Employment of Titanium dioxide thin film on NO₂ gas sensing

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Abstract. TiO₂ thin films were deposited by Spray Pyrolysis with thickness (350±5 nm) onto glass substrates at (350°C), and the film was annealed at temperatures (400 and 500°C). The structural and morphological properties of the thin films (TiO₂) were investigated by X-ray diffraction, Field emission scanning electron microscopy and atomic force microscope. The gas sensor fabricated by evaporating aluminum electrodes using the annealed TiO₂ thin films as an active material. The sensitivity of the sensors was determined by change the electrical resistance towards NO₂ at different working temperatures (200 and 300°C). It was determined that the fabricated sensor using TiO₂ thin film annealed at (400°C) with 8.28 nm particle size has high sensitivity than the thin films annealed at 500°C with 10.37 nm particle size. The sensor operated at 200 °C had also sensitive to the NO₂ gas and its sensivity increased with operated temperatures at 300°C. It was observed that the fabricated sensors exhibited reproducible and stable results.

Keywords: TiO₂; Thin Film; annealing temperature; operation temperature; gas sensor; spray pyrolysis.

1. Introduction

The Solid State gas sensors are depends on the change of the physical and/or chemical properties of their sensing materials when exposed to different gas atmospheres. Although the number of materials used to implement this kind of devices is huge, this work will be centered in studying the ones based in semiconductor properties, and more specifically in those using TiO₂ as gas sensor [1].

TiO₂ used in gas sensing is extensively because of its desirable sensitivity and mainly because of its good stability in adverse environments and versatility in detecting a wide range of toxic/flammable gases [2, 3]. Titanium (IV) Oxide (II) has phase stable, rutile (tetragonal) and two phases metastable, brookite (orthorhombic) and anatase (tetragonal). Both metastable phases become rutile (stable) when annealing the material at temperatures above 700 °C (in pure state) [4].

This Semiconductor Gas Sensors (SGS) present the property of changing the electrical conductivity upon adsorption/desorption of gas molecules at their surfaces. Interaction with ambient oxygen in an n-type SMO can trap mobile carriers (electrons) from the bulk, resulting in an electron-depleted layer (i.e., space-charge layer) at the material surface [2,5].
As suggested by several authors [6, 7], working with nanostructured materials will give a higher surface area in front of gas. Taking into account that sensing reactions take place mainly on sensors layer surface, the control of semiconductor particle size will be one of the first requirements for enhancing the sensitivity of the sensor.

Previously, reported methods for depositing thin film gas sensing materials include chemical bath deposition [8], spin-coating [9] silar [10], vacuum evaporation [11], sol-gel [12] and RF. Sputtering techniques [13] ,etc. Among all methods, spray pyrolysis method is preferred here because It is a simple method, cheap cost and easily for producing wide area deposition with suitable thickness [14]. The aim of this work was to deposited-TiO$_2$ thin films using a simple Spray Pyrolysis method and characterizes the effect of annealing temperature operation temperature on their nanostructural and sensor properties.

2. Experimental details

The TiO$_2$ thin films were prepared using spray pyrolysis method by taking a 0.1 M aqueous solution of TiC$_3$ as starting solutions. The solution was sprayed on to heated glass substrates which were kept at temperature 350°C. Film thickness (t) was measured using weighting method, and was found to be around (350 nm). The prepared films were annealed for 2h at temperatures 400 and 500 °C. The structure of the films after annealing were determined by X-ray diffraction (XRD) using X-ray diffractometer (SHIMADZU Japan) XRD600) with a Cu Kα radiation source (λ = 1.5406 Å) operated at 40 kV and 30 mA. The samples were scanned from 10 to 80°.

The surface morphology of films after annealing at 400 °C and 500 °C was carried out using Field emission scanning electron microscopy (FE-SEM) TESCAN (Czech Republic) (Zeiss-EM10C-100KV university of Tehran -Iran, and Atomic Force Microscopy (AFM) micrographs were recorded by using Cary 100 Conc plus) university of Baghdad.

Finally, the TiO$_2$ gas sensor was fabricated by evaporating aluminum as the ohmic contact electrodes on the TiO$_2$ thin films deposited using a grade mask. The gas sensitivity of a film is usually measured as the percentage change in film resistance on gas exposure, or may be defined as the ratio of its resistance in air to its steady state value in the presence of a gas. After put the sample in chamber was locally manufactured (The chamber is cylindrical in shape, with a radius of 7.5 cm, and a height of 15 cm.

3. Results and discussion

3.1. XRD analysis

The X-ray diffraction of thin films annealed at (400and 500) °C are shown in Figure 1 and 2. XRD results showed that the film was tetragonal TiO$_2$ polycrystalline after annealing according to JCPDS (Card No. 21-1272). It can be seen peaks (101) and (200) at around 25.23° and 48.10° belong to TiO$_2$ appear at the annealing temperature of 400°C and slightly deviation in the peak position with increasing of annealing temperature, may be due to the formation of different strain relief at the crystal grains[15]. It is also observed that the peaks intensity increase with increasing annealing temperature, and other weak peaks appear after annealing at 500°C, also it was found that the tetragonal phase remains stable with increasing annealing temperature, this result agreement with (Hasan et.al)[16].
The XRD peaks (101) was selected to obtain structural parameters such as strain, crystalline size C.S, dislocation density δ and number of crystallites per area are calculated by using the following relations respectively [15,17] and listed in table(1) and influence of increase annealing temp. on the structural parameters.

\[ \varepsilon = \frac{\beta \cos \theta}{4} \]  \hspace{1cm} (1)

\[ \text{C.S} = \frac{0.94 \lambda}{\beta \cos \theta} \]  \hspace{1cm} (2)

\[ \delta = \frac{1}{(\text{C.S})^2} \]  \hspace{1cm} (3)

\[ N = \frac{t}{(\text{C.S})^3} \]  \hspace{1cm} (4)

Where \( \lambda = 0.154061 \text{nm}, \) Bragg’s angle, \( \beta \) (FWHM): full width at half maximum in rad and \( t \): thickness of the film.

From the Table 1, it was generally observed that as the crystallite size increases the strain, dislocation density and number of crystallites per area in the film decreases which is a well-known phenomenon.

| Parameters | Annealing temperatures | Standard values |
|------------|------------------------|-----------------|
|            | 400                    | 500             |
| \( 2 \theta \) | (101) 25.2372 | 25.1807 | 25.2806 |
| \( 2 \theta \) | (200) 48.1091 | 47.9392 | 48.0487 |
| \( d \) Å | (101) 3.5261 | 3.5338 | 3.5200 |
| \( d \) Å | (200) 1.80779 | 1.89611 | 1.8920 |
| Strain | (101) 0.00437 | 0.00349 | ........ |
| C.S nm | 8.28 | 10.37 | ........ |
| \( \delta \) \( \times 10^{15} \) m\(^2\) | 14.5 | 9.3 | ........ |
| \( N_o \) \( \times 10^{16} \) m\(^2\) | 61.5 | 31.4 | ........ |
3.2 FESEM and AFM analysis

Figure 3 shows the Field Emission Scanning Electron Microscopic (FESEM) images of the annealed at 400 °C and 500 °C films. FESEM pattern reveals that films are uniform, good coverage of substrata surface, dense and without any cracks.

The two-dimensional (2D) AFM images for thin films with annealing temperatures are shown in Figure 4. The sample surface become rougher after annealing at 500 °C, it increased from 3.53nm for thin films annealed at 400°C to 7.63 nm for thin films annealed at 500°C as shown in table (2) this increasing may be due to increase of grain size. This results agreement with X-ray diffraction and (FESEM).

Figure 4. (2D) AFM images for annealing temperatures: (a) 400°C and (b) 500 °C.
Table 2. AFM results for thin films.

| Annealing Temp. | Roughness | RMS  | Average grain size (nm) |
|-----------------|-----------|------|-------------------------|
| 400°C.          | 3.53      | 4.08 | 47.73                   |
| 500°C.          | 7.63      | 8.81 | 74.03                   |

3.3. The gas sensitivity

The gas sensitivity of a film is usually measured as the percentage change in film resistance on gas exposure, or may be defined as the ratio of its resistance in air to its steady state value in the presence of a gas. Response (or detection sensitivity) of the sensors can be calculated as [18,19].

\[
S = \left( \frac{R_g - R_a}{R_a} \right) \times 100\% \tag{5}
\]

Where, \( R_a \) and \( R_g \) are the measured resistance under air and \( \text{NO}_2 \) (oxidizing gas), respectively.

It is possible to calculate the sensitivity of the sensor of the type metal oxides semiconductor through the interaction between the gas and the sensor surface.

3.3.1. Influence of annealing temperature on Gas sensitivity

Figure 5 shows the effect the annealing on sensitivity (S) as a function of operating time for TiO\(_2\) thin films when exposure to \( \text{NO}_2 \) gas at 200°C operating temperature. It is clear from this figure the sensitivity of the thin film annealed at 400°C (particle size of 8.28 nm) is greater sensitivity than of the TiO\(_2\) thin film annealed at 500°C (particle size of 10.37 nm) because it has a large surface area that provides more active sites for adsorption and reactivation for the gaseous species. And thin film annealed at 400°C larger roughness, the increasing in surface roughness of the films leads to increase in sensing properties this results agreement with S.H. salman [20].

![Figure 5](image_url)

Figure 5. Show the effect annealing on sensitivity (S) as a function of operating time for TiO\(_2\) thin films at 200°C operating temperature
3.3.2. Influence of operating temperature on Gas sensitivity

Figure 6 and Figure 7 Show operating temperature on sensitivity (S) as a function of operating time for TiO$_2$ thin films annealed at 400°C and 500°C (annealing temperature).

![Figure 6](image1)

Figure 6. Shows operating temperature on sensitivity (S) as a function of operating time for TiO$_2$ thin films annealed at 400°C (annealing temperature).

![Figure 7](image2)

Figure 7. Shows operating temperature on sensitivity (S) as a function of operating time for TiO$_2$ thin films annealed at 500°C (annealing temperature).

The calculated sensitivity (S) of the sensors in two cases was given in Figure 5 and 6. The sensor prepared is sensitive to NO$_2$ gas as seen in these figures. It was shown that the sensitivity of the sensors for these two measurements did not significantly change. As known the stability of the chemical gas sensors related the particle size in the film [21]. It was seen that the sensitivity increased as the operating temperature increased because decreases the surface resistance of the semiconductor thin film. Changing of their electrical properties interested in adsorption of oxygen by trapping an electron from the conduction band of the metal-oxide semiconductor. At the working temperature of the sensor below 200 °C ionized molecular (O$_2^-$) form of the oxygen can be exist while above this temperature atomic (O $^-$, O$^2-$) forms is dominated [22].

The highest response of the sensor was reached at an operating temperature of 300 °C, as % 97.4. In addition, the results indicate that the sensor has a good response with 37.46 % at a low temperature as 200 °C; these results for thin films annealed at 500°C.
Also the highest response of the sensor was reached at an operating temperature of 300 °C, as 70.8%. In addition, the results indicate that the sensor has a good response with 43.9 % at a low temperature as 200 °C, this results for thin films annealed at 400°C.

4. Conclusions

The spray pyrolysis method was successfully used to deposit a uniform and homogeneous TiO$_2$ film. The XRD data reveal that the TiO$_2$ samples are polycrystalline with tetragonal structure after annealing. The crystallite size is increased as the annealing temperature increases. The properties of TiO$_2$ thin films are suitable for various technological applications. Such as gas sensor .the sensitivity of thin films (TiO$_2$) for NO$_2$ gas depending on annealing and operating temperature.

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