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## Optical and Structural Properties of Titanium Dioxide Papered by DC Magneto-Sputtering as a NO<sub>2</sub> Gas Sensor

Sarmed Salih Al-Awadi, Amer A Ramadhan, Fuad T Ibrahim\*, Ali K Abbood  
Physics Department, College of Science, University of Baghdad, Baghdad, Iraq

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### Abstract

In this work, a reactive DC magnetron sputtering technique was used to prepare TiO<sub>2</sub> thin films. The variation in argon and oxygen gases mixing ratios (4:1, 2:1, 1:1, 1:2, 1:4) was used to achieve optimal properties for gas sensing. In addition, an analysis of the optical XRD properties of TiO<sub>2</sub> thin films is presented. High-quality and uniform nanocrystalline films were obtained at a working gas pressure of 0.25 mbar and 1:4 (Ar/O<sub>2</sub>) gas mixture. The optical properties showed a transparent thin film with uniform adherence to the substrate. The average transmission of the TiO<sub>2</sub> films deposited on the glass substrates was higher than 95% over the range of 400 to 800 nm. The optical band gap varied from 3.84 eV to 3.93 eV as a function of oxygen/argon ratios. The XRD pattern showed that the films have an amorphous structure, which is shifted to polycrystalline with increasing oxygen to argon ratio. The sensitivity, response time, and recovery time were measured for TiO<sub>2</sub> thin films using NO<sub>2</sub> oxidizing gas.

**Keywords:** TiO<sub>2</sub>, reactive DC magnetron sputtering technique, argon to oxygen, gas sensor, sensitivity

## دراسة الخصائص البصرية والتركيبية لثاني أكسيد التيتانيوم المحضر بطريقة التريذ المستمر كمتحسس لغاز ثاني أكسيد النايروجين

سرمد صالح، عامر عباس، فؤاد طارق، علي عبود

قسم الفيزياء، كلية العلوم، جامعة بغداد، بغداد، العراق

### الخلاصة

في هذا العمل، استخدم تقنية الماكنترون التريذ المستمر لتحضير أغشية رقيقة من ثاني أكسيد التيتانيوم. نسب خلط مختلفة لغازي الأركون والأكسجين (4:1، 2:1، 1:1، 1:2، 1:4) استخدمت في عملية التحضير أغشية ثاني أكسيد التيتانيوم كمتحسس بأعلى كفاءة، والذي تم دراسة خصائصه البصرية والتركيبية. حيث بينت النتائج أن استخدام نسبة خلط الأركون إلى الأكسجين (4:1) وبضغط غاز 0.25 mbar تعطيت أغشية بتوزيع نانوية منتظم وتجانس بصري عالي. أن الخصائص البصرية تبين الشفافية العالية للغشاء وأن نفاذية الأغشية بحدود 95% ضمن الطول الموجي 400-800nm. كذلك أن فجوة الطاقة البصرية 3.84-3.93eV وحسب تغير نسب خلط غازات التحضير. أن فحص الأشعة السينية للأغشية المحضرة يظهر عشوائية التركيب والذي يصبح متعدد التبلور بزيادة غاز الأكسجين إلى الأركون. كذلك تم قياس

\*Email: fuadtariq2002@yahoo.com

تحسسية وزمن الاستجابة وزمن الاسترجاع لا غشية ثاني اوكسيد التيتانيوم لغاز ثاني اوكسيد النايترجين المؤكسد.

## 1. Introduction

Titanium dioxide  $\text{TiO}_2$  films have good transmittance in the visible region along with chemical stability and high refractive index. For this reason, they are extensively used in present and future applications related to electronics, photonics, sensing, catalysis, controlled drugs, and medicine [1]. Different deposition techniques can be used to form titanium oxides films, including thermal evaporation [2], electron beam evaporation [3], plasma-enhanced chemical vapor deposition [4], spray pyrolysis [5], sol-gel method [6] and reactive DC magnetron sputtering [7]. Among these techniques, reactive magnetron sputtering has important properties because of the fact that the film can control the stoichiometry of the metal target.

In the present work, we have made an effort to prepare  $\text{TiO}_2$  nanoparticles with tetragonal pure anatase phase in a simple way, where anatase  $\text{TiO}_2$  has a wide bandgap ( $E_g \approx 3.2$  eV) with an n-type semiconductor material and poor electrical conductivity. Therefore, the nanoparticles were prepared without using chemical components, as we know that  $\text{TiO}_2$  nanoparticles as thin films are biocompatible, bio-safe, and can be used easily for medicinal industries.

This paper focuses on preparing surface conductivity of anatase  $\text{TiO}_2$  thin films deposited by a DC reactive magneto-sputtering technique. The optical properties, nanostructures, and morphology of these thin films were studied at different argon: oxygen mixing ratios. In addition, the sensitivity, response time, and recovery time were studied for the  $\text{TiO}_2$  gas sensors fabricated as a function of working temperature.

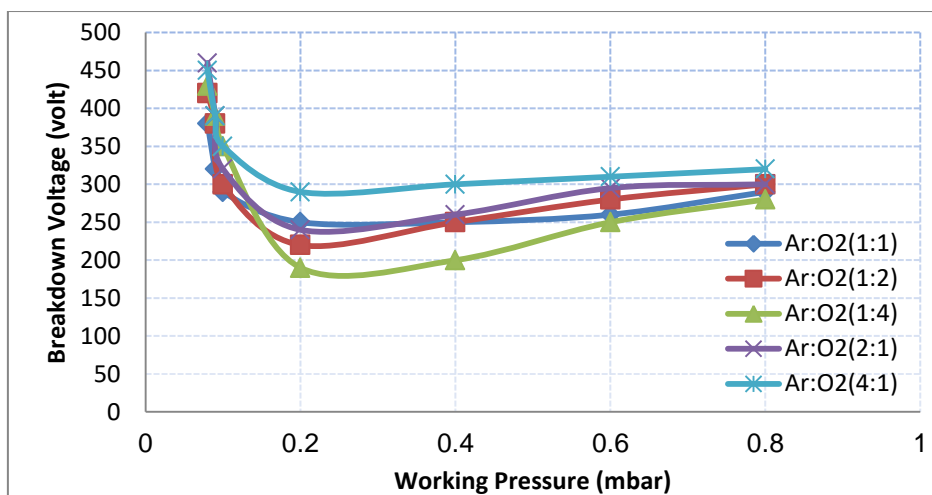
## 2. Experimental work

Details of the design and construction of the homemade reactive magneto-sputtering system, which was used for depositing  $\text{TiO}_2$  films, are explained here. Electrodes, vacuum feedthrough, electrical feedthrough, high voltage feedthrough, and gas supply feedthrough were inserted into a chamber. The chamber was pumped by two stage rotary pump (24  $\text{m}^3/\text{h}$ ) [L.H] to a base pressure of about  $5 \times 10^{-3}$  mbar. The high pressure was measured using Edward pirani gauge, which can read continuous pressure over the whole range from atmospheric to base pressure of the vacuum system.

The vacuum chamber was cleaned by using glow discharge for five minute with 10 mA discharge current to remove contaminants in electrodes and chamber. First, the chamber was evacuated using rotary vacuum pump to a base pressure of about  $5 \times 10^{-3}$  mbar, and then the chamber was filled with argon and oxygen gases (99.99% purity) to about the desired pressure (0.25 mbar). The starting material was a solid titanium target (99.9% purity). High purity argon and oxygen were mixed with different ratios of 4:1, 2:1, 1:1, 1:2, and 1:4, which were used as sputtering and reactive gases. A glow discharge was generated to prepare the  $\text{TiO}_2$  thin films by applying current of about 50mA for 90 minutes between electrodes.

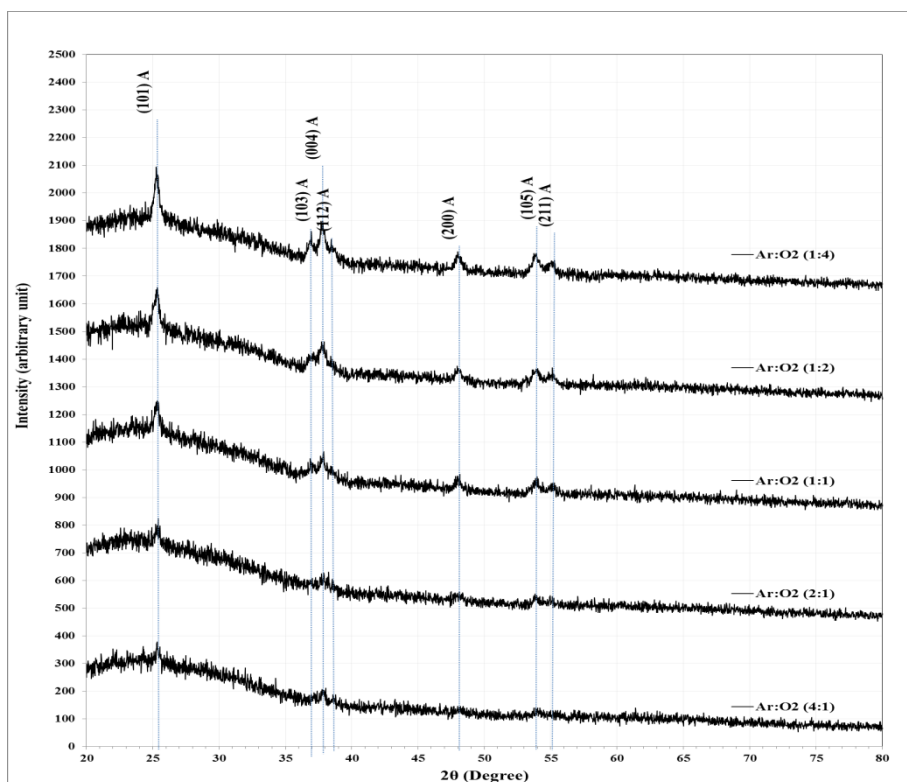
## 3. Results and discussion

In this work, two gases were used to deposit the  $\text{TiO}_2$  thin films; argon was used as a sputtered gas whereas oxygen was used as a reactive gas (oxidization gas). For this reason, the flow of Ar: $\text{O}_2$  gases mixture was examined. Figure- 1 exhibits the variation of the breakdown voltage with the applied gas pressure at three-centimeter distances between electrodes. From this figure, we can depict the optimum Ar: $\text{O}_2$  mixture flow for operating the sputtering system. At the value of argon- oxygen mixture flow equal or less than one, the paschal minimum curve had an optimum Ar: $\text{O}_2$  mixture, since the higher discharge current plasma and  $\text{TiO}_2$  thin films were transparent and had high-quality optical coatings with high hardness.



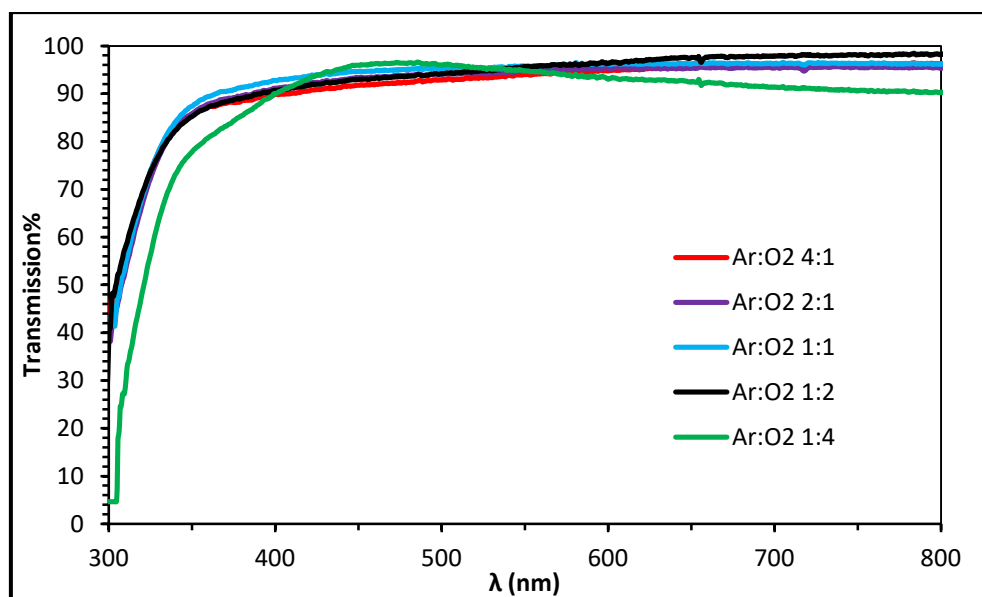
**Figure 1-** The variation of the breakdown voltage with applied gas pressure at 3cm distances between electrodes.

The effects of argon-oxygen mixture on the  $\text{TiO}_2$  thin films structure were characterized by X-ray diffraction. The XRD pattern of  $\text{TiO}_2$  thin films deposited on a glass substrate for different argon-oxygen mixture flow (4:1, 2:1, 1:1, 1:2, and 1:4) at an optimum constant working pressure of 0.25 mbar is shown in Figure- 2. Reflections from the tetragonal crystallographic phase of the anatase phase  $\text{TiO}_2$  became more defined with progressively more intense and sharp films with decreasing oxygen in respect to argon. All the diffraction peaks identified and located at 25.3, 37.79, 53.88 and 55.06 are indexed as anatase  $\text{TiO}_2$  (ASTM card no. 96-900-9087) [8] corresponding to reflections of (101), (004), (105) and (211) planes, respectively. As shown, all films are polycrystalline with the preferred orientation in (110) direction when they were deposited at a flow ratio ( $\text{Ar}/\text{O}_2$ ) of less than 1. The peak intensity was increased with increasing the flow ratio of  $\text{Ar}/\text{O}_2$  from 4:1 to 1:4. The increase in oxygen content is related to a significant increase of the density of defects. The increase in oxygen absorption might be attributed to a change in film structure from an amorphous film containing the  $\text{TiO}$  phase towards a  $\text{TiO}_2$  phase.



**Figure 2-** XRD of sputtered  $\text{TiO}_2$  thin films on a glass substrate for different Ar to  $\text{O}_2$  mixing flow.

The optical measurements of the prepared films were carried out using UV-Vis (300-800 nm) Spectroscop. The spectral dependence of the transmittance (T) was determined for all TiO<sub>2</sub> films deposited at the same conditions (d=3cm and a deposition time of 90min) at the working pressure for different argon to oxygen mixing flow, as shown in Figure- 3. The presence of these oscillations is indicative of the good optical quality of the films. All films were transparent and adherent to the substrate uniform. The average transmission of the TiO<sub>2</sub> films deposited on the glass substrates was more than 95% over the range of 400 to 800 nm. A sharp fall in the transmission at about 310 nm is due to the absorption edge of TiO<sub>2</sub> semiconductor films. The transparency of the films was decreased in the major portions of the visible range with the built-up thickness, which is also clear from the fringes in the transmission spectra. The absorption edge was slightly red shifted with increasing gas pressure. The transmittance fell rapidly in the low wavelength region with increasing film thickness, whereas the onset of absorption edge became less sharp. This may be due to the presence of bigger crystalline sizes and increased scattering due to the surface roughness [9].



**Figure 3**-Transmission spectrum as a function of wavelength for sputtering TiO<sub>2</sub> films at different argon to oxygen mixed ratio.

**Table 1**-Parameter of TiO<sub>2</sub> films prepared at different sputtering Ar/O<sub>2</sub> mixture ratio.

Ar:O <sub>2</sub>	T%	$\alpha$ (cm <sup>-1</sup> )	K	n	$\epsilon_r$	$\epsilon_i$	E <sub>g</sub> (eV)
04:01	92.82	11170	0.044	1.496	2.235	0.133	3.84
02:01	94.04	9212	0.037	1.443	2.081	0.106	3.86
01:01	95.21	7370	0.029	1.390	1.931	0.082	3.88
01:02	94.19	8982	0.036	1.437	2.063	0.103	3.90
01:04	95.94	6218	0.025	1.354	1.832	0.067	3.93

The Hall measurements showed that the n-type semiconductors for TiO<sub>2</sub> samples were deposited on the glass substrate as thin film. The Hall parameters for the n-type films included the electrical

conductivity ( $\sigma$ ), Hall coefficient ( $R_H$ ), carrier concentration ( $n_H$ ), and mobility ( $\mu_H$ ), as shown in Table- 2

**Table 2-**The Hall effect parameters for TiO<sub>2</sub>.

Ar:O <sub>2</sub>	$\sigma_{RT}$ ( $\Omega^{-1} \cdot \text{cm}^{-1}$ )	$R_H$	$n$ ( $\text{cm}^{-3}$ )	type	$\mu_H$ ( $\text{cm}^2/\text{v} \cdot \text{sec}$ )
4:1	2.064E-05	8.77E+05	7.12E+12	n	18.11
2:1	2.049E-05	2.69E+06	2.32E+12	n	55.10
1:1	2.041E-05	3.44E+06	1.82E+12	n	70.17
1:2	2.034E-05	1.75E+06	3.58E+12	n	35.49
1:4	1.987E-05	6.58E+05	9.50E+12	n	13.07

The electrical conductivity of the samples was measured at room temperature ( $\sigma_{RT}$ ). The effect of the various argon to oxygen ratios was observed as the electrical conductivity was decreased by increasing oxygen to argon ratio. On the other hand, additionally increasing oxygen to argon caused lattice sites of Titanium atoms in TiO<sub>2</sub> and resulted in more charge carriers.

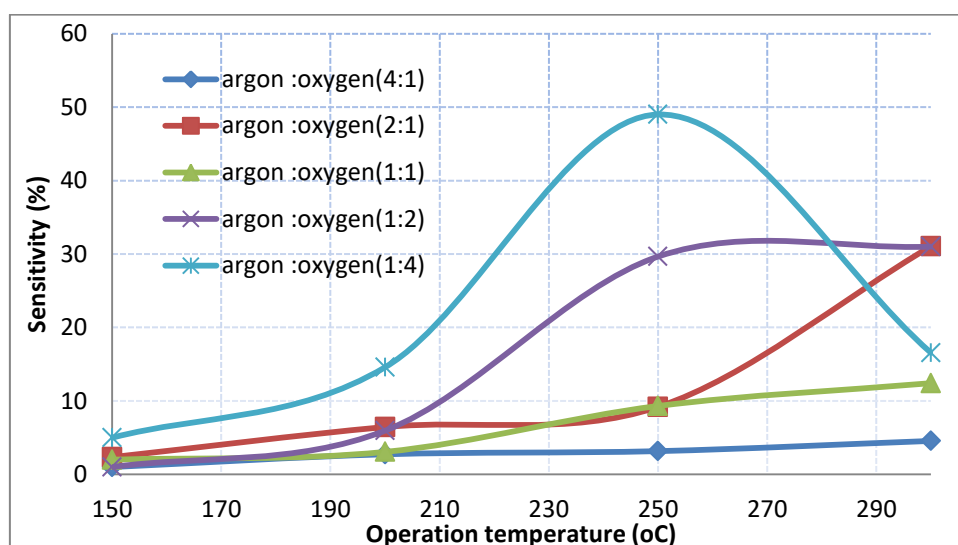
The main purpose of preparing TiO<sub>2</sub> with different argon to oxygen ratios is to support the production of much more charge carriers and hence to increase the amplitude of electrical signal when this device responds to the detected gas species. It was observed that the TiO<sub>2</sub> prepared at an equal mixed ratio of argon to oxygen showed much higher efficiently and hence provided further charge carriers for the electrical conduction, as well as increased mobility ( $\mu_H$ ) of the charge carriers. The overall variation in the density and mobility of charge carriers can be explained in terms of the placement of oxygen in the TiO<sub>2</sub> lattice. The mobility was decreased at high argon to oxygen ratios, which may be caused by the interstitial occupancy of oxygen in the TiO<sub>2</sub> lattice.

The fabricated samples were tested as gas sensors for NO<sub>2</sub> gas at different operation temperatures. The sensitivity factor ( $S$ ) was calculated by the following equation [10]:

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

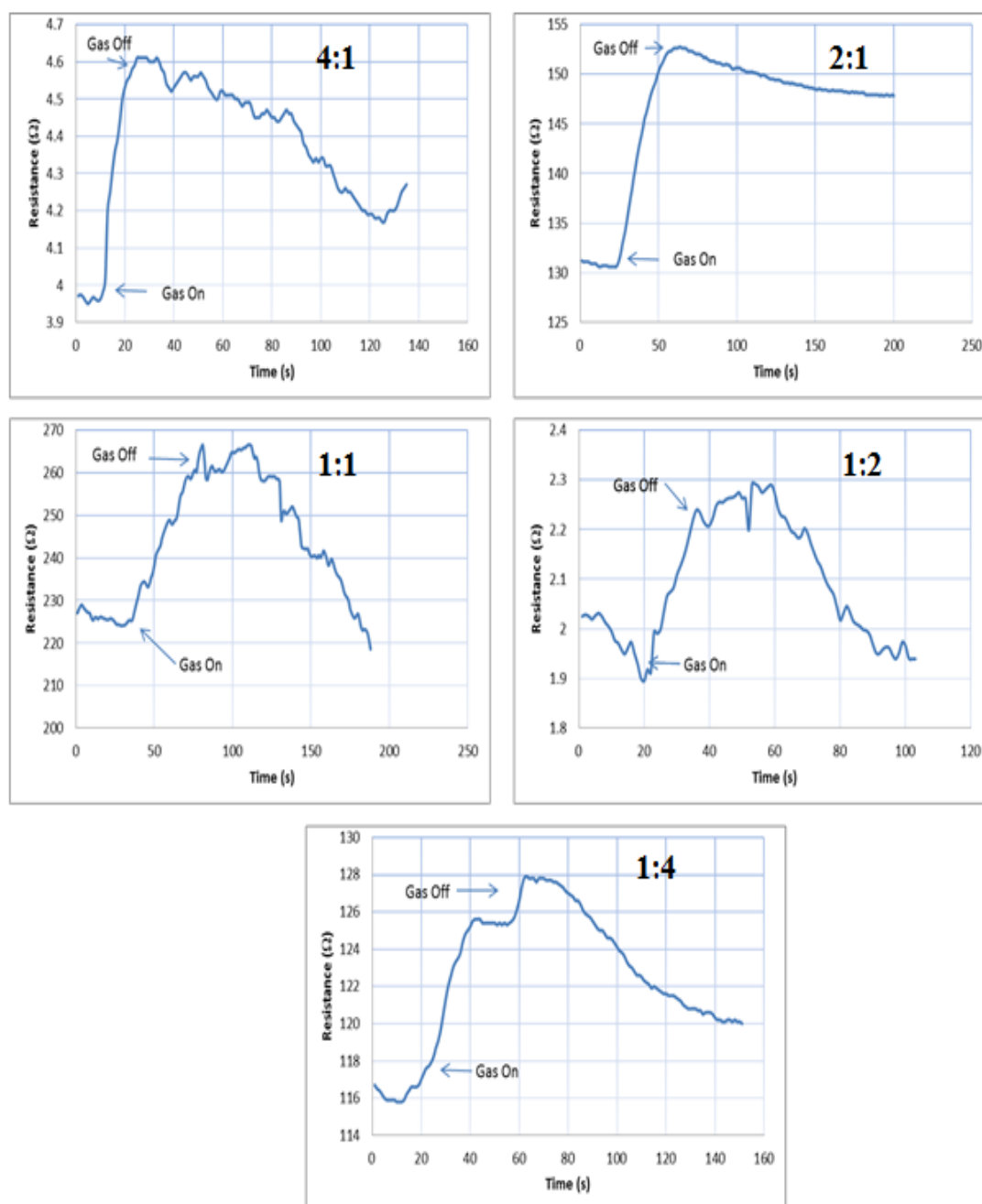
where  $R_a$  and  $R_g$  are the electrical resistance of the film in the air and in the presence of gas, respectively.

Figure-4 shows the variation of sensitivity of TiO<sub>2</sub> thin films to NO<sub>2</sub> gas with the operation temperature. The sensitivity was increasing with increasing the operation temperature until reaching its maximum at 250°C. The behaviors were identical, which means that the TiO<sub>2</sub> thin film gas sensors operate better at elevated temperatures when compared to the lower temperatures (<200°C).



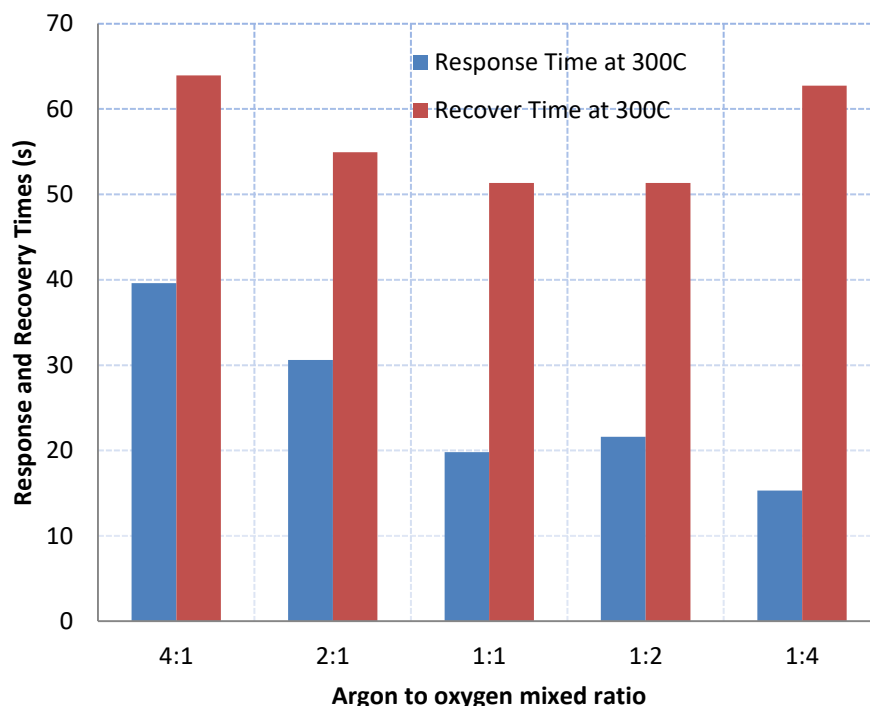
**Figure 4** -The variation of sensitivity of TiO<sub>2</sub> thin films to 3% NO<sub>2</sub> gas with the operation temperature.

In order to introduce the effects of argon to oxygen ratios on the performance of the fabricated gas sensors, the resistance of TiO<sub>2</sub> devices was measured with time, as shown in Fig. 5. This figure shows the mechanism of changing resistance with time prior to exposing the TiO<sub>2</sub> films to 3% NO<sub>2</sub> gas (66ppm). It was allowed to stabilize at an operation temperature for 15 min and the stabilized resistance was taken as  $R_a$  (Gas<sub>on</sub>). After exposing the film to the NO<sub>2</sub> gas, the resistance was decreased and taken as  $R_g$  (Gas<sub>off</sub>). The NO<sub>2</sub> gas species reacts with surface oxygen ions of the film and the oxidation process, leading to an increase in the number of free carriers. Therefore, resistance of the film increases with oxidant gases. The TiO<sub>2</sub> molecular vibration and the gas diffusion speed were increased due to an increase in temperature and hence in gas adsorption. Also, the desorption rate of the sensor surface increases and hence the sensitivity would increase with increasing temperature. The maximum gas sensitivity of TiO<sub>2</sub> films prepared in this work was ~49% at an operation temperature of 250°C.



**Figure 5-**The mechanism of changing resistance with time prior to exposing the TiO<sub>2</sub> films to 3% NO<sub>2</sub> gas .

Also, there are some desired parameters for designing gas sensors, such as response time that is defined as the time taken by the sensor to attain 90% of the maximum change in resistance on the presence of the test gas. Another important parameter is the recovery time, which is defined as the time taken by the sensor to return to 10% of the maximum resistance. The measurements of response time and recovery time were performed at a bias voltage of 6V. The results are shown in Figure- 6, which demonstrates that both parameters decrease with increasing operation temperature in case of using NO<sub>2</sub> gas



**Figure 6-** The response and recovery times as a function of Ar:O<sub>2</sub> mixed preparation condition of the TiO<sub>2</sub> films.

#### 4. Conclusions

DC reactive magneto-sputtering technique was used as a reliable and flexible technique to fabricate TiO<sub>2</sub> thin film gas sensors. The characteristics of the prepared films were highly influenced by the argon to oxygen mixed flow. The structure of TiO<sub>2</sub> films was tetragonal polycrystalline with a preferred orientation in the (110) direction (anatase phase). From optical measurements, the presence of these oscillations is indicative of the good optical quality of the films which were transparent and adherent to the substrate uniformly. The TiO<sub>2</sub> thin film gas sensors operated better at elevated temperatures when compared to the lower temperatures (<200°C). The maximum gas sensitivity of TiO<sub>2</sub> films prepared in this work was ~49% at an operation temperature of 250°C. The response time and recovery time decreased with increasing operation temperature in the case of using NO<sub>2</sub> gas.

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