thin film from 230 nm to 644 nm.

Table 2

Sensing parameters obtained for three different sensor structures: ZSO film thickness 230 nm, ZSO film thickness 460 nm and pure SnO$_2$ film thickness 500 nm at operating temperature of 90°C for 20 ppm of NO$_2$ gas.

<table>
<thead>
<tr>
<th>Structure type (Thin Films)</th>
<th>Sensor Response</th>
<th>Response Time (min.)</th>
<th>Recovery Time (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSO (230 nm)</td>
<td>$5.26 \times 10^2$</td>
<td>4.35</td>
<td>5.35</td>
</tr>
<tr>
<td>ZSO (460 nm)</td>
<td>$2.13 \times 10^3$</td>
<td>3.51</td>
<td>6.63</td>
</tr>
<tr>
<td>SnO$_2$(500 nm)</td>
<td>$4.21 \times 10^2$</td>
<td>8.96</td>
<td>9.10</td>
</tr>
</tbody>
</table>

Figure 12 (a) depicts that the changing of sensing device resistance observed in air ambience ($R_\text{a}$) designed for all developed sensor structure. At room temperature, air resistance ($R_\text{a}$) values for developed films are relatively lower (< 1 GΩ) which is beneficial for getting enhanced sensing response towards NO$_2$ gas detection. A bare SnO$_2$ film-based sensors display higher $R_\text{a}$ value of 644 MΩ at room temperature whereas pure ZnO thin film sensor structure shows a lower $R_\text{a}$ value of 82 MΩ. When ZnO was incorporated into SnO$_2$ the sensor resistance was found increased from 86 MΩ to 970 MΩ through a rise in the width of ZSO thin film from 230 nm to 460 nm respectively. Thereafter on further increasing the ZSO film thickness to 644 nm the sensor resistance, $R_\text{a}$ decreases to 182 MΩ. The variation in value $R_\text{a}$ as a function of the thickness of ZSO sensor structure may be ascribed to be surface roughness. The surface roughness profile of the prepared sensor structure is summarised in Table 3. It can be observed that the rough surface morphology of developed ZSO sensors is rising from 23 to 70 nm with ZSO film width from 230 nm to 460 nm and on further increasing the thickness to 644 nm the surface roughness
reduces. The higher value of surface roughness indicates that the 40 nm ZSO thin film is comparatively porous indicating the higher surface to volume ratio. Due to the higher porosity, there is the possibility of more adsorption of ambience oxygen onto the rough sensing surface which results in more trapping of permitted electrons from the HOMO state of ZSO thin film leading to increasing in $R_a$ value. In Fig. 12 (b) evaluate the overall performance of the sensor resistance nodes baseline temperature measuring in atmospheric ambient sensor resistance decrease with increase in temperature.

Table 3

<table>
<thead>
<tr>
<th>Thickness of films</th>
<th>Surface Roughness</th>
</tr>
</thead>
<tbody>
<tr>
<td>230 nm ZSO</td>
<td>23 nm</td>
</tr>
<tr>
<td>400 nm ZnO</td>
<td>37 nm</td>
</tr>
<tr>
<td>460 nm ZSO</td>
<td>70 nm</td>
</tr>
<tr>
<td>500 nm SnO$_2$</td>
<td>42 nm</td>
</tr>
<tr>
<td>550 nm ZSO</td>
<td>40 nm</td>
</tr>
<tr>
<td>644 nm ZSO</td>
<td>27 nm</td>
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</tbody>
</table>

It can be observed from Fig. 12 all developed sensor structure, the value of $R_a$ is observed that reduction continuously through the rise in temperature representing a characteristic semiconducting nature of ZSO nanocomposite film. Nevertheless, it was observed that all prepared sensor structured the value of $R_a$ increases with temperature ranges 50–100 ºC. The hump was observed in $R_a$ value, which may be ascribed to the translation of physisorbed oxygen ($O_2^-$) species to chemisorbed oxygen ($O^{2-}$) species at a slightly higher temperature which captures the more electron thus the $R_a$ value increases. But due to the semiconducting behaviour of the prepared sensor, the $R_a$ value reductions on moreover rising in the temperature. The value of $R_a$ is observed slight hump in the temperature range 110–190°C due to oxygen molecule to molecular oxygen ions ($O^-_2$) and then oxygen species ($O^-$) reaction bellowed;

$$O_2 + e^- \rightarrow O^-_2 + e^- \rightarrow 2O^-$$

(4)

Then, the reaction kinetics for temperature variable sensor has been observed a numeral electron capture from the transmission band, which resulting presence of hump in $R_a$ at a sensible temperature. When the sensor is exposed in the chamber after then improve detection response due to the adsorbed oxygen on SnO$_2$ thin film surface at a moderate temperature [52].
Figure 13 depict that the resistance variation ($R_g$) of sensor observed in the occurrence of NO$_2$ gas at 20 ppm as a variation of temperature for wholly the developed sensor under investigation. Since NO$_2$ gas is an oxidising gas then interact with NO$_2$ gas molecules with sensor surface leads to a rise in the value of $R_g$ for all sensor structures at all measured temperatures. The value of $R_g$ is found to decrease first with increases in temperature till 90 ºC and on the further increasing temperature, the value of $R_g$ decreases for all developed sensor structure. The decrease in the value of $R_g$ at higher temperature is due to the faster role of desorption of gas with sensor surfaces. The maximum value thickness of $R_g$ is obtained for ZSO thin-film ~ 460 nm as compared to other sensor structures. Pure SnO$_2$ and ZnO thin film sensor structures show the maximum change in $R_g$ value of 32.43 MΩ and 42 kΩ, at a working temperature of 150 and 130 ºC respectively. Still, an amalgamation of ZnO into SnO$_2$, the value of $R_g$ is found to dependent on ZSO thin film. The value of $R_g$ is found to increase to 644 MΩ with a rise in ZSO film width to 460 nm at operating temperature and consequently rise in width to 644 nm, the $R_g$ value reduces to 45.61 MΩ. The maximum value of $R_g$ obtained at 460 nm ZSO film towards 20 ppm of NO$_2$ gas can be ascribed to the observed maximum surface roughness 70 nm. The large value of surface roughness indicates the formation of ZSO thin film having a higher surface to volume ratio providing more sites to NO$_2$ gas molecules for the interaction of the ZSO thin film surface.

### 3.2 Sensing mechanism

In gas sensing mechanism found that the improved sensing response could be achieved either by getting lower the value of $R_a$ or higher value of $R_g$ according to Eq. (1). The sensing response both changes occur simultaneously and then it is additionally beneficial for sensing a characteristic of ZSO thin film. It can be found that the value of $R_a$ is lesser (Fig. 12) in the inferior temperature section (< 100°C) for SnO$_2$ thin films. When upsurge in $R_a$ was detected for the SnO$_2$ thin film with the incorporation of ZnO and becomes much higher (> 0.6 MΩ) for all the ZSO thin film of different thicknesses. We observed that rise in the value of $R_a$ may be attributed to the electronic interaction between ZnO and SnO$_2$ which could be confirmed from the variation in the bandgap of ZSO nanocomposite (UV-Visible Spectroscopy). Since, both SnO$_2$ and ZnO are n-type semiconductors, so with the incorporation of ZnO into SnO$_2$ may lead to the formation of n-n junctions. Also, the work function of ZnO (5.2 eV) is larger than that of SnO$_2$ (4.35 eV), so there is a high probability of transfer of an electron from conduction of SnO$_2$ to ZnO due to which there will be the creation of space charge region. As we know that the NO$_2$ is an oxidising gas, which captures permissible electrons from the n-type semiconducting surface of ZSO thin film, later adsorption of NO$_2$ gas and then rise in the resistance of the developed sensor.

Since, permissible electrons are captured by NO$_2$ gas from the surface of the upper (conduction) band of SnO$_2$, ZnO and ZSO. Thus, reducing the conductance of the sensor structure leading to an increase in resistance of sensor ($R_g$). At lower working temperatures (< 90 ºC), trapping of electron on adsorbed oxygen species to change the depletion layer on the upper SnO$_2$ surface. When SnO$_2$ have interacted with
exposed NO₂ then NO₂ gas molecules react with no only adsorbed O⁻ ions but also directly adsorb on semiconducting metal oxide surface i.e. tin ionic sites [53]. SnO₂ responds to NO₂ gas as mentioned below [54];

\[
\begin{align*}
NO_2 + Sn^{2+}_{\text{adsorption}} & \rightarrow (Sn^{3+} \ NO_2)_{\text{desorption}} (Sn^{3+} \ O^-) + NO \quad (5) \\
2(Sn^{3+} \ O^-)_{\text{desorption}} & \rightarrow 2Sn^{2+} + O_2 \quad (6)
\end{align*}
\]

When the oxidizing NO₂ gas concentration of trapping electron adsorbed onto the plane of SnO₂ detection device decreases (offered Sn spots). Then electrical resistance rises due to the adsorbed electrons after the top of the surface (upper band structure of SnO₂) creating NO⁻2 class. Similarly, NO₂ gas adsorbed onto ZnO surface captures electrons from the upper band of ZnO. The schematic diagram of the sensing mechanism of ZSO sensor shown with band model in Fig. 14. The process of reaction is described as follows [55];

\[
NO_{2(gas)} + e^- \rightarrow NO_{2(ads)}^- \quad (7)
\]

After capturing of the electrons, NO₂ gas molecules get converted into NO₂⁻(ads) species which further reacts with adsorbed atmospheric oxygen and desorbs the NO₂ gas depicted as under;

\[
\begin{align*}
NO_{2(ads)}^- + 2O_{(ads)}^- & \rightarrow 2O_{(ads)}^{2-} + NO_2 \quad (8) \\
NO_{2(g)}^- + e^- & \rightarrow NO_{2(ads)}^- \quad (9) \\
NO_{2(ads)}^- + 2O_{(ads)}^- + 2e^- & \rightarrow NO_{(gas)} + 3O_{(ads)}^- \quad (10)
\end{align*}
\]

Chemical processes mentioned in Eqs. (7) and (8) are continued in series which results in a further decrease in the concentration of electronics on the surface of the sensor leading to an increase in resistivity of the sensor. Thus NO₂⁻(ads) is slowly desorbed as NO gas to the atmosphere [Eq. (9 &10)].

As a result, reducing the concentration of electron depletion layers and electron growth layers will be created charge transporters to the upper band of tin oxide (SnO₂), ZnO and ZSO heterojunction interface. This will be contributed to the rise in the value of sensor resistance (Rg) as found in the current study and due to enhance in the sensing response. Therefore, it is possible that a slow sensing phenomenon can be observed and undergoes a changeable oxidising interface at on the surface of SnO₂, ZnO and ZSO films.
Through the recovery characteristic of the adsorbed \( \text{NO}^{-2} \) / \( \text{NO}_2(ads) \) species on the surface then desorb in place of \( \text{NO} \) molecules, which departure as chemisorbed oxygen ions back on sensor surface [Eq. (5) and (9)]. The absorption of oxygen species has been trapped electrons accumulated on the sensor surface. The thin film surface is still lacking allowed electrons and therefore the inventive gain of the resistance \( (R_a) \) is not recovered. Afterwards, the left behind ionosorbed molecular oxygen species with adsorbing on the surface and deliver \( \text{O}_2 \) gas giving Eq. (6) [56–58]. Dynamic Sensing Response curve at operating temperature 90 °C is shown in Fig. 15 and a possible schematic drawing for the sensing mechanism are presented in Fig. 15. The electron transferred from \( \text{ZnO} \) to \( \text{SnO}_2 \) to balance the fermi level and potential barrier are formed at ZSO heterojunction and energy levels experiences bending (Fig. 16).

### 3.3 Selectivity and reproducibility of sensor

In the gas detecting experiment, the selectivity of the developed sensor has been tested for various gasses. The sensing response was measured for incompatibility interfering gasses to 2000 ppm such as \( \text{CO} \), \( \text{Acetone} \), \( \text{IPA} \), \( \text{CH}_4 \), \( \text{NH}_3 \), \( \text{CO}_2 \) and 20 ppm \( \text{NO}_2 \) towards a working temperature of 90 °C. The developed ZSO sensor was set up to be an extremely selective and remarkable aspect to \( \text{NO}_2 \) gas. The proposed sensor (Fig. 16) exhibits a higher sensing response \( (2.1 \times 10^3) \) due to rising the value of sensor resistance demonstrating the strong specific adsorption on the surface of ZSO film and interface of \( \text{NO}_2 \) gas molecules towards lower temperature (90°C). Though, a slight reduction the value of sensor resistance was found after exposure to common interfering gases (Fig. 17) demonstrating the growth of a hugely selective to ZSO sensor for the detection of \( \text{NO}_2 \) gas.

The prepared sensor was tested ZSO sensor over a time span of 6 months almost constant. From the Fig. 18 it is clear that the sensor provides good reproducibility showed consistent sensing response \( (~2.29 \times 10^2) \) over a given period of time for 20 ppm of \( \text{NO}_2 \) gas. Thus, it can be said that the prepared ZSO film sensor is highly durable and reusable \( \text{NO}_2 \) monitoring.

### 4. Conclusion

In this study, we report upon the \( \text{SnO}_2 \) and ZSO nanocomposite thin film-based gas sensor to ppm level detection of nitrogen dioxide under various operating temperature. XRD, SEM and UV-visible characterization confirmed that the presence ZSO nanocomposite thin film and the slight adsorption in the crystal lattice produce several defects, making it an improved detection response, also, there are additional oxygen vacancies of ZSO film, which is advantageous to the adsorption of oxygen and nitrogen dioxide on the surface reaction. The average crystallite sizes were estimated as 9.8 and 8.1 nm for \( \text{SnO}_2 \) and ZSO nanocomposite thin films. The usual surface roughness of ZSO composite thin film was found to be \(~40\) nm. ZSO nanocomposite thin film-based sensor exhibited the response \( 2.13 \times 10^3 \) with sensible response time 3.51 min and recovery time 6.63 min at an operating temperature of 90°C. This value is so much higher than that reported elsewhere in the literature. It was found that ZSO sensor
with active layer prepares by sol-gel annealing work reliability at low oxygen levels with again a high gas sensitivity. Our virtual test in contradiction of the commercially accessible devices confirmed the important enhancement reached with our ZSO sensor over the current generation. In conclusion; we believed that low power consumption and low cast ZSO based nanocomposite gas detection can be sense ppm level of \( \text{NO}_2 \) sensing. Consequently, we find that low cast ZSO sensor investigated here may be used as \( \text{NO}_2 \) applications.

**Declarations**

**Conflict of Interest Statement:**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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**References**


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**Figures**
Figure 1

Overview of the sensor fabrication procedure using the spin coating method.
Figure 2

Transmittance spectra of SnO$_2$, ZnO and ZSO composite thin film.

Figure 3

Tauc plot of $(\alpha h\nu)^2$ versus $h\nu$ of SnO$_2$, ZnO and ZSO nanocomposite thin film.
Figure 4

X-Ray Diffraction of the ZnO, SnO$_2$ and ZSO nanocomposite thin film.
Figure 5

SEM image of SnO$_2$, ZnO and ZSO nanocomposite thin film.
Figure 6

A: (a-e) TEM images of SnO$_2$ and (f) Electron Diffraction Pattern of SnO$_2$.

B: (a-e) TEM images of ZnO and (f) Electron Diffraction Pattern of ZnO.

C: (a-e) TEM images of ZnSnO$_3$ and (f) Electron Diffraction Pattern of ZnSnO$_3$. 
Figure 7

Atomic force micrograph of (a-c) SnO$_2$ thin film, (d-f) ZnO thin film and (g-i) ZSO thin film.
Figure 8

2D and 3D Topographical image of the surface of ZSO thin film.

Figure 9

(a) Sensor Response to 20 ppm NO$_2$ gas as a function of temperature for the SnO$_2$, ZnO and ZSO composite films deposited with a spin coater and (b) Variation of sensor resistance ZSO (460 nm) thin film with relative humidity (%RH).
Figure 10
Variation of response time as a function of temperature for the SnO$_2$, ZnO and ZSO composite films deposited with spin coater when exposed to 20 ppm NO$_2$ gas.

Figure 11
Variation of recovery time as a function of temperature for the SnO$_2$, ZnO and ZSO films deposited with spin coater when 20 ppm NO$_2$ gas was flushed out.
Figure 12

Variation of sensor resistance in the air ($R_a$) for the $\text{SnO}_2$, $\text{ZnO}$ and ZSO films.

Figure 13

Variation of sensor resistance in presence of 20 ppm $\text{NO}_2$ gas with temperature for the $\text{SnO}_2$, $\text{ZnO}$ and ZSO films.
Figure 14
Possible NO\textsubscript{2} gas sensing mechanism of ZSO film.

Figure 15
Dynamic Sensing Response curve at operating temperature 90 °C.
Figure 16

Sensor Response of ZSO (460 nm) film sensor various target gases for different concentrations at 90 °C.

<table>
<thead>
<tr>
<th>Gas (Concentration)</th>
<th>Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO (2000 ppm)</td>
<td>1.016</td>
</tr>
<tr>
<td>Acetone (2000 ppm)</td>
<td>1.024</td>
</tr>
<tr>
<td>IPA (2000 ppm)</td>
<td>1.024</td>
</tr>
<tr>
<td>CH₄ (2000 ppm)</td>
<td>1.02</td>
</tr>
<tr>
<td>NH₃ (2000 ppm)</td>
<td>1.035</td>
</tr>
<tr>
<td>CO₂ (2000 ppm)</td>
<td>1.016</td>
</tr>
<tr>
<td>NO₂ (20 ppm)</td>
<td>2.13×10³</td>
</tr>
</tbody>
</table>

Figure 17
Selectivity of ZSO film sensor.

Figure 18

Stability study of the ZSO sensor

Supplementary Files

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