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Study of gas sensor based on TiO_2 nanostructures for the detection of NO_2 gas in air

Radhiyah Mahdi Shaker Jarrah

Department of Physics, Faculty of Science, University of Kufa, Najaf, Iraq.
Email: rathyah@yahoo.com

Abstract
In this work gas sensor based on a TiO_2 nanostructure has been investigated to employ it to detect and measurement percentage of presence of nitrogen dioxide in the air specimen. TiO_2 was fabricated using dc magnetron sputtering method, pure Ti (99.99%) used as sputtering target, the oxygen/argon rate flow rate was settled at (50:50 sccm), the chamber presser was controlled to remain it at (0.2 Pa) during the deposition process and direct voltage for the sputtering operation was 1000 V with 100W power. X-ray diffraction pattern show that the structure of all TiO_2 films is polycrystalline with three phases Anatase, Brookite and Rutile with preferential orientation in the (112) direction. For TiO_2 metal oxides, the annealed sensor exhibit variation of the conductance upon exposure to NO_2 gas and showing excellent sensitivity. The high sensitivity for NO_2 gas can be achieved with annealing the film and the sensitivity of the TiO_2 thin films changes linearly with the increase of the gas concentration. The response – recovery time of TiO_2 materials to NO_2 gas is characterized to be relatively exceedingly short. TiO_2 thin films have the highest sensitivity of 95% and exceedingly short response time of 2 s.

Keywords: Anatase; Brookite; Recovery time; Response time; Rutile; Sensitivity.

1. Introduction

Titanium dioxide (TiO2) possesses several good physical properties for instance, direct and wide band gab, high dielectric constant, strong mechanical and chemical stability. Therefore, interest in studying this kind of semiconductor is increasing. These advantages make this material is required for many applications such as solar cells, photo catalysts, gas sensors, optical coatings, etc. [1-4]

Metal oxides such as TiO2, WO3, Fe2O3, ZnO and Co_3O_4 have also been used as gas sensors. Despite these broad studies in the semiconductor sensor area, problems such as insufficient gas selectivity, slow response and recovery times, inability to detect very low gas concentrations, and degradation of the sensor performance by surface contamination still persist. Thus, there is a growing need for chemical sensors with novel properties [5, 6].

Sensors are devices that produce a measurable change in output in response to a specified input stimulus. This stimulus can be a physical stimulus, chemical or biochemical material. The output signal is typically an electrical signal proportional to the input variable. [5-7].

The presence of a reducing/oxidizing gas at the surface of certain metal oxide semiconductors changes its electrical resistance R. It is this phenomenon that has spurred the use of these materials in the detection of a gaseous ambient. [7]. There are two well – known ways for improving the gas sensing properties of these films. The first is to add noble metals for their catalytic activity and to dope the film, with many reports showing that it leads to better sensitivity and stability. [8, 9]. The second is to reduce grain size, which has been shown to increase sensitivity [10]. Consequently, there is great interest in using nanoparticles in gas sensors, since they can be used to make films with very small grain sizes

2. Experimental procedure

In this work TiO_2 is fabricated using dc magnetron sputtering method. The gases were mixing prior to the delivering them to the sputtering chamber. While flow meters were used to control the flow of gases, the oxygen/argon rate flow rate was stetted at (50:50 sccm) (stander centimeter cubic per minute).

Circular magnetron with diameter 10 cm and magnetic field reaches up to 400 gausses and variable d.c. supply (5kVand 500 mA) was designed to control the discharge characteristics. On the other hand, Pure Ti (99.99%) with a diameter of 10 cm and 0.4 cm thickness was used as a sputtering target. According to the experience, the space between target and substrate (glass plates) was adjusted at 4 cm to give best result.

The work has been started by evacuate the growth chamber and reduce the pressure to 6×10^{-4} pa, after 30 minutes the mixer of Ar (99.99%) and O_2 (99.99%) gases were introduced into the chamber, while the chamber pressure was controlled to remain it at (0.2 Pa) during the deposition process. Initially, sputtering for 10 minutes has been used as pre-sputtering process to clean the surface of the target. The direct voltage for the sputtering operation was 1000 V with 100W power.

The resulting crystalline structure of 200 nm thickness of TiO_2 films have been studied by X-ray diffraction tests, using XR-6000-Schemadzu system.

The whole sensor test system as Figure 1. The voltage of bias is 10 volts, and the pressure in range of (1×10^{-3} bar) in the chamber. The mixing of the gas with air have been controlled by flow meter. The mixing control system was fitted tightly to give the right ratio of the mixing in order to recording real sensitivity.

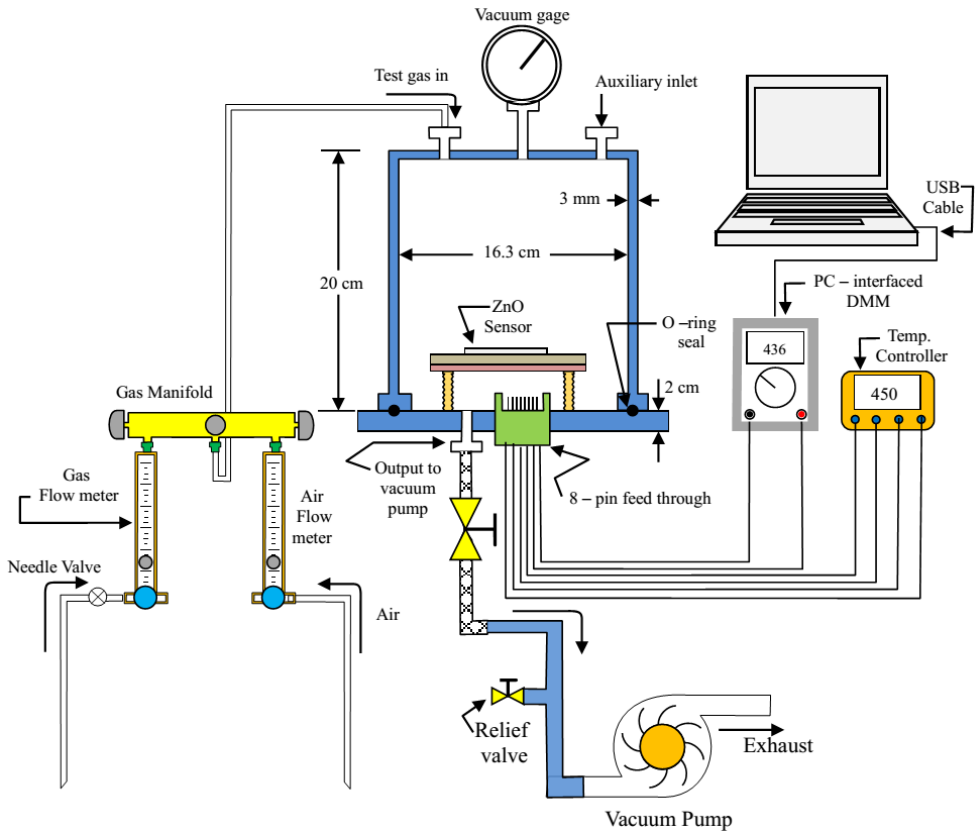

Figure 1. Gas sensor testing system.

3. Results and discussion

3.1 structure measurements

The results of XRD tests for TiO_2 predicted thin film, which was subjected to annealing using different temperatures (673K and 773K) for one hour in air, are showing in Figure 2, which indicate that all the films have multiphase Brookite (B), Anatase (A) and Rutile (R) .

The XRD spectra of the TiO_2 thin film have six peaks A (112), B (112) R (210), B (213), B (431) and A (224) [11] at angles (2θ=38.6°), (2θ=39.9°), (2θ=44.7°), (2θ=64.9°), (2θ=78.7°) and (2θ=82.4°) respectively.

The estimate of the d space using Bragg's law [12],

$$n\lambda = 2d_{hkl}\sin\theta \tag{1}$$

where λ = 1.54059Å, is the wavelength of X-ray used and d is the atomic space.

And the average of grains size have been estimated using Scherer formula [12]:

$$G = \frac{0.9\lambda}{\beta\cos\theta} \tag{2}$$

Where G is the crystallite size, β is the full width at half maximum at diffraction angle 2θ in radians, reveals the size was 27.51 nm for (as deposited) thin film and increase to 28.06 nm and 29.62 nm after annealing from 673K to 773K respectively for 2Θ~38.6 as Table 1.

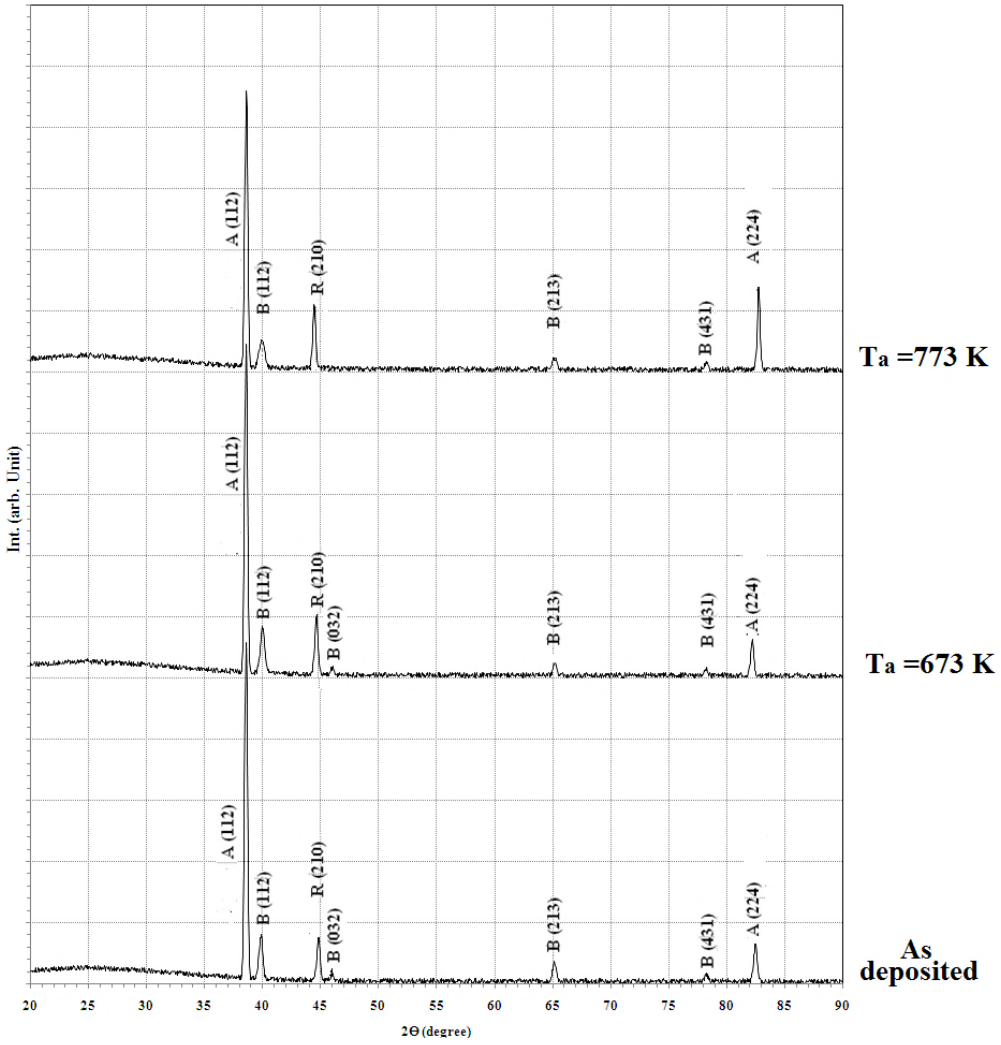

Figure 2. X -ray diffraction pattern for thin TiO_2 films deposited at different annealing temperatures Ta.

Table 1. Experimental XRD data for TiO_2 films for different annealing temperatures.

T_a (K)	2θ(degree)	d_{hkl} (Å)	Grain size (nm)	Phase	(hkl)
As deposited	38.606	2.330	27.51	Anatase	(112)
	39.961	2.254	22.48	Brookite	(112)
	44.748	2.024	28.08	Rutile	(210)
	82.413	1.169	29.91	Anatase	(224)
673	38.587	2.331	28.06	Anatase	(112)
	39.974	2.254	24.15	Brookite	(112)
	44.690	2.026	27.71	Rutile	(210)
	82.232	1.171	29.87	Anatase	(224)
773	38.587	2.331	29.62	Anatase	(112)
	39.881	2.259	21.13	Brookite	(112)
	44.412	2.038	28.6	Rutile	(210)
	82.787	1.165	31.15	Anatase	(224)

3.2 gas sensor measurements

The performance of the gas sensor is converted an analytical gas concentration into an electronic signal. TiO_2 is one of the n-type semiconductors that can be used to perform this converting, due to the impact of presence of gas molecules and its reaction with film surface on the electric resistance of the film. [13-15]. Sensing measurements are investigated at different mixing ratios (NO_2: air mixing ratio is 3%, 2%, 1%) and annealing temperature to find the sensor sensitivity for NO_2 gas. The variation of sensor sensitivity S, as calculated using the equation [16]:

$$S = \frac{|\Delta R|}{R_o} \times 100\% = \frac{R_{gas} - R_o}{R_o} \times 100\% = \frac{\sigma_{gas} - \sigma_o}{\sigma_o} \times 100\% \quad (3)$$

(where R is the electrical resistance and σ is the electrical conductance) with test gas mixing ratio is illustrated in Figure 3. It was appeared that the sensitivity increases rapidly with gas concentration region particularly at ratio less than 2%, which benefits an actuator to enabling it to detect different concentrations of combustible gases [16, 17].

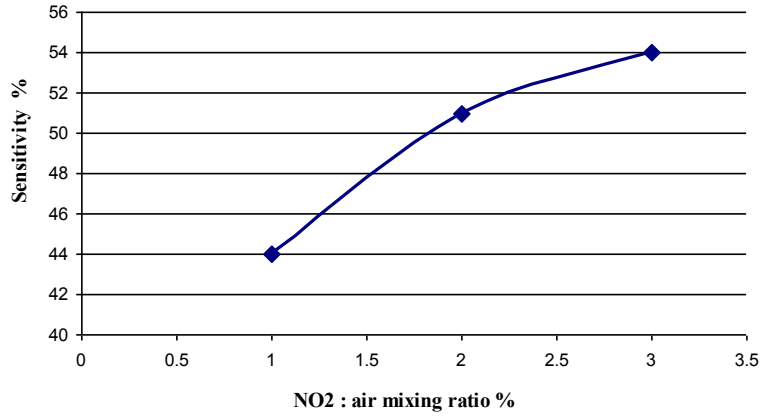

Figure 3. The sensitivity dependence of TiO_2 sensor on NO_2 gas mixing ratio.

Figure 4 exhibits the sensitivity of the sensor which increases as the NO_2 gas concentration increased from 1 % to 3% and it drops rapidly when the NO_2 gas is removed, indicating that the gas sensor has a good response for different NO_2 concentrations.

The response and recovery times of the sensor estimated from Figure 4 as defined in Figure 5. Both response and recovery time of the sensor decrease with increasing NO_2 concentration to 2% then it

should be decreased with increasing gas concentration to 3% at which the lowest response and recovery times of 2 s and 12 s are observed. The high sensitivity and the fast response time are actualizing at 2% gases concentration.

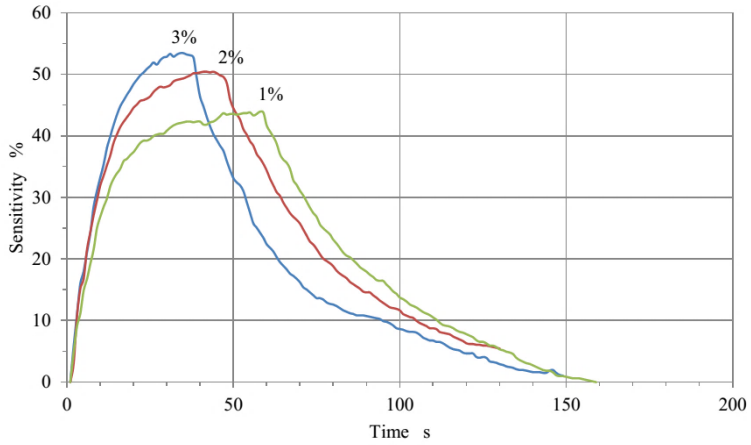

Figure 4. Transient responses upon exposure to NO_2 gas of mixing ratios of 1%, 2%, and 3% respectively.

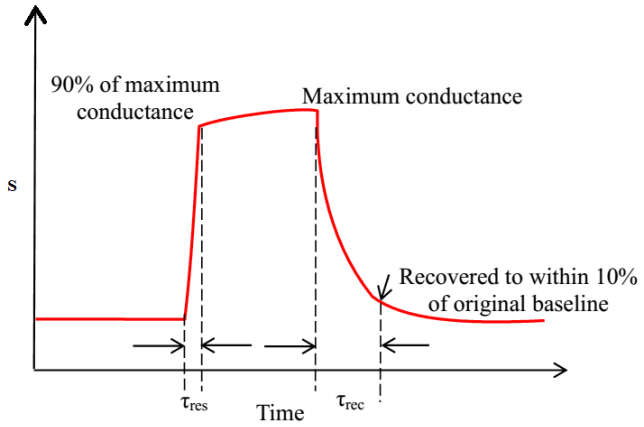

Figure 5. The response and recovery times.

The effect of annealing temperature on the sensitivity was studied with the aim of finding optimize annealing temperature. The variation of sensitivity with the annealing temperature is shown in Figure 6. The sensitivity increases as the annealing temperature increased reaching a maximum value (~ 95%) at 673K, and then it decreased with further increase in the annealing temperature. It is suggested that 673K is the best annealing temperature for high sensitivity of the sensor.

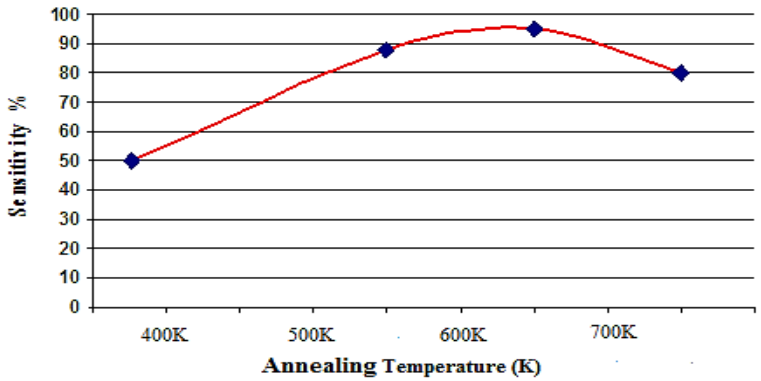

Figure 6. The variation of sensitivity with the annealing temperature.

4. Conclusion

We can be concluded that the highest sensitivity of 95% and extremely short response time of 2 s, which fit for practice since it is crucial to get fast and sensitive gas sensor capable of detecting toxic and flammable gases. The best annealing temperature for high sensitivity of the sensor found to be 673K.

5. Future suggestions

1- improving the gas sensing properties of these films by add noble metals for their catalytic activity and to dope the film, with many reports showing that it leads to better sensitivity and stability.
2- Reduce grain size, which has been increased the sensitivity.
3- Consequently, there is great interest in using nanoparticles in gas sensors, since they can be used to make films with very small grain sizes.

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