Investigation of pyrolysis method for preparing CdO:In$_2$O$_3$ thin films gas sensor for NO$_2$ gas

Abstract

A novel CdO:In$_2$O$_3$ nano composite has been synthesized by a pyrolysis method. The prepared nano composites have been carefully characterized using X ray diffraction and atomic force microscopy. The obtained results showed that the synthesized nano composite CdO:In$_2$O$_3$ at optimum conditions has excellent grains. It was found that synthesized CdO:In$_2$O$_3$ nano composite can be used as NO$_2$ gas sensing to exhibit the highest sensitivity for NO$_2$ at 200°C. The constructed sensor showed a very low detection limit of 5 ppm.

Keywords: Thin films, crystalline structure, CdO:In$_2$O$_3$ thin films.

INTRODUCTION

Cadmium oxide (CdO) has been used extensively in transparent conducting oxide, solar cells [1,2], smart windows phototransistors [3], diodes [4], transparent electrodes [5], and solid state gas sensors [6] and in many other optoelectronic applications. CdO thin films exhibit high transmission in the visible and UV regions, as well as a high ohmic conductivity. Bulk CdO shows n-type conductivity mainly due to oxygen vacancies. In the recent years, many different techniques such as thermal evaporation [7] sputtering [8], solution growth [9], pulsed laser sputtering [10], activated reactive evaporation [11] and spray pyrolysis deposition (SPD) [12-14], have been used for the preparation of CdO thin film. SPD technique provides a simple route of
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synthesizing thin films because of its simplicity, low cost experimental setup from an economical point of view. In addition, this technique could be used for the production of large-area thin film deposition without any high vacuum system. This method has good control over the thickness uniformity and good adherence to the substrate. It was observed that with doping by different types of metallic ions, the physical properties of CdO could be controlled for optoelectronic applications. So that doping with ions like In, Sn, Al, Sc, and Y, improves its n-type conductivity and increases optical band gap [15-18]. Surface roughness's, in homogeneity and intrinsic defects, etc. are the cause of the optical losses. From the practical point of view, these properties can severely degrade or modify the performances of a component. Overall, the structural and optical properties of the thin films depend on the method of the preparation. The properties of the films are influenced by the geometry of the experimental setup.

Nitrogen dioxide (NO$_2$) is one of the main harmful gases, which provokes noxious effects on environment and human health. Resistive-type sensors based on metal-oxide semiconductors have been intensively studied in the last decades due to the low cost, technological simplicity, small size, and ease of handling. Besides, thin-film gas sensors show high performance features such as high stability and fast response. Furthermore, the compatibility with micromachined structures allows sensor miniaturization, reduction of the production cost, and power consumption [19-21].

In this context, our work deals with gas-sensing properties of thin films of (CdO) (In$_2$O$_3$) mixed oxide for NO$_2$ detection. Spray pyrolysis technique was selected to prepare the oxide films since it is an inexpensive and simple technique, which allows obtaining a wide range of nano structured oxides with high surface area.

**Experimental**

CdO:In$_2$O$_3$ thin solid films were prepared using the spray pyrolysis technique (Figure 1), which is a versatile technique that can be used to produce thin solid films. With this method the particle’s size can be easily controlled by changing the concentration in the starting solution and the atomization parameters.

Chemical spray pyrolysis is one of the major techniques used to deposit a wide variety of materials including metal or alloy oxides. Generally, spray pyrolysis deposition system which is mainly consists of the following four sections: (a) the reactants and carrier gas assembly connected to the spray nozzle at the entrance of the reaction chamber, (b) the reaction chamber in which there is a resistive heater used to heat the substrate to the required temperature for thin film deposition, (c) the temperature controller that monitors the deposition temperature and controls the desired substrate temperature and (d) the exhausting gas module. The substrate temperature was measured using a K-type thermocouple to an accuracy of ± 1 K. The film were prepared on clean glass substrates, the slides first cleaned in distilled water in order to remove the impurities and residuals from their surfaces, followed by rinsing in chromatic acid (for two day), to introduce functional groups called nucleation and/or epitaxial centers, which formed the basis for layer films growth. Then the samples were washed repeatedly in deionized water, and finally put in ultrasonic agitation with distilled water for 15 min then dried. 0.1M CdO:2%In thin films were prepared from solutions of cadmium acetate...
Cd(CH₃COO)₂·2H₂O diluted with methanol and distiller water in the ratio 1:1 and doping CdO solution in a ratio of (2%) with 0.1 M from mixture of InCl₃ and water distiller. The deposition of CdO:In thin films 0.1M molar concentrations were carried by spraying an aqueous solutions onto a heated glass substrates at (350±10°C). The optimized deposition parameters such as spray nozzle substrate distance (29cm), spray time (5s) and the spray interval (50s) were kept constant. The pressure of the carrier gas (N₂) was 4 mbar. The crystalline structure of the films was confirmed by X-ray diffraction (XRD, Shimadzu, DIFRACTOMETER / 6000,) with Cu Kα radiation λ = 1.5406Å).

Film thickness was measured after evaporation by optical interferometer method, using He-Ne Laser λ =0.632 μm and the thickness were determined using the formula:

\[ d = \frac{\Delta x \cdot \lambda}{x \cdot 2} \quad \ldots (1) \]

Where :d is the thickness of sample, x is fringe width, Δx is the distance between two fringes and λ is the wavelength of He-Ne laser light, and its values are 400±10 nm. AFM analysis is also studied for the sample by using atomic force microscopy (AFM), model A2000.

**Sensor construction and test**

In this research, glass substrates (2.5 cm × 2.5 cm × 0.2 cm), prepared with an inter digitized electrodes were used as sensing device. Fig. 1(a,b) shows the sensor configuration. The homogenous thin films as sensing layer was tested. Silver paste was used to fix two contact wires. The thickness of the thin films film was measured to be 400±10 nm. For sensor test, the sensor chip (Fig. 1) was inserted into the isolated box which filled by N₂ gas. The temperature of sensor chip was adjusted in 135 °C and a constant voltage of 60 V was applied by a power supply instrument into the two output wires of sensor chip. Finally, NO₂ gas was injected into the box. Internal atmosphere of the box was circulated by a small fan to make a homogenous gas. After stabilizing, the current of sensor circuit was determined by a high sensitive galvanometer. The determined current was related to the electrical resistance of the sensor. The sensor resistance was related to the NO₂ concentration in the box.
Results and Discussion

Structural properties

Figure 2 shows the X ray diffraction (XRD) patterns of the prepared CdO:2%In film of molar concentrations (0.1M). The pattern show polycrystalline of cubic CdO structure (NaCl structure) and CdO:In films are composed of crystallites of CdO and In$_2$O$_3$ (JCPDS Card 2010). XRD shows neither the formation of CdO and In$_2$O$_3$ nor mixed phases. It can be clearly seen that the film is preferentially orientated along (222) crystallographic directions, and this is in agreement with the result obtained by others on film prepared by sputtering [22], vacuum evaporation [23] and spray pyrolysis [24]. In figure (3:A,B), a typical 5×5 mm$^2$ sized AFM image of CdO:In$_2$O$_3$ film surface is shown. The film crystallites are well shape and uniform in size. It was observed, from 2D, 3D image that, the films exhibit a surface columnar morphology, which can be a consequence of crystalline preferential orientation. AFM images indicate that the used preparation conditions of the films are more favorable to obtain sample with excellent shape as it shown in figure (4). The Granularity cumulation distribution chart and the distribution pattern of CdO: In$_2$O$_3$ grain size of the sample are shown in figure (5), (6) which deals that the grain size are about ~125 nm.

Figure (2) The X ray diffraction (XRD) patterns of the prepared CdO: In$_2$O$_3$ thin films
Table (1): The structural properties of CdO:In$_2$O$_3$ thin films

<table>
<thead>
<tr>
<th>Sample</th>
<th>2θ (deg)</th>
<th>D (Å)</th>
<th>I / I$_0$</th>
<th>FWHM (deg)</th>
<th>Identification with (hkl)</th>
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</thead>
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<tr>
<td>CdO:In$_2$O$_3$</td>
<td>29.8248(CdO)C</td>
<td>2.9932</td>
<td>44</td>
<td>0.262</td>
<td>111</td>
</tr>
<tr>
<td></td>
<td>30.3733(In$_2$O$_3$)C</td>
<td>2.9404</td>
<td>50</td>
<td>0.220</td>
<td>222</td>
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<tr>
<td></td>
<td>37.0240(In$_2$O$_3$)C</td>
<td>2.4261</td>
<td>56</td>
<td>0.205</td>
<td>411</td>
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<tr>
<td></td>
<td>48.5733(CdO)C</td>
<td>1.8728</td>
<td>28</td>
<td>0.366</td>
<td>220</td>
</tr>
</tbody>
</table>

Figure (3(A,B)) AFM micrographs characteristic of CdO: In$_2$O$_3$ thin film
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Figure (4) The shape of CdO:In$_2$O$_3$ grains

Figure (5) Granularity cumulation distribution chart of CdO:In$_2$O$_3$ sample
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Figure (6) The distribution patterns of the grain size for CdO: In$_2$O$_3$

Figure (7) shows the resistance of sensor with time at different operation temperature. Our results show increasing in the resistance values with increasing operation temperature.

A relatively short response time and recovery time at different operation temperature was noticed at 5ppm NO$_2$ gas concentration. The explained behavior also predicts the response of the material to the presence of oxidizing gases, which results in an increase of the resistance. Figure 7. depicts the sensor response to NO$_2$ measured in the temperature interval 50°C–300°C for the different samples studied. The sensor response (S) in our case is defined as the resistance ratio, and being the sensor resistance in presence of the target gas and air, respectively. The gas concentration was fixed at 5 ppm, is observed that the sensor resistance rises in presence of NO$_2$ for all temperatures and a well-defined maximum on sensor response is achieved at about 200°C. The observed behavior may be understood by considering that the kinetic of the surface interaction is thermally activated and determined by the concurrence of several processes of adsorption, reaction, and desorption of previously adsorbed molecules of NO$_2$. At temperatures below 200°C, the sensor response change might be attributed mainly to the adsorption and/or reaction of NO$_2$ molecules on the solid surface according to the following mechanisms as it in [25].

The ratio of measured resistance before and after exposing the sensor surface to gas gives sensitivity [26]. Table (2) refers to the response and rapid time for sensor. The sensitivity of sensor can be calculated from the relation (2).

$$S\% = \frac{(R_{air}(\Omega) - R_{gas}(\Omega))}{R_{air}(\Omega)} * 100\%$$

Where
$R_{\text{air}}$, $R_{\text{gas}}$ is resistance in air and gas for NO$_2$ vapor. The sensing properties were studied at low concentrations of gases vapor (5ppm). This result obtained in that methods are promising for the preparation of sensitive and low cost gas sensor. Figure (8) shows the sensitivity to NO$_2$ gas with different operation temperature. The sensitivity S% increased with increasing operating temperature T.
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Figure (7) the resistance vs. time for different operation temperature for NO$_2$ gas sensor

Table (2) The CdO:In$_2$O$_3$ thin films sensor properties to NO$_2$ gas at different temperature

<table>
<thead>
<tr>
<th>Temp(°C)</th>
<th>response time(sec)</th>
<th>recover time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>37.8</td>
<td>210.6</td>
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<tr>
<td>100</td>
<td>32.4</td>
<td>79.2</td>
</tr>
<tr>
<td>200</td>
<td>18.9</td>
<td>51.3</td>
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<tr>
<td>300</td>
<td>18.9</td>
<td>50.4</td>
</tr>
</tbody>
</table>
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Figure (8) The sensitivity of CdO:In$_2$O$_3$ sensor for different operation temperature to NO$_2$ gas

Conclusions

A novel NO$_2$ gas sensor based on (CdO) (In$_2$O$_3$) mixed-oxide thin films deposited by spray pyrolysis has been studied. The sensor follows a typical surface-controlled gas-sensing model. A different behavior was observed when the sensor surface was exposed to exam at different temperatures. Thus, the sensor resistance reaches maximum at temperature (200°C), while it decreases with further increase of temperature to (300°C) as a consequence of different surface interaction mechanisms. The sensitivity S% increased with increasing operating temperature.

References