CeO$_2$ activated ZnO-TiO$_2$ thick film for CO$_2$ gas sensor

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Abstract: Nanocrystalline ZnO-TiO$_2$ (molar ratio 9:1, 7:3, 1:1, 3:7 and 1:9) synthesized by hydrothermal method. The synthesized materials were used to prepare the thick films and gas sensing characteristics of prepared thick films for 286 ppm CO$_2$ gas was investigated at different operating temperature. ZnO-TiO$_2$ (3:7 molar ratio) thick film respond more to CO$_2$ gas as compared to other investigated films. Further ZnO-TiO$_2$ (molar ratio 3:7) thick film was activated by using 0.1M, 0.2M, 0.3M and 0.4M CeO$_2$ solution. The sensing response of all CeO$_2$ activated films to 286 ppm CO$_2$ gas was studied at different operating temperature. It is found that 0.3M CeO$_2$ activated ZnO-TiO$_2$ thick film exhibited good response to CO$_2$ gas at operating temperature 290 $^\circ$C with quick response time (~ 24 s) and less recovery time (~ 72 s). Also film exhibited long time stability and repeatability. The experimental results indicate that the 0.3M CeO$_2$ activated ZnO-TiO$_2$ thick film is a very promising material that fulfils the practical requirements for the fabrication of CO$_2$ gas sensors with good sensing characteristics.

Keywords: Carbon dioxide gas, Cerium oxide, Gas sensor, Thick film, ZnO-TiO$_2$

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I. Introduction

In general it is believed that green house gases are responsible for global warming. Global warming affects the eco-system, which may lead to disastrous consequences for life on earth. Among the green house gases carbon dioxide (CO$_2$) play key role because it is the most man-made emission. Since last few years, great efforts have been taken to reduce the global warming. CO$_2$ monitoring and controlling have been essential to save the world from the effects of global warming and other hazards. It is important to measure the CO$_2$ concentration in the ppm range for many other applications such as early fire detection, air quality control, food quality control, etc. [1]. The number of options that could be employed to mitigate increases in CO$_2$ atmospheric levels is limited and will need to include its storage, capture and disposal. Hence it is high time to develop CO$_2$ sensors with excellent response, small response time, fast recovery, higher stability and more economic.

The physical and chemical properties of materials depend on synthesis routes, governed by the synthesizing conditions. In literature, for synthesis of nanomaterials several routes are described, such as chemical, mechanical, gas phase and molten salt synthesis, etc. Hydrothermal technique is one of the chemical synthesis routes that allow in fabrication of shaped and size oriented materials without melting steps. There are a number of advantages of this technique such as: the short duration of the experiments as compared to classical synthesis methods, crystal size and the level of agglomeration can be controlled, costs of the instrument and energy requirement is low as compared to other synthesis routes and it is an eco-friendly method [2-4].

There have been numerous research publications reporting the successful application of metal oxides in the gas sensor [4-7]. In metal oxide based gas sensors, gas-sensing mechanism is surface controlled phenomena. There are many parameters of materials for gas sensor applications such as adsorption ability, catalytic activity, sensor response, stability, etc. Semiconductor metal oxides like ZnO, SnO$_2$, Fe$_2$O$_3$, In$_2$O$_3$, etc. have been investigated for detection of gases [8-10]. However very few of them are suitable to fulfil all these requirements. To overcome these limitations recently researchers are focused on composite materials, like SnO$_2$-ZnO [11], Fe$_2$O$_3$-ZnO [12], ZnO-CuO [13], etc. In addition to binary metal oxides there are number of ternary and complex metal oxides which have emerged as promising candidates for gas detection [14-16]. It has been recognized that sensors developed by mixing of two components together are more sensitive than individual component. This is due to a synergistic effect between two metal oxides [12]. Preparation of mixed oxide lead to the alteration of the electronic structure of the system which causes changes in the bulk as well as in the surface properties [17]. Surface properties are expected to be affected by new boundaries between grains of different chemical composition. It is anticipated that all these phenomena will contribute favorably to the gas-sensing mechanism [18, 19].
Adequate selection of specific impurities can provide careful control of the sensor operating temperature with an optimum response for a specific gas. Materials like CuO, Fe₂O₃, Cr₂O₃, etc. when dispersed onto the semiconductor oxide films, enhance the sensor response to the gas [14, 20, 21]. Cerium oxide (CeO₂) is most reactive rare earth metal oxide and it has a fluorite structure, with each Ce⁴⁺ surrounded by eight equivalents, nearest O²⁻ ions that form the corner of a cube. When Ce⁴⁺ ions are replaced by lower valence cations, oxygen vacancies or lattice defect will be created that can be most reactive site on the surface. The surface and bulk oxygen vacancies occur in CeO₂ are suitable sites for adsorption [22, 23]. CeO₂ has an additional importance in the applications of heterogeneous catalysis because of its redox couple Ce³⁺/Ce⁴⁺ and high capacity of store oxygen [23]. The objective of this work is to study the CO₂ gas sensing properties of ZnO-TiO₂ thick film and report the effect of CeO₂ activation on CO₂ gas sensing properties of ZnO-TiO₂ thick film.

II. Material and Method

2.1 Synthesis of nanocrystalline ZnO-TiO₂ and preparation of thick film.

Synthesis of nanocrystalline ZnO-TiO₂ with molar ratio 9:1 (sample A), 7:3 (sample B), 1:1 (sample C), 3:7 (sample D) and 1:9 (sample E) and its characterization by using X-ray diffraction (XRD, XPERT-PRO) and transmission electron microscope (TEM, Techai G2 20) were discussed in our publication [20]. Also formulation of thixotropic paste and preparation of thick films from synthesized material samples (A-E) were discussed in our publication [20].

2.2 Activation of thick film

The thick film of ZnO-TiO₂ (molar ratio 3:7) was activated by dipping it into 0.1M, 0.2M, 0.3M and 0.4M aqueous solutions of Cerium(III) chloride heptahydrate (CeCl₃·7H₂O) for 30 min. These films were dried in air and fired in heating furnace at 450 °C for 24 h. These films are termed as CeO₂ activated ZnO-TiO₂ thick films.

For the measurements of gas sensing properties of all these thick films, silver electrodes were used for electrical contacts. Gas sensing measurements were carried out on computer-controlled static gas-sensing system. A small Ni-Cr alloy coil was used for heater and a chromel–alumel thermocouple used to monitor temperature. Keithley 6487 picometer current source was used to measure the sensor current. Test gas was injected into the chamber through an inlet port. The sensor response was defined as the ratio of resistance in air to that in target gas [24].

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

Where,

- **S** - Sensor response
- **Rₐ** – Resistant of sensor element in air
- **Rₔ** – Resistant of sensor element in target gas

III. Results and Discussion

3.1 Materials Characterization

The surface morphology and nature of ZnO-TiO₂ molar ratio (A) 9:1, (B) 7:3, (C) 1:1, (D) 3:7 and (E) 1:9 thick films were analyzed by using scanning electron microscope (SEM, JEOL JSM 6380A). SEM micrographs of ZnO-TiO₂ thick films are shown in Fig. 1. It can be seen that, presence of pores indicate that porosity is present and surface roughness of films increases with increase in concentration of TiO₂.

The elemental composition of CeO₂ activated ZnO-TiO₂ (molar ratio 3:7) thick film and ZnO-TiO₂ (molar ratio 3:7) thick film were analyzed by using an energy dispersive spectrometer (EDS). Fig. 2 shows EDS spectrum of (A) ZnO-TiO₂ (3:7 molar ratio) thick film and (B) 0.3M CeO₂ activated ZnO-TiO₂ (3:7 molar ratio) thick film. From the spectrum, it can be seen that in ZnO-TiO₂ (3:7 molar ratio) thick film there are no other elements than O, Ti and Zn and in 0.3M CeO₂ activated ZnO-TiO₂ (3:7 molar ratio) thick film there are no other elements than O, Ti, Zn and Ce. The percentage of elements present in ZnO-TiO₂ (3:7 molar ratio) thick film and 0.3M CeO₂ activated ZnO-TiO₂ (3:7 molar ratio) thick film is shown in table 1. The less percentage of O atoms in the CeO₂ activated film shows that there are lattice defects such as oxygen vacancies.

Fig. 3 shows scanning electron microscope image of (A) ZnO-TiO₂ (3:7 molar ratio) thick film and (B) 0.3M CeO₂ activated (3:7 molar ratio) ZnO-TiO₂ thick film. It shows that the CeO₂ distribution in the microstructure is uniform with open porosity. Hence the surface to volume ratio became maximum this help to enhance the sensor response.
CeO$_2$ activated ZnO-TiO$_2$ thick film for CO$_2$ gas sensor

**Figure 1**: SEM images of ZnO-TiO$_2$ thick films with molar ratio (A) 9:1, (B) 7:3, (C) 1:1, (D) 3:7 and (E) 1:9.

**Figure 2**: EDS spectrum of (A) ZnO-TiO$_2$ (molar ratio 3:7) thick film and (B) 0.3M CeO$_2$ activated ZnO-TiO$_2$ (molar ratio 3:7) thick film.

**Table 1** Composition of 0.3M CeO$_2$ activated ZnO-TiO$_2$ (molar ratio 3:7 thick film) and ZnO-TiO$_2$ (molar ratio 3:7) thick film.

<table>
<thead>
<tr>
<th>Element</th>
<th>0.3M CeO$_2$ activated ZnO-TiO$_2$ (molar ratio 3:7)</th>
<th>ZnO-TiO$_2$ (molar ratio 3:7)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Norm. wt.%</td>
<td>Atom. at. %</td>
</tr>
<tr>
<td>O</td>
<td>30.11</td>
<td>61.64</td>
</tr>
<tr>
<td>Zn</td>
<td>33.67</td>
<td>18.94</td>
</tr>
<tr>
<td>Ti</td>
<td>26.36</td>
<td>17.03</td>
</tr>
<tr>
<td>Ce</td>
<td>9.86</td>
<td>2.59</td>
</tr>
</tbody>
</table>


3.2 Gas sensing characteristics

Fig. 4 illustrates the response of ZnO-TiO$_2$ thick films with molar ratio (A) 9:1, (B) 7:3, (C) 1:1, (D) 3:7 and (E) 1:9 to 286 ppm CO$_2$ gas. The thick films were maintained at different operating temperatures in the range of 30 °C to 325 °C and tested for 286 ppm CO$_2$ gas. From the figure it can be seen that within the studied temperature range, among the tested compositions, ZnO-TiO$_2$ (3:7 molar ratio) thick film exhibited maximum response of 2.68 towards 286 ppm CO$_2$ gas at 305 °C.

Regarding the sensing mechanism of semiconductor oxide based materials, the sensing mechanism and change in electrical transport properties are generally involved the adsorption and desorption process of oxygen molecules on the surface of materials and/or direct reaction of lattice oxygen or interstitial oxygen with test gases [28-32]. When ZnO-TiO$_2$ film is exposed to air, oxygen molecules interact with the film to form adsorbed oxygen ions like O$_2^-$ or O$^-$ or O$_2^+$ by capturing electrons from the conduction band and this interaction decreases the concentration of electrons in the conduction band. The processes are as follows [33]:

\[
O_2 \text{ (gas)} \leftrightarrow O_2 \text{ (ads)} \tag{2}
\]

\[
O_2 \text{ (ads)} + e^- \leftrightarrow O_2^- \text{ (ads)} \tag{3}
\]

\[
O_2^- \text{ (ads)} + e^- \leftrightarrow 2O^- \text{ (ads)} \tag{4}
\]

\[
O^- \text{ (ads)} + e^- \leftrightarrow O^{2-} \text{ (ads)} \tag{5}
\]
When the film exposed to CO$_2$, CO$_2$ interact with the adsorbed oxygen species present on the film surface. The response of ZnO-TiO$_2$ thick film to CO$_2$ can be explained by the interaction of CO$_2$ gas with film surface. In this interaction the adsorption of CO$_2$ accounts for the consumption of oxygen and this reaction leads to decrease in film resistance. The sensing response was improved with increasing amount of TiO$_2$ content in the film. This indicates that there would be increase in amount of chemisorbed oxygen ions. This is due to electrons induced by Ti$^{4+}$, entering into ZnO lattice can form more chemisorbed oxygen ions on the surface of film [24]. Fig. 4 indicates that ZnO-TiO$_2$ (3:7 molar ratio) thick film exhibited highest sensing response to 286 ppm CO$_2$ gas at 305 °C among the all investigated compositions of ZnO-TiO$_2$ thick films. At the optimum amount of TiO$_2$ in thick film, TiO$_2$ species would be distributed uniformly and sufficient to promote the catalytic reaction effectively. Also presence of pores indicates that porosity and surface roughness of films increases with increase in concentration of TiO$_2$. This would have increased the sensing response of film on the exposure of CO$_2$ gas.

Fig. 5 shows the response of 0.1M, 0.2M, 0.3M and 0.4M CeO$_2$ activated ZnO-TiO$_2$ (3:7 molar ratio) films to 286 ppm CO$_2$ gas at different operating temperatures. The figure illustrates the fact that the CO$_2$ gas sensing response measured in the studied temperature range significantly changes with different concentration of CeO$_2$. The thick film activated by 0.3M CeO$_2$ exhibited maximum response of 31.17 to 286 ppm CO$_2$ gas at 290 °C. The improved sensing response can be attributed to synergistic effects. At high temperature or in the reduced state or in pure CeO$_2$, lose some amount of oxygen and, generate oxygen vacancies [34],

$$2 \text{CeO}_2 \rightarrow \text{Ce}_2\text{O}_3 + \text{O}^- \quad (6)$$

Although it was anticipated that CeO$_2$ could lose oxygen during reduction at high temperature. When CO$_2$ come in contact with CeO$_2$ activated surface, to form carbonates as a product through the participation of surface oxide ions: [1, 35]

$$\text{O}^2- + \text{CO}_2 \rightarrow \text{CO}_3^{2-} \quad (7)$$

These carbonates disappear when they are exposed to oxidizing conditions [35]. Sensor response improves with increasing presence of high-activity catalyst CeO$_2$, up to 0.3M CeO$_2$ activation. While an opposite influence happens with further increase in content of CeO$_2$ due to the fact that it could embarrass the mobility of the carriers to across [36].

Figure 4: Response of ZnO-TiO$_2$ molar ratio (A) 9:1, (B) 7:3, (C) 1:1, (D) 3:7 and (E) 1:9 thick films to 286 ppm CO$_2$ gas.
**CeO2 activated ZnO-TiO2 thick film for CO2 gas sensor**

**Figure 5:** Response of 0.1M, 0.2M, 0.3M and 0.4M CeO2 activated ZnO-TiO2 (3:7 molar ratio) thick film toward 286 ppm CO2 gas.

In practical applications, a response and recovery time of sensor for the particular gas is the important factors. Response and recovery times are defined as the time required reaching 90% of the final stable value. Fig. 6 illustrates response and recovery time of 0.3M CeO2 activated ZnO-TiO2 (3:7 molar ratio) thick film to 286 ppm CO2 gas at 290 °C. It indicates that response time and recovery time of sensor are 24 s and 72 s respectively. The quick response would be due to faster oxidation of CO2 gas. The CeO2 catalyses the reaction and promotes the rapid transfer between the adsorbate and substrate. This result may be recommended for practical applicability of the sensor to detect CO2 gas.

**Figure 6:** Response and recovery time of 0.3M CeO2 activated ZnO-TiO2 (3:7 molar ratio) thick film to 286 ppm CO2 gas at 290 °C.

Fig. 7 demonstrates the stability of 0.3M CeO2 activated ZnO-TiO2 (3:7 molar ratio) thick film to 286 ppm CO2 gas at 290 °C for the period of six months in the interval of 30 days. It is observed that there is no noticeable deviation in the sensor response. This is due to presence of TiO2 [37].
CeO$_2$ activated ZnO-TiO$_2$ thick film for CO$_2$ gas sensor

Figure 7: Stability of 0.3M CeO$_2$ activated ZnO-TiO$_2$ (3:7 molar ratio) thick film towards 286 ppm CO$_2$ gas at 290 °C.

The response of 0.3M CeO$_2$ activated ZnO-TiO$_2$ (3:7 molar ratio) thick film towards different gases (286 ppm each) like NH$_3$, CO$_2$, H$_2$S & LPG at optimal operating temperature is shown in Fig. 8. The sensor shows excellent response at 290 °C towards CO$_2$ but a very poor response toward LPG, NH$_3$ and H$_2$S. The excellent sensing response of the sensor element to CO$_2$ gas is because CO$_2$ molecules easily react with sensor element as compared to the other tested gases at optimum operating temperature 290 °C.

Figure 8: Response of 0.3M CeO$_2$ activated ZnO-TiO$_2$ (3:7 molar ratio) thick film towards NH$_3$, CO$_2$, H$_2$S and LPG at 290 °C.

IV. Conclusions

On the basis of experimental results and its discussions, the following conclusions can be made:
(i) The sensing response of nanocrystalline ZnO-TiO$_2$ (molar ratio 9:1, 7:3, 1:1 and 1:9) thick films to 286 ppm CO$_2$ gas was relatively poor than ZnO-TiO$_2$ (3:7 molar ratio) thick film.
(ii) CeO$_2$ activated ZnO-TiO$_2$ (3:7 molar ratio) thick films exhibited enhanced sensing response at comparatively lower operating temperature to 286 ppm CO$_2$ gas than ZnO-TiO$_2$ (3:7 molar ratio) thick film.
(iii) 0.3M CeO₂ activated ZnO-TiO₂ (molar ratio 3:7) thick film exhibited excellent sensing response 31.17 to 286 ppm CO₂ gas at 290 °C.

(iv) The thick film based on 0.3M CeO₂ activated ZnO-TiO₂ (molar ratio 3:7) exhibited excellent response to CO₂ gas selectively as compared to other gases like LPG, H₂S and NH₃. Also it exhibited quick response time (24 s) to CO₂ gas, rapid recovery time (72 s) and long time stability at 290 °C.

(v) CO₂ gas sensor based on CeO₂ activated ZnO-TiO₂ (molar ratio 3:7) thick film was found to be sensitive to the operating temperature and the amount of the dopant. Hence 0.3M CeO₂ activated ZnO-TiO₂ (molar ratio 3:7) thick film fulfils the practical requirement for detecting CO₂ gas.

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