Enhanced hydrogen gas sensitivity employing sputtered deposited NiO thin films

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Abstract

In this work, nickel oxide thin films have been successfully deposited on glass substrates by sputtering technique at different temperatures, and explored as a fast response sensor to hydrogen reducing gas.

The nickel oxide sensor exhibits an increase of the conductance upon exposure to hydrogen gas of various concentrations at different operating temperatures. Pure sputtered NiO sample showed excellent sensitivity S of 1488% to hydrogen gas at the optimum H_2: air concentration of 3.75%.

The variation of the operating temperature of the film has led to a significant change in the sensitivity of the sensor with an ideal operating temperature of about 275℃ after which it began to saturate with increasing temperature and test was terminated. The variation of NiO sensor sample with H_2: air gas ratio concentration showed linear relationship up to 3% after which saturation of S occurred.

Key words

Nickel oxide, Sputtering, Thin film, Sensitivity.

Article info.

Received: Feb. 2016
Accepted: May. 2016
Published: Sep. 2016

تحسسية محسنه لغاز الهيدروجين باستخدام اغشية اوكسيد النيكل الرقيقة المرسبة بالترذيذ

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الخلاصة

في هذا البحث، تم تحضير اغشية لاوكسيد النيكل على قواعد زجاجية باستخدام طريقة الترذيذ وتم تفحصها كمتحسس سريع الاستجابة لغاز الهيدروجين المحتزل عند درجات حرارية مختلفة.

ولقد اظهر متحسس اوكسيد النيكل زيادة في التوصيلية بتعرضه لغاز الهيدروجين عند تراكيز و درجات حرارة مختلفة. اظهرالنموذج النقي لاوكسيد النيكل تحسسية فائقة مقدارها 1488% لغاز الهيدروجين عند تركيز 3.75%.

ان تغير درجات الحرارة لهذا المتحسس ادى الى تغير ملحوظ في الحساسية حيث كانت درجة الحرارة المثالية للاشتغال حوالي 275 درجة مئوية بعدها بدات الحساسية بالتشبع بزيادة درجات الحرارة. ان تغير حساسية المتحسس مع نسبة تركيز غاز الهيدروجين في الهواء اظهرت علاقة خطية حتى تركيز 3% وبعدها تحدث حالة اشباع للتحسسية.

Introduction

The ever growing human society continues to impose more and more complexities and severe life threats especially those related to the public health. To overcome such problems, scientists always try to mimic "simulate" human senses in a step to lessen the effects of these threats. Both liquids and gases are chemical materials of special important. Chemical gas sensors simulate the human nose function. Principally, a gas sensor is gas-dependent resistor, i.e., its resistance R changes in respond to a specific gas concentration present in the nearly environment. Although there are different types of gas resistive

sensing elements, those based on semiconducting metal oxide (SMO) are at the forefront. The current research demonstrates the sensing effect of Nickel Oxide thin film structures exposed to reducing hydrogen gas at various concentration and temperatures.

Nickel oxide (NiO) is an attractive material due to its excellent chemical stability, as well as optical, electrical and magnetic properties. It has been used as antiferromagetic material [1], material for electrochromic display devices [2] and functional layer material for chemical sensors [3]. Furthermore, it is a p-type semiconductor conductivity films due to its wide band-gap energy ranging from (3.6 to 4.0) eV [4].

Among the different methods currently used to obtain NiO metal oxide of superior quality, sputtering was adopted in the current study. The crystallite size as calculated in accordance with Debye-Scherer formula is given bellow [5].

$$D = \frac{k\lambda}{\beta cos\theta} \qquad (1)$$

where k=0.89, λ is the wavelength of the radiation being equal to 1.504$A°$, β is the full width at half maximum (FWHM) in radian and θ is the Bragg diffraction angle in degree as obtained from 2θ values corresponding to maximum intensity peak in the XRD pattern.

The performance of the annealed NiO dements upon exposure to a hydrogen gas was tested at numerous affecting characterization parameters including gas concentration, temperature, rise and recovery times.

The response of a sensor upon the introduction of a particular gas species is called the sensitivity(S). The most general definition of sensitivity is applied to solid –state chemi-resistive gas sensors is a change in the electrical resistance (or conductance) relative to the initial state upon exposure to a reducing or oxidizing gas component. The sensitivity depends on many factors including the background gas composition, relative humidity level, sensor temperature, oxide microstructure, film thickness and gas exposure time. One of the most common methods is to report(S) the ratio of the electrical resistance in air (R_{AIR}) to the resistance measured when a gas is introduced(R_{GAS}) as given in Eq. (2) [6]:

$$S = \frac{\mathrm{R_{AIR}}}{R_{GAS}} = \frac{G_{GAS}}{G_{AIR}} \qquad (2)$$

where R is the electrical resistance and G is the electrical conductance and the subscript "AIR" indicates that background is the initial dry air state and the subscript "GAS" indicates the analytic gas has been introduced.

Another common approach to report S is shown in Eq. (3) and (4) [7]

$$S=\frac{\Delta R}{R^{\circ}} \times 100\% = \frac{R_{GAS}-R_{AIR}}{R_{AIR}} \times 100\% \qquad (3)$$

$$S=\frac{\Delta G}{G^{\circ}} \times 100\% = \frac{G_{GAS}-G_{AIR}}{G_{GAS}} \times 100\% \qquad (4)$$

The response time(τ_{res}) of a gas sensor is defined as the time it takes the sensor to reach 90% of maximum/minimum value of conductance upon introduction of the reducing/oxidizing gas [8]. Similarly, the recovery time (τ_{rec}) is defined as the time required recovering within 10% of the original baseline when the flow of reducing or oxidizing gas is removed.

Experimental procedure

Thin NiO film were deposited on glass substrate by radio frequency magnetron sputtering from NiO target in Ar plasma using RF power of 140W at ambient 100 ℃ substrate temperatures. The distance between the

target and substrate was 25 cm. The chamber was evacuated to an initial pressure of 4×10^{-4} mbar. Sputtering deposition was performed of Ar gas pressure of 2×10^{-2} mbar.

NiO Hydrogen sensing measurement

The sensing characteristics for the prepared nickel oxide film were explored in hydrogen ambient. For this purpose the testing unit, illustrated in Fig. 1.was consisting mainly of a vacuum-tight stainless steel cylindrical test chamber of diameter 163mm and of height 200mm with the bottom base made removable and of O-ring sealed. The effective volume of the chamber is 4173cc; it has an inlet for allowing the test gas to flow in and an air admittance valve to allow atmospheric air after evacuation. Another third port is provided for vacuum gauge connection a multi-pin feed through at the base of the chamber allows the electrical connections to be established to the sensor and the heater assembly. The heater assembly consists of hot plate and a k-type thermocouple inside the chamber in order to control the operating temperature of the sensor. The thermocouple senses the temperature at the surface of the film exposed to the analyte gas. The PC interfaced multi meter, of type UNI-TUT81B, was used to register the variation of the sensor conductance (reciprocal of resistance) exposed to predetermined air-hydrogen gas ratio mixing. The chamber can be evacuated using a rotary pump to a rough vacuum off. A gas mixing manifold was incorporated to control the mixing ratios of the test and carrier gases prior to being injected into the test chamber. The mixing gas manifold is fed by zero air and test gas through a flow meter and valve arrangement. This arrangement of mixing scheme was done to ensure that the mixture entering the test chamber is premixed thereby giving the real sensitivity.

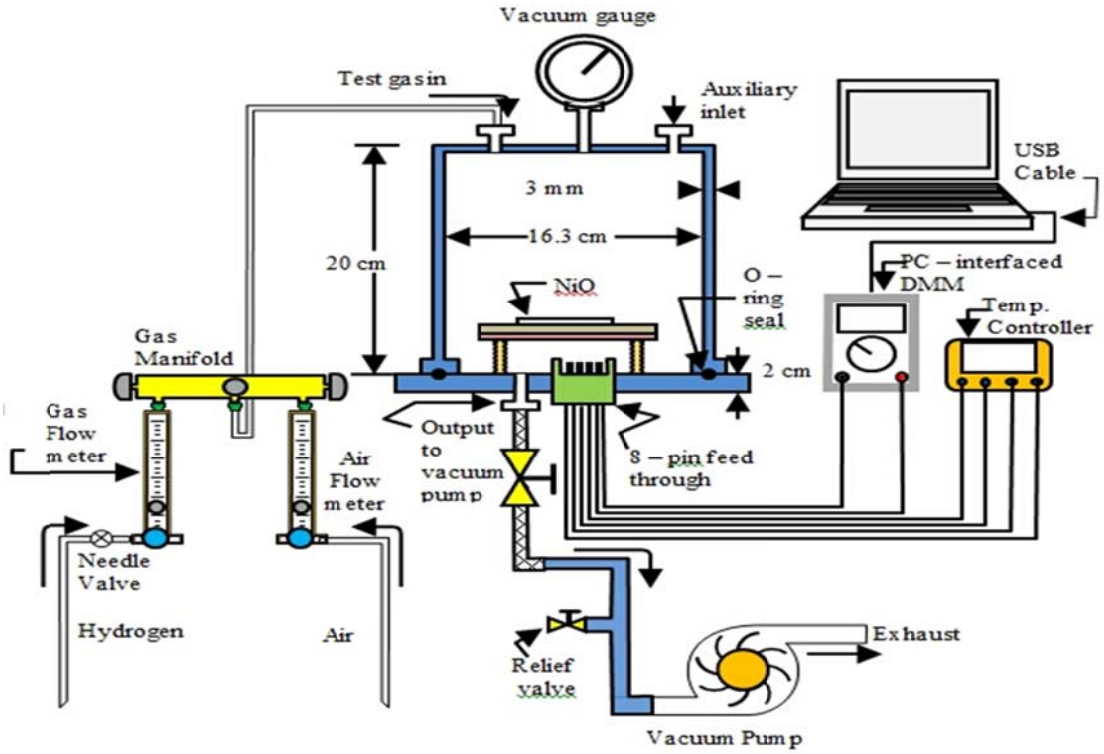

Fig.1: Gas sensor testing system.

Results and discussions

X-Ray diffraction studies

The sputtered Nickel Oxide thin film was characterized by pattern x-ray diffraction and the result is presented in Fig. 2 after annealing at 400 ℃. The XRD pattern exhibits prominent peaks at 37, 43 and 64 degrees, respectively. The crystallite size as calculated in accordance with Eq.(1) which is summarized in Table 1.

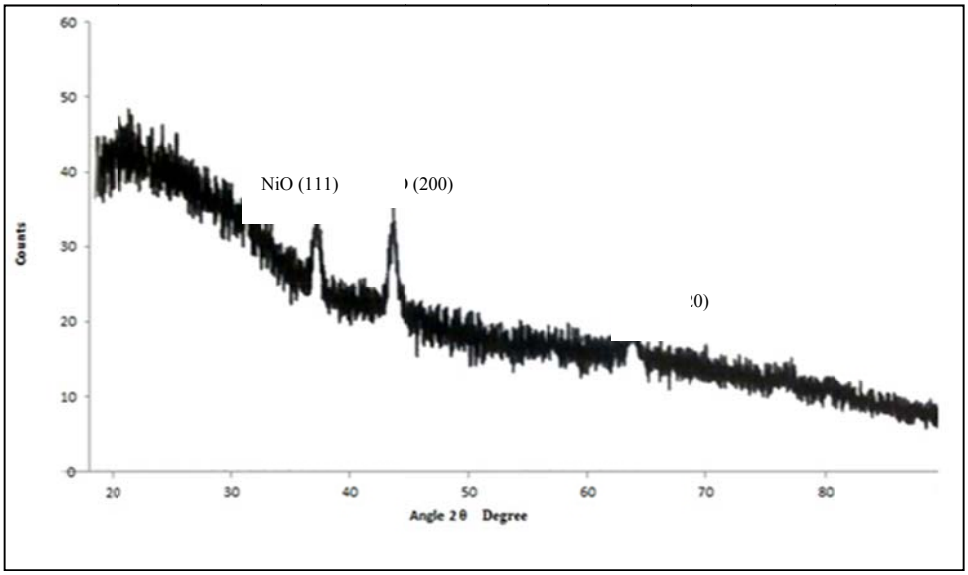

Fig. 2: X-ray diffraction pattern of sputtered NiO film annealed at 400 ℃.

Table1: Grain size data.

Peak no.	2Theta (deg)	FWHM (deg)	Crystallite size D (^oA)	Dislocation ($^oA^{-1}$)	Strain (ϵ)
1	37	3.1	26.088	0.03833	0.040427
2	44	3.2	25.849	0.03868	0.034558
3	64	1.9	47.595	0.02101	0.0132677

(AFM) Results

The 3D AFM micrographs of Nickel oxide (NiO) thin film are shown in Fig. 3 and 4. The size of the scanned area was (1591× 1584) nm^2. AFM results shows that the surface of pure NiO film is relatively smooth and regular and consists of small cluster with diameters, in the range of 105.15nm, distributed over the scanned area and the average roughness of the surface was 2.68nm, roughness depth 8.51nm. From the Fig.3, some grains merge and take the cylindrical shape.

From XRD measurements, the (D) refers to the crystallite size which is so much lower than the value estimated from the AFM that represents the grain size.

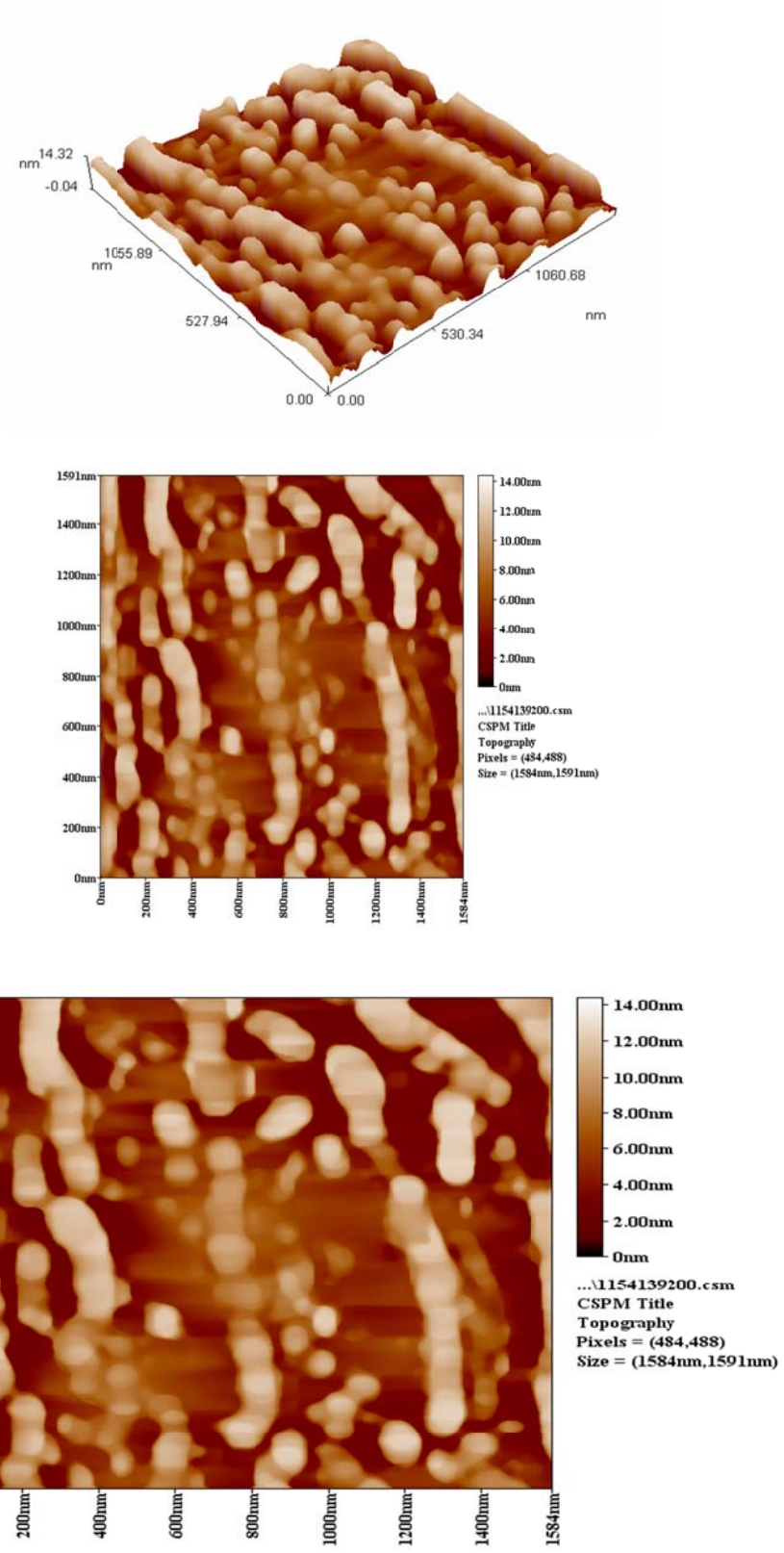

Fig. 3: 3D AFM surface morphology graphs of sputtered NiO sample.

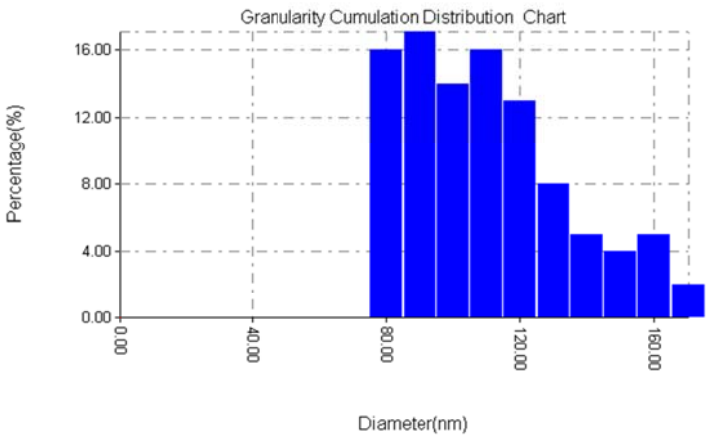

Fig. 4: Topographic structures in 3D view for NiO pure.

Sensing characteristics of pure NiO towards hydrogen gas

Fig. 5 (a and b) shows two sensing pulses at 30/80 and 60/80 H_2: air concentration, respectively.

Furthermore, the sensing rise and recovery times for the such two pulses are (25.25s, 18.7s) and (140.5s, 315.8s), respectively. These values were obtained according to the following: $\tau_{rise} = t_2 - t_1 = t_2(0.9\Delta I) - t_1(Baseline)$

where "Baseline" refers to the time instant at which the gas is introduced (H_2 ON).

$\tau_{rec} = t_2 - t_1 = t_2(0.9\Delta I) - t_1(H_2 OFF)$

as can be clearly noticed from the Fig.5a, there is a sudden reduction in the measured current as H_2 gas is introduced (H_2 ON) referring to an increase in film's resistance Fig. 5b.

This effect is observed in the exposed of temperature area elevated to (275℃) [9], where the oxygen is absorbed at surface of the metal oxide that enables an electron trapping. The charge carrier density is reduced which leads to an increase in the resistance of the Nickel oxide sample.

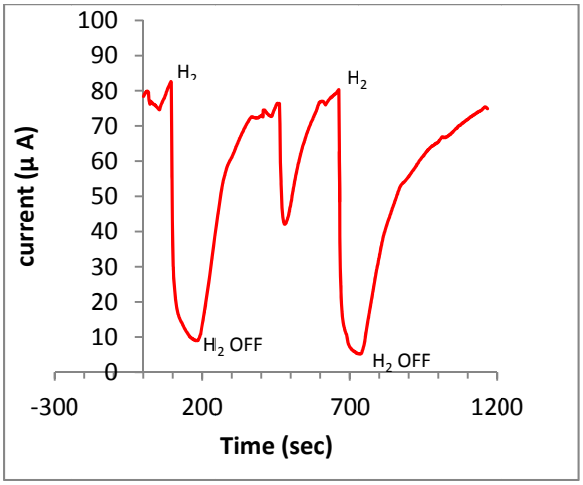

Fig. 5a: Sensing behavior of pure NiO sample at 4.8V bias voltage and 275 ℃ to traces of H_2 reducing gas mixing ratio.

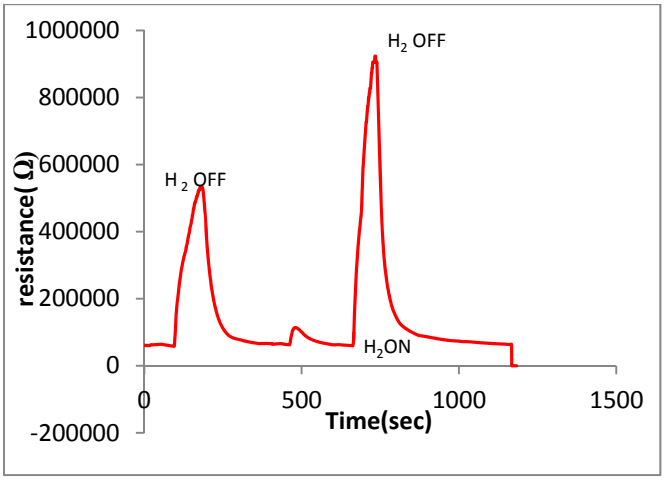

Fig. 5b: The variation of resistance of NiO sample at 4.8V bias voltage and 275 ℃ to traces of H_2 gas mixing ratios.

Fig. 6 shows the change of sensor sensitivity S, as taken by using Eq. (3) with gas mixing ratio C. The sensitivity of the sensor is linear in the low gas concentration region up to 3% after that the sensitivity tends to saturate in the high gas concentration. One applicable use of such behavior is as an actuator by enabling it to detect different concentrations of combustible gases as shown in the Fig. 6 [10].

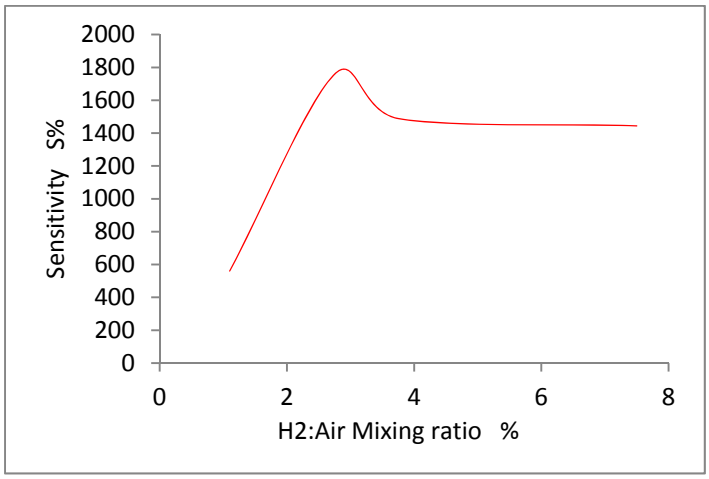

Fig. 6: The sensitivity of as sputtered NiO sensor on exposure to different hydrogen gas mixing ratios.

Operation temperature of the sensor

The high temperature required for the sensor operation (400 ℃) is the basic disadvantage of Nickel oxide gas sensors.

As a result, the effect of the operation temperature on the thin film sensitivity was studied.

Fig. 7 shows the variation of sensitivity with the operating temperature. The sensitivity goes up as the operating temperature increases, reaching a maximum value at ~300℃ and it reaches saturation with further going up in the operating temperature. The optimum operating temperature obtained was 275 ℃ which are recommended for high sensitivity.

In addition to sensitivity, response time is temperature dependent because the chemical kinetics controlling the solid-gas interface reaction is temperature dependent [11].

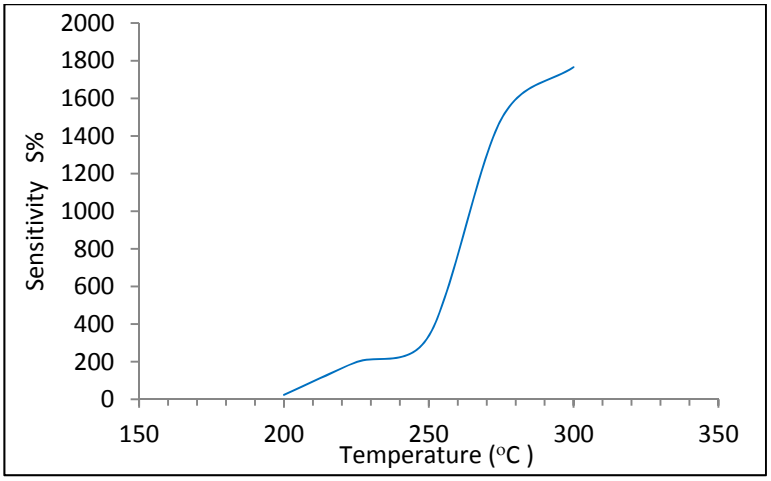

Fig. 7: The variation of sensitivity with the operating temperature of the Nickel Oxide gas sensor.

Conclusions

In this study, Nickel oxide thin film was successfully deposited on glass substrate at 400 ℃ prepared by sputtering technique, some conclusions can be summarized:

1-Nickel oxide thin film sensors demonstrated high sensitivity to hydrogen gas.

2-For sputtered NiO element to work as an hydrogen gas sensor, it is advisable to operate it at temperature of ~300℃. Thus, the variation of the operating temperature of the prepared samples led to a significant change in the sensitivity of the sensor with an ideal operating temperature of about 275℃. After which sensor sensitivity decreased.

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