Fabrication of Cr₂O₃: ZnO Nanostructure Thin Film Prepared by PLD Technique as NH₃ Gas Sensor

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Received: 4/8/2020 Accepted: 9/10/2020

Abstract
Chromium oxide (Cr₂O₃) doped ZnO nanoparticles were prepared by pulsed laser deposition (PLD) technique at different concentration ratios (0, 3, 5, 7 and 9 wt %) of ZnO on glass substrate. The effects of ZnO dopant on the average crystallite size of the synthesized nanoparticles was examined by X-ray diffraction. The morphological features were detected using atomic force microscopy (AFM). The optical band gap value was observed to range between 2.78 to 2.50 eV by UV-Vis absorption spectroscopy, with longer wavelength shifted in comparison with that of the bulk Cr₂O₃ (~3eV). Gas sensitivity, response, and recovery times of the sensor in the presence of NH₃ gas were studied and discussed. In the present work, we found that the sensitivity was increased upon increasing the concentration ratio from 3 to 5% wt of ZnO, whereas it was decreased again over that value. Also, we found that the sensitivity was increased when increasing operating temperature, while the response time was decreased. The optimum concentrations ratio for NH₃ gas sensitivity at 5% wt ZnO revealed sensitivity of 66.67% and response time of 14s at operating temperature of 300°C and 700mJ PLD energy.

Keywords: Cr₂O₃; ZnO Nanostructure, PLD technique, structural, optical properties, Sensitivity.

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الخلاصة

لما تم تصنيع غشاء رقيق من أوكسيد الكرم (Cr₂O₃) المطابع بأوكسيد الزنك (ZnO) والتي تم تحصين بلغة تركيز النبض وسنسين تتراوح من 0 إلى 9% (3, 5, 7, 9) %، تم اختبار تأثير نسبة تركيز الأوكسيد الزنك في مجال الحجم البليوري للنيئوية Cr₂O₃. Use of Chromium Oxide (Cr₂O₃) and Zinc Oxide (ZnO) nanoparticles in Pulsed Laser Deposition (PLD) technique to prepare Cr₂O₃: ZnO nanostructured thin film. The influence of ZnO dopant on the average crystallite size of the synthesized nanoparticles was examined by X-ray diffraction. The morphological features were detected using atomic force microscopy (AFM). The optical band gap value was observed to range between 2.78 to 2.50 eV by UV-Vis absorption spectroscopy, with longer wavelength shifted in comparison with that of the bulk Cr₂O₃ (~3eV). Gas sensitivity, response, and recovery times of the sensor in the presence of NH₃ gas were studied and discussed. In the present work, we found that the sensitivity was increased upon increasing the concentration ratio from 3 to 5% wt of ZnO, whereas it was decreased again over that value. Also, we found that the sensitivity was increased when increasing operating temperature, while the response time was decreased. The optimum concentrations ratio for NH₃ gas sensitivity at 5% wt ZnO revealed sensitivity of 66.67% and response time of 14s at operating temperature of 300°C and 700mJ PLD energy.

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Introduction

Semiconductor metal oxide received a lot of interest in recent years, because of its structure and optical, electrical, and chemical properties. Among the various semiconductor metal oxides, Cr$_2$O$_3$ is one of the successful semiconductors and broadly studied compounds due to its wide band gap (~3 eV) [1]. Cr$_2$O$_3$ has a p-type semiconductor nature at lower temperatures [2]. This kind of p-type metal oxide semiconductors with broad optical band gap may be decent candidates for many applications in gas sensors and optical storage systems [3]. Such applications of Cr$_2$O$_3$ material depends on its structure, phase, shape, size and synthesizing techniques, along with the addition of suitable dopants to them, such as zinc oxide [4]. For example, the composite of nanomaterial with large surface area to volume (lesser particle size) and high chemical actions has been an important area of active research [5]. The sensing properties of this metal oxide were proved for some flammable or deadly gases, such as NO$_2$ and NH$_3$. Advances in nanotechnology generally provide an increasing response of semiconductor metal oxides because of high surface area. Thin films of nanostructure provide high sensitivity and faster response times [6].

The average crystallite size (D) was estimated by Scherrer’s equation [7], as follows.

$$D = \frac{K\lambda}{\beta \cos\theta}$$

where $K = 0.9$ is Scherer's constant, $\lambda$ is X-ray radiation's wavelength ($\lambda = 1.54056$ Å), $\beta$ is the peak full width at half maximum (FWHM) in radians, and $\theta$ is the Bragg diffraction angle at which FWHM is measured.

The optical band gap energy (E$_g$) of the as-synthesized nanoparticles is obtained from the UV-Vis spectra by using the Tauc’s relation [8]:

$$\frac{\alpha h \nu}{A(h \nu - E_g)} = n$$

where $\alpha$ represents the absorption coefficient, $h\nu$ is photon energy, $A$ is constant (absorbance) and the exponent $n = \frac{1}{2}$ for direct transition.

Sensing measurements are carried out by measuring the $R_s$ resistance of thin films in air resistance ($R_a$) in the presence of NH$_3$ gas. Evaluating gas sensitivity (S%) and response time (S) for reducing gas can be obtained from equations 3 and 4, respectively.

$$S\% = \left| \frac{R_a}{R_s} \right| \times 100$$

$$S = \left| \frac{R_a}{R_s} - 1 \right|$$

In this paper, we present the results of studying Cr$_2$O$_3$ doped with ZnO to find probability and optimal conditions for PLD of nano-crystalline films on glass substrate. The crystallite size, morphology, and optical properties of the as-synthesized Cr$_2$O$_3$ doped with ZnO nanoparticles are investigated and discussed. The thin films prepared are studies for the sensing properties to NH$_3$ gas.

Experimental Part

Un-doped Cr$_2$O$_3$ films and those with different doping concentrations of ZnO (3, 5, 7 and 9 % wt) with high purity (99.99%) were pressed less than 6-8 Ton to form a target product with 2 cm diameter and 0.5 cm thickness. The films were deposited by Nd:YAG laser Second Harmonic Generation, with a laser wavelength of 1064 nm, on glass substrates at room temperature and oxygen pressure of 0.01 to 0.5 mbar. Pulse laser depositions energy was 700 mJ and the frequency of laser pulse was 6 Hz, with about ~2 cm distance between the target and the substrate. The laser beam was focused on the target inside the chamber in 45° angle. The glass substrates were cleaned by ethanol and thereafter rinsed with distilled water in an ultrasonic device. The crystallite structures of the as-synthesized nanoparticles were characterized through XRD $\gamma$ (model D2 PHASER BRUKER, power diffraction systems, Germany) with Cu-K$_\alpha$ radiation ($\lambda = 1.54056$ Å), voltage = 40 kV, current = 30 mA, and scanning 2θ range of 20° to 80°. Morphological images of the thin film surfaces were measured using an AFM (SPM, Model AA3000, Angstrom Advanced Inc, USA) which can provide information about
average diameter, root mean roughness (RMS) and average roughness. The wavelength range of the optical absorbance spectrum (190–1100) nm was recorded by spectrophotometer (SHIMADZU UV-1800, Japan).

RESULTS AND DISCUSSION
Structural Properties
The X-ray diffraction patterns of the as-deposited nanoparticles are shown in Figure-1.

A highly crystalline nature was observed in the spectrum for the as-deposited thin films, whereas the lattice referred to hexagonal axes [9]. It was observed that the crystalline size in planes (012), (104) and (110) was increasing when increasing the concentration from 3 to 7 wt%, while it was decreased over that value. New peaks were observed in the XRD image for a material which represents zinc oxide when concentration ratios of 7 and 9 wt% were used at planes of 100, 012 and 110 in the hexagonal phase, as show in Figure-1. The restrained quantity of ZnO atoms exists due to the effect of ZnO doping decreasing peak intensity of Cr$_2$O$_3$ nanoparticle due to an interstitials sharing the oxygen with Cr atoms and hence recede the crystallinity size, a result which is in agreement with that reported by Mohanapandian [10].

Morphological properties
Three-dimensional images and the distribution of granularity accumulation for Cr$_2$O$_3$:ZnO at the used different concentration ratios of ZnO deposited on glass substrate, with dimensions of 2.5×2.5 cm$^2$, are demonstrated in Figure-2. The grain size was increased when increasing the concentration ratio of ZnO from 3 to 7 % wt, whereas it was decreasing over that value. The images of AFM displayed that all films were of a granular structure. The granular films showed a greater surface area, which is decent for thin film gas interaction and results in higher sensitivity, where the sensitivity of gas has a proportional relationship with the thin film roughness, which is in agreement with the results of Deshpande [11].
Figures 2- AFM image and the chart of grain density distribution for Cr$_2$O$_3$:ZnO thin films.

Values of maximum and average RMS roughness were 3.55 and 2.98 nm, respectively, at 5% wt doping, as shown in table 1. The increases in roughness of thin films may be due to the presence of several hillocks, which are faceted and distributed randomly on the relatively smooth structure densification of the deposition processes [12].

Table 1-Average Diameter, Average roughness and RMS roughness for Cr$_2$O$_3$: ZnO thin films

| ZnO Ratio | Average Diameter (nm) | Average Roughness (nm) | RMS roughness (nm) |
|-----------|-----------------------|------------------------|-------------------|
| 0         | 65.89                 | 0.455                  | 0.558             |
| 3         | 78.32                 | 1.22                   | 1.41              |
| 5         | 82.54                 | 2.98                   | 3.55              |
| 7         | 89.14                 | 1.65                   | 1.83              |
| 9         | 53.47                 | 2.99                   | 3.5               |

Optical properties

Figure-3 shows that the transmission spectra of different concentration of ZnO-doped Cr$_2$O$_3$ nanoparticles were decreased with the increase in the concentrations ratio, whereas they were increased with increasing wavelength.
The spectra show a higher absorption coefficient in the wavelength of 360 nm, as shown in Figure-4, which was increased when increasing the concentration ratio from 3 to 9% wt. The absorption coefficient was decreased with increasing wavelength.

Figure 4 - The relation between the absorption coefficient and wavelength for un-doped Cr$_2$O$_3$ and Cr$_2$O$_3$: ZnO thin films

Figure 5 shows the relation of $(\alpha h\nu)^2$ versus $h\nu$, where the extrapolation of the linear portions of the curves to the $h\nu$ axis results in $E_g$. 
Figure 5-Optical energy gap for Cr$_2$O$_3$: ZnO thin films at different ratios of ZnO

The estimated transmissions (T) and absorption coefficient (α) at a wavelength of 550 nm and the values of the energy band gap (E$_g$) are given in Table-2.

**Table 2- energy gap for Cr$_2$O$_3$: ZnO thin films**

| ZnO ratio% | E$_g$ (eV) |
|------------|------------|
| 0          | 2.78       |
| 3          | 2.75       |
| 5          | 2.65       |
| 7          | 2.60       |
| 9          | 2.50       |

The absorption peaks showed a longer wavelength shift as the concentration of the ZnO dopant in the host Cr$_2$O$_3$ matrices increased from 0 to 9% wt, when compared with the bulk system (~3eV) [13,14]. Hence, the E$_g$ was gradually decreased from 2.78 eV at 0% wt to 2.50 eV at 9% wt. The observed E$_g$ value of the pure Cr$_2$O$_3$ nanoparticles was 2.78 eV. These results are in agreement with the reported values, while showing a marginally lower value than that for the sample prepared by other techniques [15, 16].

**Properties of gas sensors**

The variation in resistance for the thin films with time, after gas on and gas off, is shown in Figure-6. The resistance increasing and decreasing with time after gas on and gas off respectively of all films.
a- Un-doped Cr$_2$O$_3$

b- Cr$_2$O$_3$ doped with 3 wt% of ZnO
c- Cr$_2$O$_3$ doped with 5 wt% of ZnO

d- Cr$_2$O$_3$ doped with 7 wt% of ZnO
e-Cr$_2$O$_3$ doped with 9 wt% of ZnO

Figure-6 Variations of resistance of thin film as a function of time of three different operating temperatures for a-pure Cr$_2$O$_3$, b-doped with 3 wt%ZnO. c- doped with 5 wt%ZnO. d- doped with 7 wt%ZnO. e- doped with 9wt%ZnO.

The reason of this behavior can be attributed to the Cr$_2$O$_3$ mechanism of sensing associated to the ion sorption of gas type over the surface, leading to charge transfer between the gas and surface molecules and changes in the electrical conductance. Hence, NH$_3$ is reducing gas in the environment. When the gas sensor is under the ambient reducing gas, the electrons obtained from the chemical reaction in the process of forming the adsorbed oxygen ion are given back to the conduction band. For the p-type metal oxide semiconductor sensor, the electrons go to the valence band and recombine with the holes, which results in reducing the carrier concentration (holes) and an increased reduction in electrical conductance [17-18].

Figure-7 and Table-3 show that the sensitivity is increased and the response time is reduced with increasing the doping ratio of ZnO from 0 to 7 wt%. The maximum value of sensitivity was equal to 66.67% at 0.07% wt and operating temperature of 573K. Furthermore, when operating temperature was increased from 473 K to 573 K, the sensitivity was also increased, which is in agreement with the results of Starke [19].
Figure 6-Variation of sensitivity for NH\(_3\) gas with ZnO ratios at different temperatures for films

Table 3 shows the response time reduction with increasing the doping ratio of ZnO from 0 to 7\% wt, while it was increased again at 9\%, with 573 K, where the response time was 10s at 7\% wt and 573K [20-27].

**Table 3** Sensitivity, response time, and recovery time for Cr\(_2\)O\(_3\): ZnO thin films at different operating temperatures

| Temp.(K) | ZnO ratio\% | Sensitivity (%) | response time (s) | recover time (s) |
|---------|-------------|----------------|------------------|-----------------|
| 473     | 9           | 18.99          | 8.00             | 40.00           |
|         | 7           | 19.35          | 30.00            | 58.00           |
|         | 5           | 23.68          | 30.00            | 50.00           |
|         | 3           | 22.73          | 9.00             | 40.00           |
|         | 0           | 3.23           | 40.00            | 30.00           |
|         | 9           | 12.16          | 7.00             | 66.00           |
|         | 7           | 50.00          | 20.00            | 40.00           |
| 523     | 5           | 18.75          | 33.00            | 68.00           |
|         | 3           | 20.95          | 8.00             | 48.00           |
|         | 0           | 1.58           | 30.00            | 45.00           |
|         | 9           | 13.79          | 18.00            | 30.00           |
|         | 7           | 66.67          | 10.00            | 28.00           |
| 573     | 5           | 22.73          | 20.00            | 43.00           |
|         | 3           | 5.56           | 28.00            | 41.00           |
|         | 0           | **3.57**       | **30.00**        | **40.00**       |

**Conclusions**

The characterization of structural, optical, and gas sensors properties for ZnO-doped C\(_2\)O\(_3\) thin films were investigated in an reducing ammonia gas sensor prepared by simple and cost-effective PLD technique. The XRD measurements showed that the lattice may be referred to as having a hexagonal phase with a maximum intensity for Cr\(_2\)O\(_3\):ZnO in plane (104) at 5\% wt. The AFM images of all films illustrated a granular structure. Increasing the concentration ratio of ZnO into the Cr\(_2\)O\(_3\) resulted in an increase in the roughness of the deposited thin films, with a higher roughness at 0.05\% wt doping ratio. The optical energy gap was decreased with increasing the concentrations ratio of ZnO. The 5\% wt ZnO-doped Cr\(_2\)O\(_3\) thin film had the highest sensitivity to NH\(_3\) gas, which was 66.67\% at 573 K.
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