Study of Utilization of Ferric Oxide Thin Films as a Nitrogen Dioxide Gas Sensor

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Abstract:

In this work, we investigate and synthesis a (NO_2) gas sensing properties of Ferric oxide (Fe_2O_3) thin films are prepared using magnetron DC- sputtering technique, using different thicknesses concurring various deposition times. Each film is tested with different sample temperature (200, 250 and 300) ^oC in order to enhance gas sensitivity. The results reveal that the films sensitivity increases as the film thickness decreases (lower grain size), and the gas sensitivity increases also with the increasing operating temperature.

Keywords: gas sensor, NO_2, DC-sputtering, Fe_2O_3 thin film

1- Introduction:

The gas sensor is an essential device used to detect the environmental contamination produced from industrial plants such as thermal electric power stations, chemical factories and vehicles which are emitting pollutant gases such as Nitride Dioxide (NO_2), Carbon Dioxide (CO_2), Carbon Monoxide (CO), sulfur dioxide (SO_2),…etc.[1]. So that, gas sensors employed in order to detect such pollutants and exhibit its types, quantities and levels of unlicensed emissions according to the universal standard. Diminish the risks and diseases of employee at sites of those establishments and treat the reasons of emission over the allowed levels [2]. There are several researches addressing various materials such as zinc oxide (ZnO)[3], titanium oxide (TiO_2)[4], Indium dioxide (In_2O_3)[5] and SnO_2[6]…etc, as well as Ferric Oxide (Fe_2O_3) thin films[7] used to achieve (NO_2) gas sensors with optimum specifications and sensing efficiency. The choice and preparation of the sensor materials required for making NO_2 gas sensor and the manufacturing method rely upon several parameters of gas sensors[8], the most critical of which are low resistance, availability, large reaction surface, total cost of chemical component, surface modification and micro-structure of sensing layers in order to achieve detector with high sensitivity. The sensor sensitivity can be calculated by the following relations:[9]

$$S = \frac{[\Delta R]}{R_o} \times 100\% = \frac{R_{gas} - R_{air}}{R_{air}} \times 100\% \qquad (1)$$

Where (R) refers the electrical resistance, and the subscript (air) refers to that background which is the initial dry air state and the subscript (gas) refers to the gas which has been under study.

The response of gas sensors is generally regarded as a first order time response. The first step in sensor analysis is to insert air as a reference gas through the sensor to obtain a baseline. Next, the sensor is exposed to the test gas (NO_2), which causes changes in the output signal until the point that the sensor achieves consistent state. Finally, the gas is flushed out of the test chamber utilizing the air flow and the sensor returns back to its baseline, figure (1). The time during which the sensor is exposed to the test gas is referred to as the response time, while the time it spent to return to its baseline with air is called the recovery time [10].

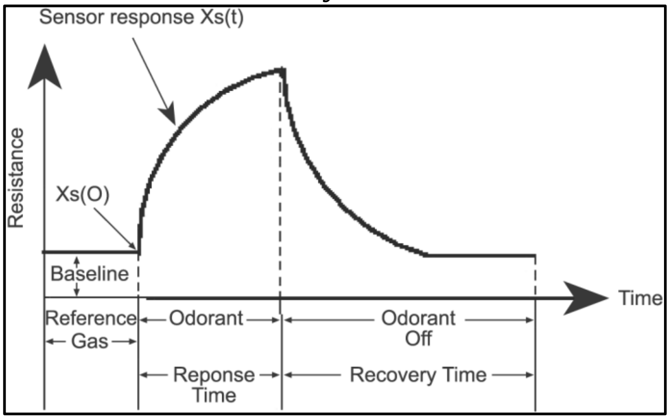


Figure (1): schematic trace of gas sensor response

The response time (τ_{res}) of a gas sensor is assessed by the duration time it takes to accomplish 90% of its peak value of conductance upon introduction of the reducing/oxidizing gas. Likewise, the recovery time (τ_{rec}) is assessed by the duration time it takes to return to within 10% of the original baseline when the flow of reducing or oxidizing gas is expelled. The aim of this study is to utilize different Fe_2O_3 thin film thickness effects as a NO_2 gas sensor with high efficiency and investigate the optimum operating temperature.

2- The Experiment:

The deposition procedure for Fe_2O_3 thin film preparation utilizing magnetron DC-Sputtering technique with various deposition time, and the plasma deposition system are explained in detail in a previous work [11], briefly, the diameter of the target is 50 mm, approximately 3mm thick and the distance between the electrodes of about 5cm. the Ferric Oxide are made in pullet as a target cathode of 99.99% purity. The sputtering action is initiated by evaluating the chamber pressure to a lower than (1×10^{-5} mbar), and injected with argon gas which is being a noble gas that reacts with neither target nor mutual specimen. The DC- power supply is then switched ON in order to establish the required current and cathode bias voltage. Surface finishing and nature of the glass substrate used for deposition is very important since it influences the properties of the film enormously, so that the substrate was ultrasonically cleaned with acetone and air blown to dry before inserting it inside the chamber. The target was sputtered with (Ar^+) plasma at different deposition time so as to achieve different film thickness as shown in table (1).

Table (1): sample thickness and grain size as a function of deposition time as achieved from the previous work.[11]

P=8×10^{-2} mbar, I=10 A, V=2kV			
sample	**Deposition time (hour)**	**Thickness (nm)**	**Grain size (nm)**
1	1	102.69	61
2	1.5	111.1	67
3	2	114.87	97
4	3	115.54	120

3- Gas Sensor Apparatus and Materials:

The sensitivity parameter measurements essentially are given from the response time and recovery time of the prepared Fe_2O_3 gas sensor; reasonable setup is set up for this reason. Figure (2) indicates the demonstrated gas sensor testing framework, which it comprises of: A test chamber made of stainless steel material and cylindrical shape of (6594 cc) effective volume (30 cm diameter x 35 cm height); an inlet port where established in order to enable the test gas (NO_2) to flow in, and a valve to permit the air to flow after evacuation. The heater, thermocouple and sensor electrodes, all are connected to electrodes by using a multi-pin feed through located at the base of the chamber.

In order to control the operating temperature of the sensor, a heater comprises of hot plate and a thermocouple (k-type) inside the chamber. A digital multimeter (Uni-T UT81B) are interfaced with a PC laptop are used to enroll the current data acquired from the sensor during the gas flow. The air and/or the test gas is fed through a tube upon the sensor inside the chamber utilizing a flow-meter and needle valve arrangement, figure (2).

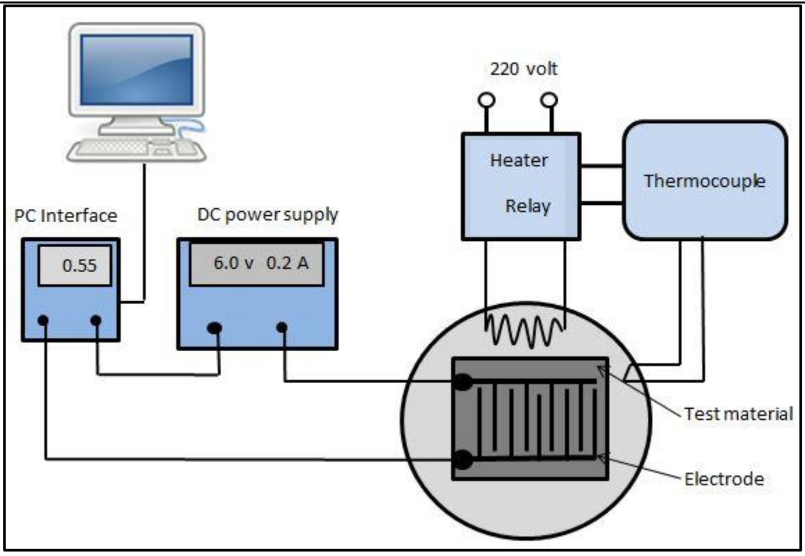


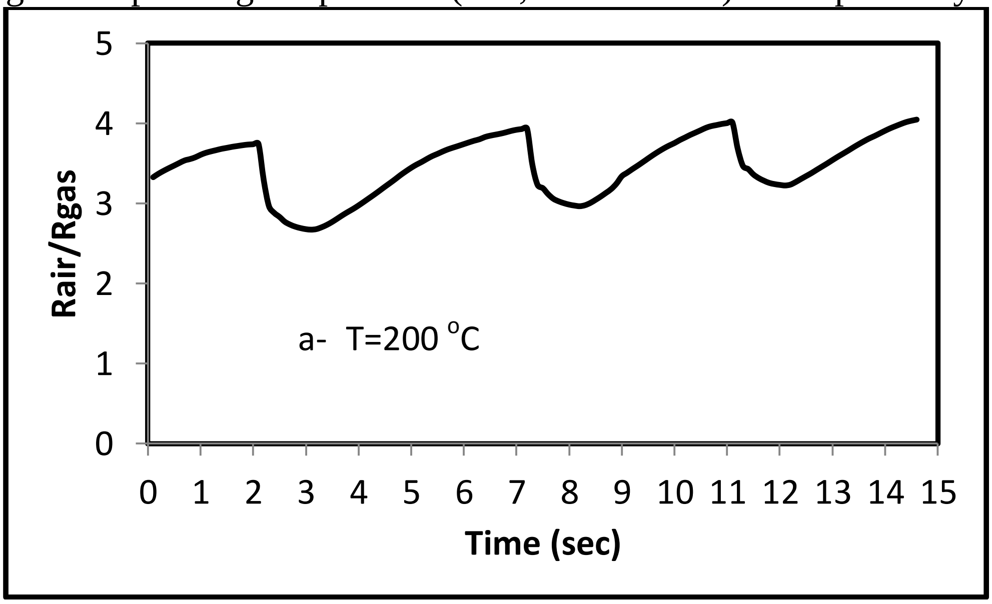
Figure (2): scheme of the used gas sensor testing setup.

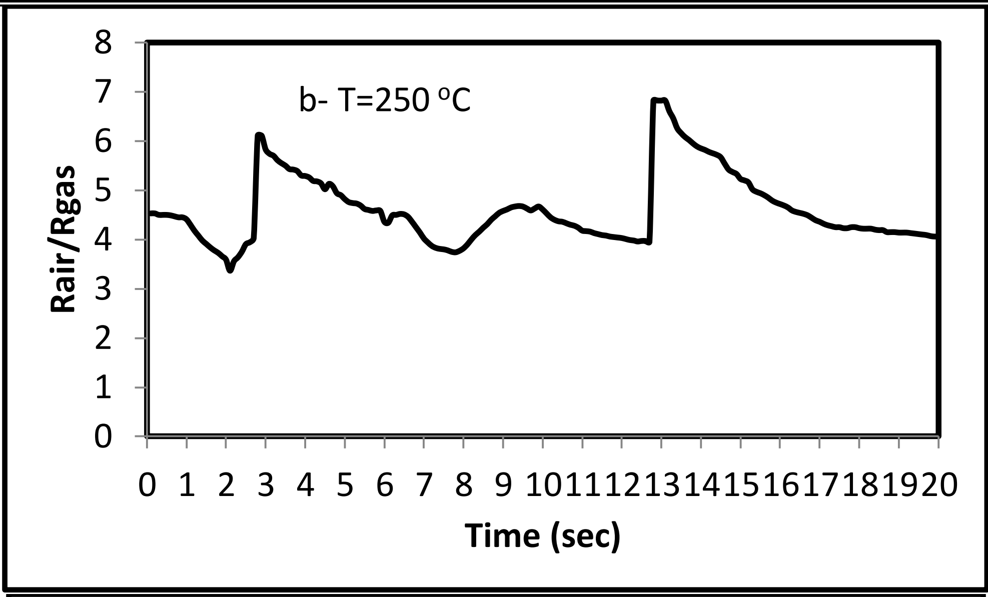
4- Results and discussions:

The structural analysis of Fe_2O_3 thin films reveals a well rhombohedra structure. And the surface morphology study reveals that the surfaces of the films becomes rougher as the film thickness increases, i.e. a thicker films leads to a larger grain size, as in our previous study[11].

The sensitivity of Fe_2O_3 thin films with different thickness for NO_2 gas has been investigated. The testing gas were fed into the chamber and recording the change in resistance values of samples with time, the concentration of NO_2 gas was closed to 6 ppm.

From the gas sensing measurements, in general, it is obvious that all Fe_2O_3 thin films obey the role of increasing in film resistivity as exposed to oxidizing NO_2 gas. The figure (3) shows sensor response at 6 volt bias voltage and operating temperature (200, 250 and 300) ^oC respectively.





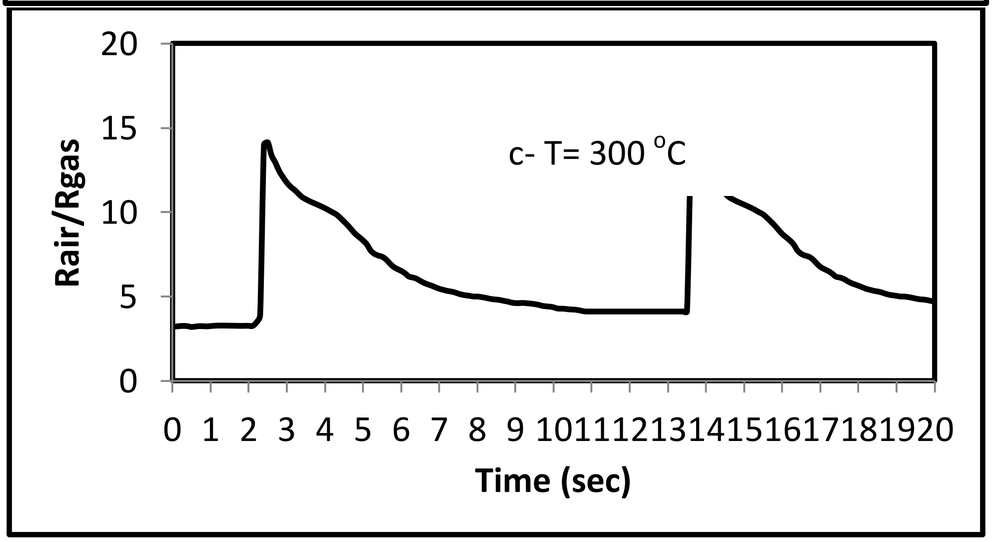


Figure (3): The gas sensor (of t_1=102.69 nm) response at 6 volt bias voltage and operating temperature ((a) 200, 250 (b) and 300 (c)) ^oC.

The effects of the operating temperature on the film sensitivity were examined. The films are initially tested to confirm its semiconducting behavior. The sensors are located on a heater base and their resistances are measured as the sample temperature values varies from (200-300) ^oC in a dry air environment. The figure (4) demonstrates the variation of sensitivity as a function of operating temperature of the Fe_2O_3 films deposited with various thicknesses. The temperature variation reveals that the resistance of the films diminishes as the temperature increases, which will confirm the typical negative temperature Coefficient of resistance (NTCR) due to thermally-excited charge carriers in semiconductors. From table (1), as well as film thickness increases, the grain size increases too, so that, the sensitivity of sample increases with decreasing sample grain size.

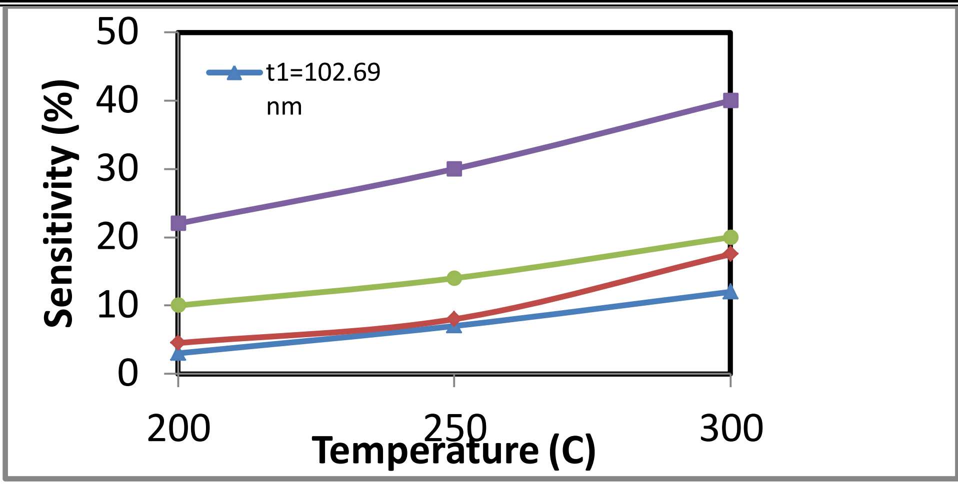


Figure (4): the sensitivity variation with operating temperature for each sample thickness

Figure (5) shows the impact of the grain size on the sensitivity at constant operating temperature (250)^{o}C. This figure reveals that the reduction of the film thickness, i.e. decrease in particle size led to increase in the sensitivity value. This is attributed to the possible reason of increasing the surface to volume ratio, and the high porosity which is generally preferred for the gas sensing applications. The reduction in the grain size allows the space charge to cover large volume of the grain boundaries giving large area for adsorption O^{-},O^{-2}. Thus an extensive variation in the barrier and resistance can improve the reactivity at low temperature. Moreover, the surface states density increment with reduction in the particle size, or the density of surface states can help in lowering the operating temperature.

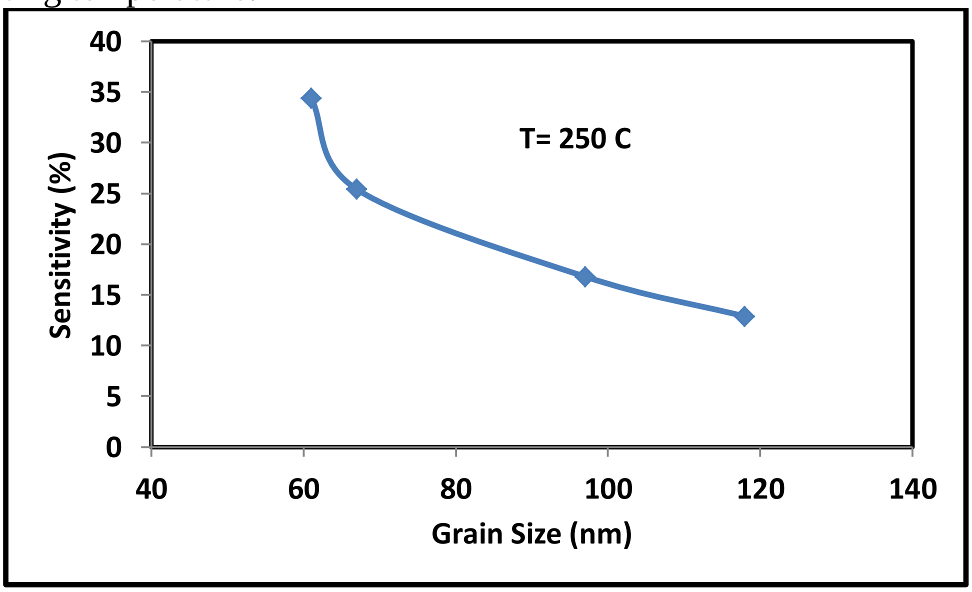


Figure (5): The sensitivity vs. sample grain size at operating temperature T = 250 ^{o}C.

In a similar manner, the recovery time (when the target gas is pulled out) is also measured. The response and recovery times of the sensor as a function of testing gas (ON/OFF) are illustrated in table (2). Both response and recovery times of the sensors have the same behavior, that is, as the operating temperature increases, both of them were decreased with increasing operating temperature at which the most minimal response and recovery times of (0.9)&(5) sec respectively (at sample of minimum thickness and grain size with operating temperature T=300 ^{o}C) are observed.

Table (2): the response and the recovery time variation with operating temperature

sample	200 ^{o}C		250 ^{o}C		300 ^{o}C	
	Response Time (sec)	**Recovery Time (sec)**	**Response Time (sec)**	**Recovery Time (sec)**	**Response Time (sec)**	**Recovery Time (sec)**
1	4	1.6	1.2	6	0.9	5
2	5	8	6	7.5	0.2	7
3	5.6	8.3	5.7	7	1.3	7.2
4	5.7	8.5	5.9	6.9	1.8	7.5

5- Conclusions:

It is obvious that the iron oxide thin film has proved its usefulness, and it is recommended for use in the detection of nitrogen oxides gas. The results showed that the sensitivity increases and the response time decreases as the particle size of the film is becoming smaller. In addition, its characteristics improved when operating in high temperature environment.

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دراسة وإستخدام أغشية أوكسيد الحديد كمتحسس لغاز ثاني أوكسيد النايتروجين

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الملخص:

في هذا البحث تم دراسة خصائص التحسسية لغاز ثنائي أوكسيد الناتروجين (NO_2) من أغشية أوكسيد الحديد النانوية (Fe_2O_3) المحضرة بطريقة الترذيذ الماكنتروني بتيار مستمر (Magnetron DC-Sputtering) على قاعدة زجاجية وبأسماك مختلفة أعتمادا على ظروف الترسيب. تم قياس تحسسية هذه الاغشية لدرجات حرارة مختلفة (200, 250, 300 ^{o}C). وقد بينت نتائج هذه الدراسة زيادة التحسسية الغازية كلما كان الغشاء أقل سمكاً (حجم حبيبي أصغر)، وكذلك زيادة التحسسية الغازية بزيادة درجة حرارة التشغيل.

الكلمات المفتاحية: متحسس الغازات، NO_2، الترذيذ بالتيار المستمر، أغشية أوكسيد الحديد Fe_2O_3.