INTRODUCTION

As per the safety environment and to maintain the concentration of toxic and flammable gases those are potentially create the problem in industrial era and their employees health issue not only them but also the peoples those are live near to them [1]. However, the gas sensor given guarantee to healthy environment, safe production and have ability to identify the specific gas from the type of chemical gases even the concentration of the gas is very small [2]. Metal oxides especially doped metal oxides has been utilized as gas sensing material because this dopant controlling the electrical, optical and constructive properties of material and which act as charge carrier to help an enhance the electricity supply due to the demand of industrial era those are having the huge potential applications in daily life [3].

The sensitivity property of metal oxides has been improved with the help of additive in the metal oxides by reducing the particle size or by changing the functioning temperature, here humidity also effect on the metal oxide sensitivity [4,5]. The gas molecule oxidation and reduction nature also show valuable effect on gas sensing material [6]. For the development of highly sensible gas sensing material the dimension of the material is very important or considerable because of specific geometry with small grain size to generate the large surface area which help to develop the good interconnection between the gas and metal oxides hence the nanotechnology is a significant role in the field of gas sensors [7]. The sensors are having numerous advantages such as small size, high reliability, low budget and low power consumption [8]. SnO2 has exceptional chemical stability, optical stability, electrical conductivity, and a wide band gap of 3.6 eV at ambient temperature [9,10]. There have been numerous methods investigated to improve the sensing capability of pure SnO2, including coating with a noble metal such as (Au, Pt and Pd) to act as a sensitizer [11-13]. Due to the high cost of noble metals, it raises the price of making sensors. To overcome this problem, another flexible method to enhance the gas sensing capabilities of pure SnO2 is to either load or dope it with another metal oxide to create a SnO2 nanocomposite [14,15].

The sensor’s mechanism is an oxidation-reduction reaction between the target gas and the SnO2 surface, resulting in a change in SnO2 resistance with gas concentration [16]. In comparison to other metal ions, cobalt has inhibitory effects on crystalline development and assumes a crucial part in the detecting capabilities of sensors. Furthermore, cobalt demonstrates inherent...
attributes of excellent corrosion resistance, ferromagnetism
and adequate thermal and electrical conductivity. The SnO₂ has
ionic radii of Co²⁺ (0.58 Å), and Sn⁴⁺ (0.64 Å) the ionic radius
of Co²⁺ is less than that of Sn⁴⁺ [17]. Consequently, it is possible
to anticipate the substitution of Co ions at the Sn⁴⁺ site within
the SnO₂ system. Consequently, there is an elevation in oxygen
deficit and a reduction in the grain size of SnO₂, both of which
are anticipated to impact the characteristics of pure SnO₂. In
this study, a Co dopant has been used to alter the electrical
characteristics of SnO₂ and enhance its gas sensing capabilities.

**EXPERIMENTAL**

**Synthesis of Co doped SnO₂ nanomaterials:** Sample
with normal composition of Co doped SnO₂ were synthesized
by using the co-precipitation method. First colloidal solution
was prepared with SnCl₄·5H₂O with deionized water stirring
for 1 h at room temperature. After the preparation of colloidal
solution, added CoCl₂·2H₂O with constant stirring for 1 h and
then required amount of NH₄OH were added dropwise with
constant stirring to maintain the pH 9 of mixture. For chemical
homogeneity, the dropping rate was regulated as 5 drops per
second. The solution was then mixed under constant stirring
for 2 h until the precipitate were formed. The mixture was filtered
on simple filter paper and then washed with three or five times
with deionized water. Then resulting mixture was again washed
with deionized water followed by the drying the mixture in
oven for 2 h at 80 ºC in order to remove the excess chlorine.
The obtained material was grounded into fine powder in mortal
and piston and annealed at 500 ºC for 2 h in a muffle furnace. After that dry this film for 45 min in infrared lamp and then
heated for 2 h at 500 ºC in a muffle furnace. After room
temperature cooling at next day, thick film sensors materials
were used for exciting gas sensing properties.

**Characterization:** The elemental analysis and surface
morphology of the synthesized material were investigated by
JEOL-JEM 2300 (LA) scanning electron microscope instru-
ment having an electron dispersion spectroscope (SEM-EDS)
facility. The X-ray powder diffraction analysis were carried
out by Phillips X-ray diffractometer in a diffraction angle range
2θ = 10 to 80º using CuKα radiation with a wavelength of
1.540598 Å.

**RESULTS AND DISCUSSION**

**SEM and EDS analysis:** The scanning electron micro-
scopy (SEM) images exhibit a high degree of nanoparticle
aggregation, characterized by a closely packed arrangement,
together with a micro-surface that displays roughness and
porosity (Fig. 1). Furthermore, it was observed that both
undoped SnO₂ and Co-doped SnO₂ exhibit the presence of
minute gaps or cavities on their respective surfaces, which are
distributed throughout the material. These voids can serve
as highly effective adsorbents in the context of gas sensing
research. The gas sensing capacity of specific sensors can

Fig. 1. SEM images of (a) undoped SnO₂, (b) Co-doped SnO₂, (c) EDS spectra of undoped SnO₂, (d) EDS spectra of Co-doped SnO₂, EDS
report of mapped data and (e) Co-doped SnO₂ nanoparticles.
be enhanced by the occlusion of smaller adsorbate gas molecules across the surface through chemisorption or physisorption [19]. The effective confirmation of doping of cobalt in SnO\textsubscript{2} was achieved by the utilization of elemental mapping analysis. Fig. 1e illustrates the observation of the presence of dopant on the SnO\textsubscript{2} matrix.

XRD studies: The structural arrangements of Co-doped SnO\textsubscript{2} were studied using PXRD at the angle of 2\theta between 10\(^{\circ}\) to 80\(^{\circ}\). The Co doped SnO\textsubscript{2} shows several Bragg’s reflection peaks at different 2\theta angle of 26.70\(^{\circ}\), 34.00\(^{\circ}\), 38.11\(^{\circ}\), 51.97\(^{\circ}\) (Fig. 2), which can be indexed to (110), (101), (020) and (121) planes, respectively. The observed diffraction peak were observed as orthorhombic structure [20]. Here, the grain size of the synthesized material Co-doped SnO\textsubscript{2} was calculated by using Debye-Scherrer’s equation \(T = \frac{0.94\lambda}{\beta \cos \theta}\), where \(T\) = average particle size, \(\lambda\) = wavelength, \(\theta\) = Diffraction angles, \(\beta\) = full-width half maximum. The obtained average particle size (T) was found to be 17.9 nm.

Gas sensing properties of undoped and Co-doped SnO\textsubscript{2} thick films: The gas sensors employed in this study were screen printed thick films consist of undoped SnO\textsubscript{2} and Co-doped SnO\textsubscript{2}. These films were specifically designed to detect hazardous gases like H\textsubscript{2}S, NH\textsubscript{3}, C\textsubscript{2}H\textsubscript{5}OH and NO\textsubscript{2} under optimum conditions.

**Optimum operating temperature condition:** The most important property of prepared gas sensor material is the operating temperature because it gives information about the gas sensing process of the gas towards the surface of the material [21]. Fig. 3 shows the optimum gas response at the temperature ranged from 200 to 40 \(^{\circ}\)C cooling cycle. The response curves show the gas response for undoped SnO\textsubscript{2} for tested gases like H\textsubscript{2}S, NH\textsubscript{3}, C\textsubscript{2}H\textsubscript{5}OH and NO\textsubscript{2}. The undoped SnO\textsubscript{2} sensor exhibited a significant response to hydrogen sulphide (H\textsubscript{2}S) vapours at 120 \(^{\circ}\)C with a recorded response rate of 64.20%. Similarly at 160 \(^{\circ}\)C, the sensor also give a response rate of 48.40% to NH\textsubscript{3} gas, 20% to C\textsubscript{2}H\textsubscript{5}OH gas vapours and 10% to NO\textsubscript{2} vapours (Fig. 3a). These findings highlighted the sensitivity of undoped SnO\textsubscript{2} sensor towards various gases at different operating temperatures. Simultaneously Fig. 3b shows the Co-doped SnO\textsubscript{2} sensor response for the same gases, out of which the highest the response was recorded for C\textsubscript{2}H\textsubscript{5}OH vapours at 120 \(^{\circ}\)C with 68.30% response, then 35.20% response was recorded for H\textsubscript{2}S gas at 120 \(^{\circ}\)C, NO\textsubscript{2} gas vapours showed a 12.20% response at 120 \(^{\circ}\)C and NH\textsubscript{3} vapours showed 7.20% at 120 \(^{\circ}\)C for Co-doped SnO\textsubscript{2} sensor.

Fig. 4 shows the maximum response in undoped and Co doped gas sensors have been given by H\textsubscript{2}S and ethanol vapours, respectively. The selectivity of other gases was calculated in ratio with respect to H\textsubscript{2}S for undoped SnO\textsubscript{2} sensor and C\textsubscript{2}H\textsubscript{5}OH for Co-doped SnO\textsubscript{2} sensor. Thus, H\textsubscript{2}S is highly selective for undoped SnO\textsubscript{2}, while C\textsubscript{2}H\textsubscript{5}OH is selective for Co-doped SnO\textsubscript{2} gas sensors.

The concentration of gas variation and response recorded for undoped SnO\textsubscript{2} and Co-doped SnO\textsubscript{2} are shown in Fig. 5. A linear relationship for tested gas H\textsubscript{2}S for undoped SnO\textsubscript{2} sensor and C\textsubscript{2}H\textsubscript{5}OH for Co-doped SnO\textsubscript{2} was found upto 300 ppm gas concentrations for both the sensors. It can be seen that there is a gradual increase in the gas response for 100 ppm to 300 ppm for undoped SnO\textsubscript{2} and Co-doped SnO\textsubscript{2} sensors. However, a sharp decline in the sensitivity from 300 ppm to 500 ppm gas concentration in both sensor was also observed.

Another two properties of gas sensor are the response time and recovery time. Fig. 6 shows the response and recovery time.
Fig. 4. Graphical representation of response of (a) undoped SnO$_2$ and (b) Co doped SnO$_2$ sensors for various gases

Fig. 5. Gas concentration in ppm variation for (a) undoped SnO$_2$ and (b) Co-doped SnO$_2$ sensor

Fig. 6. Response and recovery time of (a) undoped SnO$_2$ and (b) Co-doped SnO$_2$ gas sensor
of the both gas sensors working at the optimum temperature, with gas concentration of 50 µg/L at 40 ºC and humidity 20%.

The transient response characteristics of undoped SnO₂ thick film towards 300 ppm of H₂S at the optimum temperature of 160 ºC shows the fast response of 35 s and recovery time 70 s. The enhanced response and recovery time in Co-doped SnO₂ can potentially be attributed due to the heightened reactivity of C₂H₅OH vapour with adsorbed oxygen in the presence of Co sites on the surface as well as the high porous structure of the sensor. Enhanced gas diffusion through the grain boundaries would facilitate prompt oxidation of gas, resulting in a rapid response. The response and recovery durations of sensors are the crucial characteristics in determining their suitability for various applications.

In order to evaluate the stability and reproducibility of the undoped and Co-doped SnO₂ sensors, we conducted measurements of its response to an H₂S concentration of 300 ppm at 160 ºC for undoped SnO₂ sensor. For Co-doped SnO₂ sensor, we measured their response to a C₂H₅OH concentration of 300 ppm at 120 ºC on the 5th, 10th, 15th, 20th, 25th and 30th day following the initial measurement. Fig. 7 demonstrates that both undoped SnO₂ and Co-doped SnO₂ sensors had a response rate of around 95% of their initial performance on the 30th day. This result demonstrates the stability and reproducibility of the sensor material, which favours its use in the industrial settings [22].

In the comparative study of undoped SnO₂ and Co-doped SnO₂, it was observed that as undoped SnO₂ have less response than Co-doped SnO₂ for NH₃, H₂S, NO₂ and C₂H₅OH vapours. In literature, different methods has been reported for the preparation of Co-doped SnO₂ having different sensing properties for different gases as well as volatile vapours (Table-1).

Furthermore, a number of researchers have documented the sensing capabilities of Co-doped SnO₂ in relation to NH₃ and C₂H₅OH gases. These studies have explored the impact of varying Co-doped SnO₂ through the utilization of diverse synthesis techniques. However, it is important to emphasize that these investigations necessitated higher concentrations in parts per million (ppm) compared to the reported findings with the present research work. Hence in this work, Co-doped SnO₂ get the good results as compare to earlier reported similar material (Table-2). In literature, the co-doped SnO₂ with other gases such as H₂S and NO₂ has been previously described, specifically in case of Co-doped SnO₂ [26] and In-doped SnO₂ [27]. However, in this study, we present the first report on the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Analyzed gas</th>
<th>Operating temp. (°C)</th>
<th>Response (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped SnO₂</td>
<td>H₂S</td>
<td>120</td>
<td>64.20</td>
</tr>
<tr>
<td></td>
<td>NH₃</td>
<td>160</td>
<td>48.40</td>
</tr>
<tr>
<td></td>
<td>C₂H₅OH</td>
<td>160</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>NO₂</td>
<td>160</td>
<td>10</td>
</tr>
<tr>
<td>Co-doped SnO₂</td>
<td>H₂S</td>
<td>120</td>
<td>35.20</td>
</tr>
<tr>
<td></td>
<td>NH₃</td>
<td>120</td>
<td>7.20</td>
</tr>
<tr>
<td></td>
<td>C₂H₅OH</td>
<td>120</td>
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</tr>
<tr>
<td></td>
<td>NO₂</td>
<td>120</td>
<td>12.20</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Samples</th>
<th>Synthesis method</th>
<th>Gas analyte</th>
<th>Opera. temp</th>
<th>Conc. (ppm)</th>
<th>Response</th>
<th>Retention time</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5-3 wt% Co-doped SnO₂</td>
<td>Co-precipitation</td>
<td>C₂H₅OH</td>
<td>250</td>
<td>2000</td>
<td>120</td>
<td>3s/15s</td>
<td>[23]</td>
</tr>
<tr>
<td>Graphite supported Co-doped SnO₂</td>
<td>Flame spray pyrolysis</td>
<td>C₂H₅OH</td>
<td>350</td>
<td>1000</td>
<td>2147</td>
<td>1s</td>
<td>[24]</td>
</tr>
<tr>
<td>5 mol %</td>
<td>Solvothermal</td>
<td>NH₃</td>
<td>28</td>
<td>150</td>
<td>10.7</td>
<td>10s/150s</td>
<td>[25]</td>
</tr>
<tr>
<td>Co-doped SnO₂</td>
<td>Co-precipitation</td>
<td>H₂S</td>
<td>120</td>
<td>300</td>
<td>35.20</td>
<td>–</td>
<td>Present work</td>
</tr>
<tr>
<td>Co-doped SnO₂</td>
<td>Co-precipitation</td>
<td>NO₂</td>
<td>120</td>
<td>–</td>
<td>12.20</td>
<td>–</td>
<td>Present work</td>
</tr>
</tbody>
</table>

Fig. 7. Gas sensing material response
modification of SnO₂ with cobalt and observed the encouraging results.

Conclusion

In this work, undoped and Co-doped SnO₂ nanomaterials were synthesized by the chemical co-precipitation method. After annealing at 500 °C, both sensors were investigated for the sensing of four different gases viz. NH₃, H₂S, NO₂ and C₂H₅OH. The thick films of undoped and Co-doped SnO₂ were prepared by screen-printing technology. The good responses for H₂S and C₂H₅OH gases were recorded for undoped SnO₂ and Co-doped SnO₂. For undoped SnO₂ sensor, the gas response was recorded to be 64.20% at 160 °C for H₂S gas. The gas response of Co-doped SnO₂ shows gas response towards C₂H₅OH to be 68.30% at 120 °C. The enhanced gas response in the Co-doped SnO₂ sensors compared with the undoped SnO₂ is due to decreased band gap energy, more surface area and improved active site. Finally, it can be concluded that Co-doped SnO₂ sensors is an effective sensor at moderately high temperatures for C₂H₅OH vapours.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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