Modified Cadmium Stannate Nanostructured Thin Films Prepared by Spraying Technique for the Detection of Chemical Warfares

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Abstract: In present study spray pyrolysis technique was employed to prepare pure and doped CdSnO₃ thin films. The spray pyrolyzed thin films were observed to be nanostructured in nature with particle size less than 10 nm and characterized to investigate its structural, microstructural, and chemical properties by means of XRD, SEM/EDS, TEM and surface profilometry. Pure and Zn doped CdSnO₃ nanostructured thin films were tested against THE simulants of chemical warfare agents (CWA). The Zn doped nanostructured thin films showed good sensing performance towards the simulants as compared to the pure thin films. The effect of nanocrystalline nature on simultant-sensing properties of pure CdSnO₃ and Zn-doped CdSnO₃ thin films was discussed and interpreted.

Keywords: Spray pyrolysis technique, Nanostructured CdSnO₃ thin films, Zn doping, CWA simulant, simulant response, speed of response and recovery.

I. INTRODUCTION

Nanostructured metal oxide-based gas sensors have been a major area of extensive research because of their use in detecting several toxic, inflammable, odorless gases and deadly Chemical warfare agents (CWA) and its simulants over the past decades [1-11]. Chemical warfare agents can be defined as a chemical which is intended for use in military or civilized area operations to kill, seriously injure, or incapacitate humans or animals through its toxicological effects [12,13]. As a result of high toxicity of chemical warfare agents (CWAs), fast and correct detection of CWAs is a great urge to protect living beings. Due to high toxicity of CWA, structural analogs i.e. simulants are generally used for research purpose.

The gas sensing properties are totally dependent upon the reaction between semiconducting metal oxides and target gas. Mechanism of gas-sensing involves the redox reaction at the metal oxide surface, leading to the change in the depletion layer of the grains that ultimately change the electrical resistance of the metal oxide. For the change in electrical resistance of the metal oxide, there are many possible reactions; the most commonly accepted reaction that leads to changes in electrical resistance is the adsorption of gases on the metal oxide surface. Adsorption is nothing but a surface effect and nanostructured metal oxides possess high surface to volume ratio, which enhances this effect [14-16].

Metal oxide gas sensors improve their sensitivity and response/recovery time due to nanocrystalline nature of the material associated, which is the most attractive quality of nanomaterials. Basically the improvements are because of the high surface area to volume ratio and smaller crystallite size compared to conventional microcrystalline materials [17]. Despite of binary semiconducting metal oxide e.g. ZnO, SnO₂, TiO₂ etc, perovskites (ABO₃) with good thermal stability are also interesting materials for gas sensing. The flexibility for introduction of variety of dopant for the enhancement of sensing properties is only due to the cations size difference between A and B. These interesting characteristics of perovskites also make them promising candidate for catalytic applications [18]. Cadmium Stannate (CdSnO₃) based gas sensors are efficient for detection of reducing gases such as C₂H₂, H₂O, and ammonia (19-21) etc. Various techniques such as thermal decomposition, ball milled, co-precipitation method, low-temperature ion exchange, solid-state reaction, CVD, Sputter deposition, Electron Beam Technique [22-28] etc. have been employed to prepare CdSnO₃ thin films. In the present investigation, spray pyrolysis technique was employed to prepare pure and zinc doped CdSnO₃ thin films because the technique is simple and involves low cost equipments and raw materials. The technique involves a simple technology in which an ionic solution (containing the constituent elements of a compound in the

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form of soluble salts) is sprayed over heated substrates [29]. By this method, dopants can be easily introduced into the matrix of the film by using appropriate precursors [30]. Additives or dopants enhance the properties of the sensors, such as sensitivity, selectivity, lowering the operating temperature, response and recovery time etc [31-33]. The morphology and microstructure of the films were investigated by x-ray diffraction (XRD), energy dispersive x-ray (EDX) analyzer, transmission electron microscopy (TEM) and surface profilometry. In this work we tested sensors to sense dimethyl methylphosphonate (DMMP), a simulant -Sarin gas (Nerve agent), 2-chloroethyl ethyl sulfide (2-CEES) and chloroethyl phenyl sulfide (CEPS) simulates of -Mustard gas (blister agent) namely, [34].

The electrical and gas sensing tests were carried out by indigeneous gas sensing system [35]. Measurements were carried out at different operating temperatures, ranging from 250 to 400 °C. The operating temperature of the sensors was adjusted by a regulated dc power supply to the heater.

II. EXPERIMENTAL

Figure 1 shows the schematic diagram of spray pyrolysis system. Samples were prepared by simple and versatile spray pyrolsis technique. In this technique, the precursor solution was sprayed onto a heated substrate using air as carrier gas. The setup consists of spray nozzle, heater, air compressor, flow meter, power supply, temperature indicator and thermocouple. The CdSnO$_3$ thin films were prepared by spraying the solution mixture of aqueous solutions of: cadmium tertranitrate (Cd(NO$_3$)$_2$·4H$_2$O - 0.1 M) and tin pentachloride (SnCl$_4$·5H$_2$O - 0.1 M). Each solution was sprayed for 5 minutes and the films so obtained were referred to as S1, Z2 and Z3 respectively. The undoped and doped films were fired at 500 °C for 1h, prior to characterization and gas sensing studies. CEES/DMMP/CEPS (4 ppm) in gaseous form was used to test sensing performance of the pure and Zn-CdSnO$_3$ based sensors.

The gas response of the sensor to reducing gases is defined as $S = \frac{I_g}{I_a}$ which $I_a$ and $I_g$ are the current in air and in test gas, respectively. The response time is defined as the times needed for the sensor-current to change by 90% of the difference from the maximum value to the minimum after the test gas injection. The recovery time is the times required for the sensor-current to change by 90% of the difference from the minimum value to the maximum after exposure of gas [36].

III. RESULTS AND DISCUSSION

A. Structural Analysis

Figure 2 shows the X-ray diffraction of sample S1. Several peaks in graph for S1 were observed to be nearly matching with to perovskite type CdSnO$_3$ (JCPDS file No. 34-0758 and 34-0885). The symbols, sphere and square corresponds to hexagonal and orthorhombic phase of CdSnO$_3$ in figure 2. Hexagonal phase is the most dominant, whilst the orthorhombic phase is present to a lesser extent. The diffractogram (figure2) indicates that the prepared CdSnO$_3$ thin films are amorphus in nature. The Zn doped X-ray diffraction doesnot show any peak corresponding to the zinc. The reason may be the very low content of zinc in CdSnO$_3$.

B. Quantitative elemental analysis
Table 1. Elemental composition data of sample S1 and Z1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cd</th>
<th>Sn</th>
<th>O</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>19.53</td>
<td>33.88</td>
<td>46.5</td>
<td>---</td>
</tr>
<tr>
<td>Z1</td>
<td>09.97</td>
<td>21.83</td>
<td>67.90</td>
<td>0.31</td>
</tr>
</tbody>
</table>

The table 1 shows the Elemental composition of pure and doped samples. The films were observed to be nonstoichiometric in nature.

C. Thickness Measurement

Thickness of the samples were measured using surface profiler. Table 2 shows the thickness and roughness of samples as follows:

Table 2. Thickness and roughness of samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (nm)</th>
<th>Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>454</td>
<td>110.1</td>
</tr>
<tr>
<td>Z1</td>
<td>417.8</td>
<td>73.2</td>
</tr>
</tbody>
</table>

It is clear from the table that the Zinc doping has lowered the thickness and surface roughness as compared to the undoped samples.

D. Microstructural Study:

Figure 3 (a) and (b) shows the transmission electron microscopic images of sample S1 and Z1 respectively. Average particle size for sample S1 and Z1 were calculated from TEM images are 3.55 and 4.33 nm respectively. It is clear from the image 3 (b) that the zinc doping in CdSnO3 transforms the particle shapes into specific morphology- like hexagonal and square.

IV. ELECTRICAL PROPERTIES OF THE SENSORS

A. I-V Characteristics:

The working temperature was varied within the range of 250 °C - 450 °C. Figure 4 depicts I-V curves of S1 and Z1 samples. Linear nature of I-V curve of sensor shows good ohmic contact. The ohmic contact is very important to the gas sensing properties, because the sensitivity of the gas sensor is affected by contact resistance [37].
B. Sensing responses of modified and unmodified samples:

![Image](image1.png)

**Figure 5(a). Response of S1 and Z1 to 2-CEES.**

![Image](image2.png)

**Figure 5(b). Response of Z1 to 2-CEES, DMMP and CEPS.**

Figure 5(a) shows the responses of the S1 (undoped) and Z1 (Zn doped) sensors upon exposure to 4 ppm DMMP, 2-CEES and CEPS. The response to 2-CEES in case of S1 (S = 6) and Z1 (S = 15.56) were higher than the response to DMMP and CEPS. Also, Zn doping in CdSnO3 enhances the simulant response. Sample Z1 observed to be more sensitive and selective to 2-CEES than the other two simulants as shown in figure 5(b).

C. Selectivity and speed of response of modified and unmodified sensors

![Image](image3.png)

**Figure 6(a). Selectivity profile of Z1.**

![Image](image4.png)

**Figure 6(b). Response and recovery profile of Z1.**

Figure 6 (a) shows the selectivity profile of sample Z1 for 2-CEES (4 ppm) at 350 °C. The dynamic response transients are shown in figure 6 (b). The response time of Z1 to 2-CEES was observed to be 4 sec. While the recovery time to off Z1 to 2-CEES was recorded as 100 sec.

V. DISCUSSION

The sensing mechanism is based on the effect of surface reactions of gas species on electron/hole concentration on the conduction band of the sensing material and creating a space charge layer, depending on whether it is an n- or p-type semiconductor. Such a depletion layer modifies the electrical conduction barrier at the grain boundaries. The bulk conductivity of the sensing material is the average of resistivity of bulk particles and grain boundaries. In microcrystalline materials the depth of the space charge layer is negligible compared to the grain diameter. In nanocrystalline materials, however, the depth of the space charge layer could be comparable to the
grain radius and the whole grain could be considered as a depleted layer. The electrical conduction is therefore controlled by the whole grain conductivity and the material becomes sensitive for very small gas concentrations in the surrounding atmosphere. This sensing mechanism relies on the fact that the electrical characteristics of materials depend on the amount of chemisorbed molecules. In air, the surface of a semiconducting material is covered with adsorbed oxygen layer. The process involves as shown in equations (1) and (2), physisorption of oxygen molecules in air, which then capture electrons from the near-surface region of the semiconductor[38]:

\[
\begin{align*}
1/2 \text{O}_2(g) & \rightarrow \text{O}(\text{ads}) \\
\text{O}(\text{ads}) + 2e^- & \rightarrow \text{O}^2-(\text{ads})
\end{align*}
\]

The well accepted sensing mechanism for n-type semiconductor sensors involves three-step process i.e. an adsorption-oxidation-desorption process.

An ion radius of Zn\(^{2+}\) (0.073 nm) has similar to that of Sn\(^{4+}\) (0.071 nm) and smaller than Cd\(^{2+}\) (0.095 nm), so that it can be incorporated into the CdSnO\(_3\) lattice easily by substituting for Sn\(^{4+}\) or Cd\(^{2+}\). Zn as dopant results in surface modification and the formation of more oxygen vacancies, which can facilitate the enhancement of gas-sensing properties. It may be due to an ability of Zn ion to substitute Sn/Cd ions easily. It may be because of smaller ionic radius of Zn\(^{2+}\) (0.073 nm) than Cd\(^{2+}\) (0.095 nm) and close to Sn\(^{4+}\) (0.071 nm) [39-41].

The resistance of the film is very high when oxygen ions are adsorbed on heated Zn doped CdSnO\(_3\) (sample Z1) surface at higher temperatures above 300 \(^\circ\)C due to abstraction of surface electrons. The exposed 2–CICH\(_2\)CH\(_2\)SCH\(_2\)CH\(_3\) (2-CEES), would be first divided into the \(\text{S}^2\text{CH}_2\text{CH}_3\) and CICH\(_2\)CH\(_3\) radicals as eq. (3). Through both chlorine and sulfur moieties (which have unpaired electrons), these radicals would try to adsorb onto the film onto Lewis acid sites (i.e. metal ions). The radicals would act as a Lewis base (electron donors) and could interact with Lewis acid sites (i.e. metal ion) in the process of adsorption. Due to oxidation, the byproducts like CO\(_2\), Cl\(_2\), H\(_2\)O, and SO\(_2\) would be released and electron would return back to metal oxide surface shown in eq (4) and (5). The process may be represented in scheme [42].

Decomposition of 2-chloroethyl ethyl sulphide (2-CEES)

\[
\text{2-CEES} \rightarrow \text{CICH}_2\text{CH}_3\text{S}^2\text{CH}_2\text{CH}_3 \quad (3)
\]

Oxidation of chloroethylene and return of electrons back to the film

\[
\begin{align*}
2\text{CH}_2\text{CH}_2\text{Cl} + 8\text{O} & \rightarrow 2\text{CO}_2 + \text{Cl}_2 + 4\text{H}_2\text{O} + 8e^- \quad (4) \\
\text{Oxidation of ethylsulphide and return of electrons back to the film} & \quad (5)
\end{align*}
\]

Thus, in whole process of adsorption, dissociation and oxidation, electrons are returned back to material and film resistance is increased. This process is therefore for detection of exposed CEES.

VI. CONCLUSIONS

Pure and Zn doped CdSnO\(_3\) thin films, prepared (1) using a simple spray pyrolysis technique, were observed to be nanostructured in nature. The (2) particle size of the films was observed to be below 10 nm. Due to nanocrystallinity and Zn doping, the CdSnO\(_3\) sensor showed good response to 2-CEES at an operating temperature 350 \(^\circ\)C as compared to pure CdSnO\(_3\) sensor. The sensor responded rapidly to 4 ppm of 2-CEES (response time 4 sec). The recovery time was 100 sec. The Zn doped nanostructured CdSnO\(_3\) thin films prepared by using spray pyrolysis technique is a promising sensor candidate for the detection of CWA simulants.

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