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Room temperature hydrogen gas sensor based on nanocrystalline SnO_2 thin film using sol–gel spin coating technique

Imad H. Kadhim[1,2] · H. Abu Hassan[1]

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Abstract High-quality nanocrystalline (NC) SnO_2 thin film was grown on SiO_2/Si substrate by sol–gel spin coating technique at low temperature. X-ray diffraction and field emission scanning electron microscopy results observed the high quality of the produced NC SnO_2 thin film. A metal–semiconductor-metal (MSM) H_2 gas sensor was fabricated utilizing palladium (Pd) metal and NC SnO_2 thin film. Hydrogen (H_2) sensing capabilities of the NC SnO_2 thin film were examined at room temperature (RT), and the sensitivity was 600 % in the presence of 1000 ppm of H_2. The sensing measurements for H_2 gas at different temperatures (RT to 125 °C) were repeatable for over 50 min. The sensor showed a sensitivity of 1950 % at 125 °C upon exposure to 1000 ppm of H_2. A significant variation in the sensitivity of the NC SnO_2 thin film sensor was noticed at different concentrations of H_2 at different operating temperatures. These high sensitivities are attributed to the increase in adsorption/desorption of gas molecules, which were achieved by increasing the porosity of the NC SnO_2 thin film surface by adding glycerin to the sol solution. The high sensitivity of this H_2 gas sensor at RT indicated that it has the capability to be used as a portable RT gas sensor.

✉ Imad H. Kadhim
imad.usm.iq@gmail.com

[1] Nano-Optoelectronics Research and Technology Laboratory, School of Physics, Universiti Sains Malaysia, 11800 Penang, Penang, Malaysia

[2] Ministry of Education, Baghdad, Iraq

1 Introduction

The electronic-nose for sensing toxic and inflammable gases has become very necessary due to the wide usage of these gases [1]. In the current global economy, hydrogen gas (H_2) has become a main subject for the development of new sustainability due to its being considered a more efficient and clean energy source. As a result, it is used instead of a dependence on oil in automobiles, fuel cells, aircraft, and chemical industries applications [2, 3].

In the past decades, different kinds of gas sensors have been developed to detect H_2 gas at different sensing temperatures [4]. A solid-state gas sensor based on metal oxide wide band gap semiconductor materials emerged with high robustness and reliability for gas detection. Tin dioxide SnO_2 is the most interesting metal oxide semiconductor due to its large energy gap (3.6 eV) at 300 K [5]. Gas sensors that are operated at room temperature (RT) have many benefits, such as low power consumption [6], a long lifetime [7] and safe use in flammable environments [8]. Therefore, researchers have focused on developing gas sensor materials that employ functions at RT. However, the development of the sensitivity and selectivity of gas sensors is still a challenge in terms of their practical applications [9]. One of these challenges is the doping process, where different metals, including palladium (Pd) [10], Copper (Cu) [11] and antimony (Sb) [12], are doped into SnO_2. This process is used to enhance the sensing-performance of a gas sensor. But doping into thin films can only be achieved via long and complicated preparation steps, which contribute towards the increase in cost of the sensing device [13]. Previous studies have attempted to increase the sensitivity of devices without doping. Cantalinia et al. [14] showed that the porosity in the thin film allows for increasing the adsorption and desorption of gas molecules

on the surface of a device. Abdullah et al. [15] noted that the sensitivity increased at high operating temperatures because of an increase in the adsorption/desorption of gas molecules.

The sol–gel spin coating technique is widely used to synthesize SnO_2 thin film, because of its many advantages as compared with other techniques, advantages such as ease of process, low cost and low reaction temperature [16]. Kadhim et al. [5] showed that the addition of glycerin to the sol solution when preparing SnO_2 thin films using the sol–gel spin coating technique contributes to the increase in porosity and elimination of cracks for thin films. Usually, the gas sensing measurements were conducted at high operating temperature [17]. Hamaguchi et al. [18] reported that H_2 gas sensing response and recovery times became much longer whenever the ambient temperature is decreased.

In this paper, a simple technique was used to synthesize NC SnO_2 thin film on an insulating silicon dioxide (SiO_2) layer of approximately 1 μm thick formed on silicon (Si) substrate. The main goal is to take advantage of the high porosity that is produced in NC SnO_2 thin film by adding glycerin to the sol solution in order to fabricate a NC SnO_2 thin film sensor, which has high robustness and reliability for the detection of H_2 gas at different concentrations with high performance at RT.

2 Experimental details

A p-type Si (100) wafer (10 mm × 10 mm) was cleaned via the Radio Corporation of America (RCA) technique and heated to 900 °C for 7 h by a tube furnace to obtain a 1 μm thick layer of SiO_2 by wet air flow. The NC SnO_2 thin film was synthesized via the sol–gel spin coating technique [5, 16]. The sol solution was synthesized by dissolving 0.1 M of tin (II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$) into 70 mL of pure ethanol (C_2H_5OH). Furthermore, glycerin ($C_3H_8O_3$) was added at a volume ratio of (1:12) to the sol solution for the elimination of cracks and enhancement of film porosity; then, the sol solution was put in a closed beaker [5]. The mixture in the beaker was stirred using a magnetic stirrer for 3 h and maintained at 70 °C for 8 h. The preparation of the sol solution was completed at RT for the remainder of the 24 h. Then, the resulted sol solution was spin-coated on a SiO_2/Si substrate at a rotation speed of 3000 rpm for 30 s. Afterward the as-grown film was oven-dried at 100 °C for 10 min. In order to obtain a high thickness, the spin coating and drying process were repeated 10 times for the sample. Furthermore, to realize the crystallization of SnO_2, the thin film was annealed at 500 °C in air for 2 h.

The fabrication of the metal–semiconductor-metal (MSM) device was implemented by radio frequency (RF) sputtering of a Pd grid by a shadow mask on top of the NC SnO_2 thin film. NC SnO_2 thin film characterization was achieved using X-ray diffraction analysis (XRD) PANalytical X' pert Pro MRD equipped with a Cu Kα radiation of ($\lambda = 0.154060$ nm), and field-emission scanning electron microscopy (FESEM) (Leo-Supra 50VP, Carl Zeiss, Germany). Gas sensing was performed using a homebuilt gas chamber manufactured from an acrylic plastic box, and the heat was supplied using a small ceramic heater that was connected to a thermocouple temperature controller. The current source (2400 Source Meter, Keithley, Cleveland, OH, USA) is connected to a PC, which was utilized for measuring the electrical current passing through the sensing device, which was set to a bias voltage of 0.5 V. Furthermore, the total flow H_2 gas rate was kept constant at 1000 sccm during all sensing measurements with each pulse equal to 5 min.

3 Results and discussion

3.1 Characterization of the nanocrystalline SnO_2 thin film

The XRD patterns indicated different reflection peaks that agree with standard bulk SnO_2 having a tetragonal rutile structure (JCPDS card No. 041-1445) with lattice constants of $a = 4.737$ Å and $c = 3.185$ Å [5]. Several diffraction peaks related to the (110), (101), (200), and (211) planes of the NC SnO_2 thin film can be observed in Fig. 1. Moreover, the other peak related to the Si substrate emerged at $2\theta = 69.2°$. Small nanoparticles can be observed in polycrystalline thin film with uniform distribution the SnO_2 thin

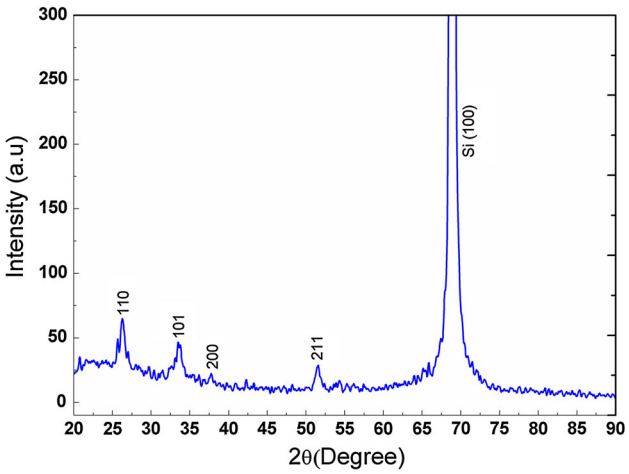

Fig. 1 XRD patterns of NC SnO_2 thin film annealed at 500 °C

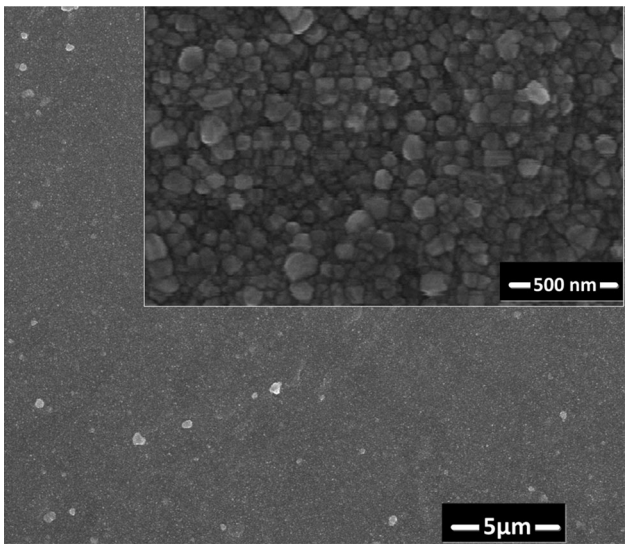

Fig. 2 FESEM images of NC SnO_2 thin film annealed at 500 °C

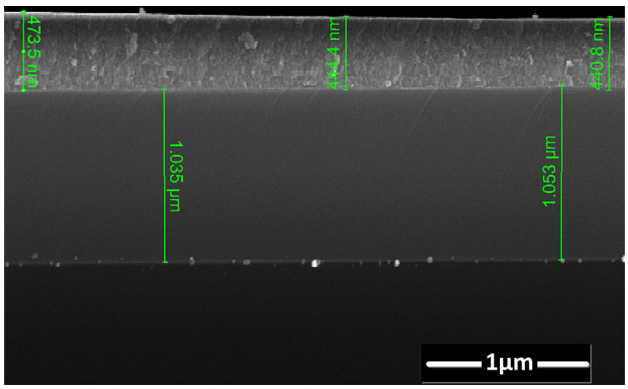

Fig. 3 Cross-section FESEM image for as-grown SnO_2 thin film synthesized from sol solution at 70 °C for 8 h aging heat time

film as shown in Fig. 2. This occurred due to the annealing of the thin film at 500 °C, which results in the improvement of the crystallinity [19, 20].

The crystallite size was calculated using the Debye–Sheerer formula Eq. (1) [5].

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where β the full width at half-maximum (FWHM) of (110) the main peak, θ presented Bragg angle. In addition, the lattice constants (a, c) were calculated using Eq. (2).

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (2)$$

where d: is the lattice plane spacing of NC SnO_2 that obtained from XRD measurement, h, k, and l: are the Miller indices. The strains (ε_a, ε_z) of NC SnO_2 was calculated along the (a -axis and c -axis) using Eq. (3) [21] as follows:

$$\varepsilon_z(\%) = \frac{c - c_o}{c_o} \times 100 \quad (3)$$

where c: is the lattice constant of the strained atoms, and c_o: is the standard lattice constant of the crystalline material (the same measurement for ε_a). The values for lattice constants, crystallite size, and strain are memorized in Table 1.

The obtained strains were low-positive values (0.2714, 0.1679 %) that indicate to the tensile strain [22], and the high quality of the examined film.

Figure 3 shows that the average thickness of the as-grown SnO_2 thin film was approximately 450 nm. In addition, approximately 1 µm thick layer of SiO_2 is shown on the top of the silicon substrate. This high thickness of the thin film is attributed to the high viscosity of the sol solution which was generated by the 8 h aging heat time [23].

3.2 Hydrogen sensing characterization

The schematic diagram of the NC SnO_2 thin film gas sensor is shown in Fig. 4, which shows the Pd finger contacts deposited on the top surface of the NC SnO_2 thin film. The Pd mask includes two electrodes; each electrode contains four fingers, the distance between every two neighbouring fingers is 0.4 mm, and the width of each finger is 0.35 mm. The Pd contact has the ability to dissociate H_2 molecules to H atoms that can diffuse on the NC SnO_2 surface and react quickly with different adsorbed oxygen species via negative charges [15].

In ambient air, the NC SnO_2 thin film surface adsorbs oxygen (O_2) molecules. This generates an increase in resistivity. This phenomenon is related to electron capture by O_2 ions from the SnO_2 conduction band at different operating temperatures according to the following reactions [24]:

Table 1 Properties of the NC SnO_2 thin film grown on SiO_2/Si substrates after annealing at 500 °C

FWHM (degree)	(110) 2θ (°)	Crystallite size (nm)	Lattice parameters		ε_a%	ε_c%
			a (Å)	c (Å)		
0.5259	26.570	15.52	4.74986	3.19035	0.2714	0.1679

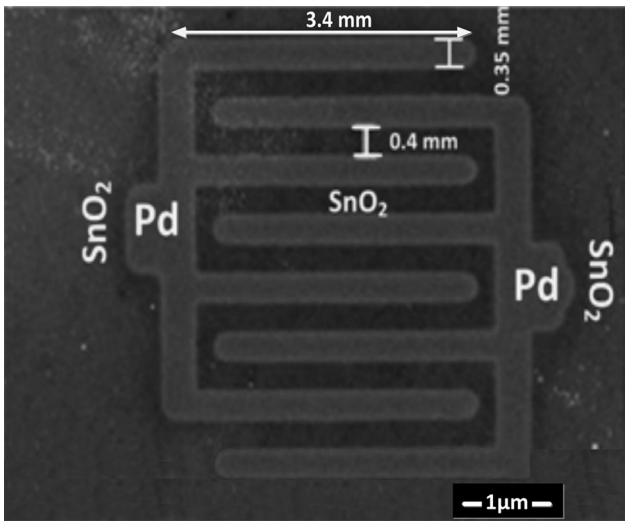

Fig. 4 Image of Pd grid contact deposited on the NC SnO_2 thin film

$$O_2(gas) \rightarrow O_2(ads.), \quad (4)$$

$$O_2(ads.) + e^- \rightarrow O_2^- \quad \text{T less than } 100\,^{\circ}\text{C} \quad (5)$$

$$O_2^- + e^- \rightarrow 2O^- \quad \text{T between 100 to } 300\,^{\circ}\text{C} \quad (6)$$

When H_2 molecules were dissociated to H atoms on the Pd contact, which diffused into the surface of NC SnO_2 thin films, and reacts very rapidly with different adsorbed oxygen species by negative charges. This results in facilitating the interaction between H_2 molecules and the chemisorbed O_2 ions. This reaction will increase the conductivity of the NC SnO_2 thin film by releasing electrons in chemisorbed O_2 to the SnO_2 conduction band as shown in the following reactions [15, 25]:

$$2H_2 + O_2^-(ads.) \rightarrow 2H_2O + e^- \quad (7)$$

$$4H + O_2^-(ads.) \rightarrow 2H_2O + e^- \quad (8)$$

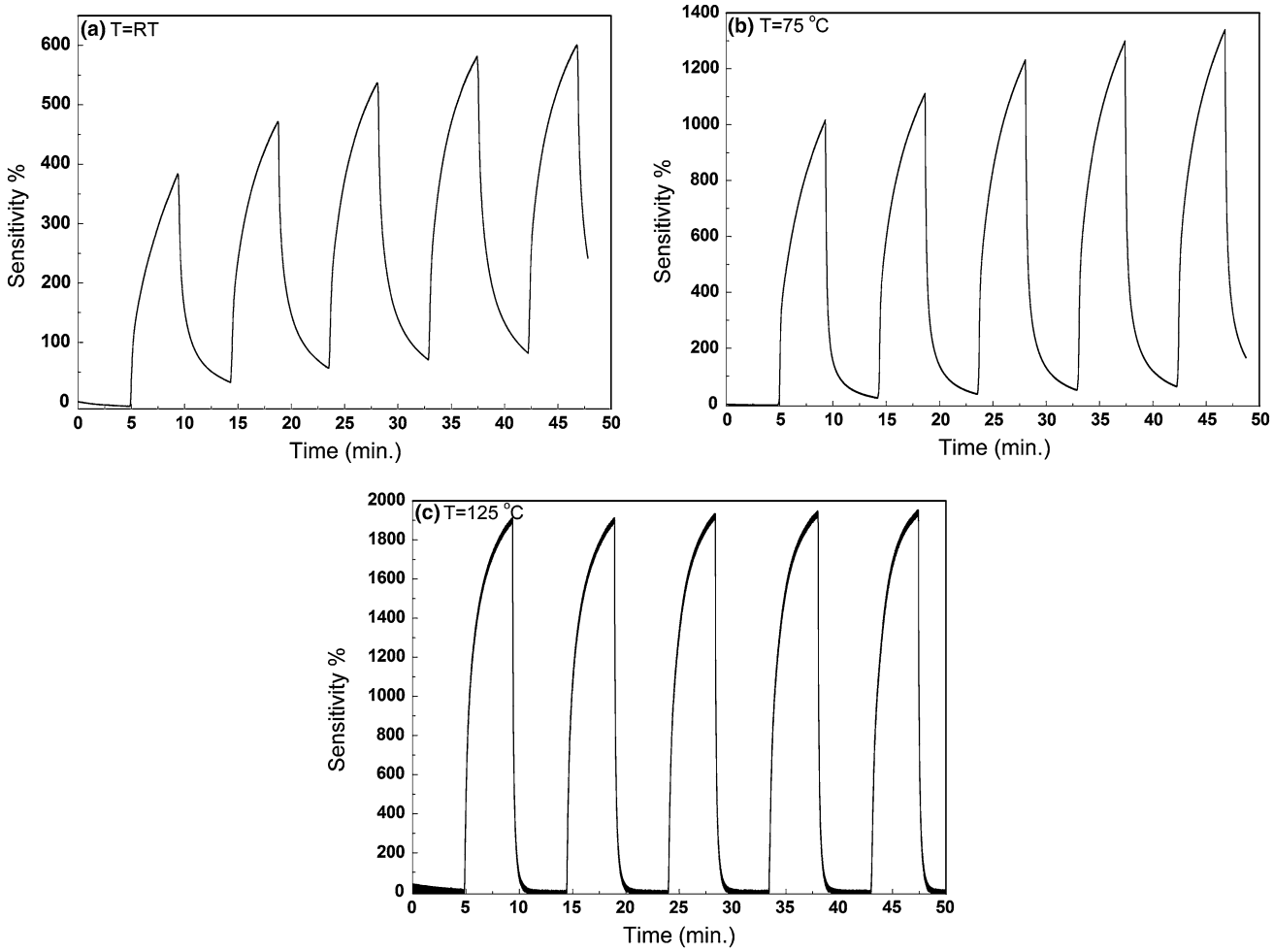

Fig. 5 The sensitivity and repeatability of NC SnO_2 thin film sensor on SiO_2/Si substrates upon exposure to successive pulses of 1000 ppm H_2/N_2 gas and dry air at different sensor temperatures: **a** RT, **b** 75 °C, and **c** 125 °C

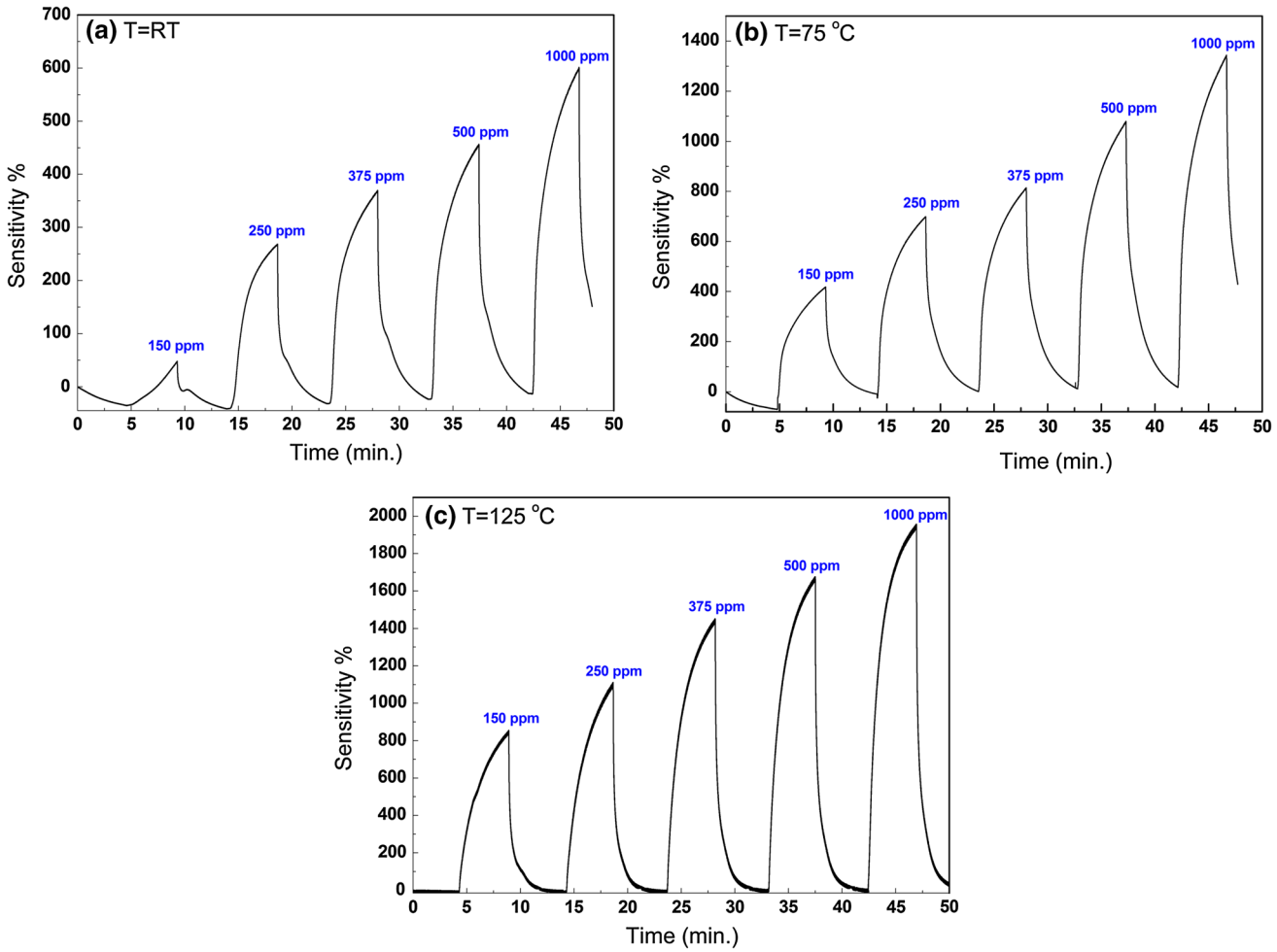

Fig. 6 The sensitivity and repeatability of NC SnO_2 thin film sensor on SiO_2/Si substrates under exposure to different concentrations of H_2 (150–1000 ppm) at different sensor temperatures: **a** RT, **b** 75 °C, and **c** 125 °C

The sensitivity of a gas sensor is defined as the change in the conductivity of the sensing material upon exposure to a reducing gas. It can also be defined as the electric current passing through a NC SnO_2 thin film, which is computed by the following equation [15, 26]:

$$S(\%) = \frac{(I_g - I_{air})}{I_{air}} \times 100 \quad (9)$$

where S is the sensitivity, I_g is the current measured in the presence H_2 gas, and I_{air} is the current measured in air.

Figure 5 shows the sensitivity of the NC SnO_2 thin film grown on the SiO_2/Si substrate at different operating temperatures in the presence of 1000 ppm of H_2 for 5 min. The sensitivity of H_2 gas detection at RT was 600 % with less repeatability for over 50 min as shown in Fig. 5a. The decreased repeatability and poor recovery over time happened because of the residual H_2 gas on the NC SnO_2 thin film surface due to the low operating temperature. Increasing operating temperature to 75 and 125 °C lead to improvement in sensitivity and repeatability of H_2 gas detection as shown in Figs. 5b, c, where the sensitivity at 125 °C was increased to 1950 %. This enhancement in the sensitivity occurred because of a improvements in the

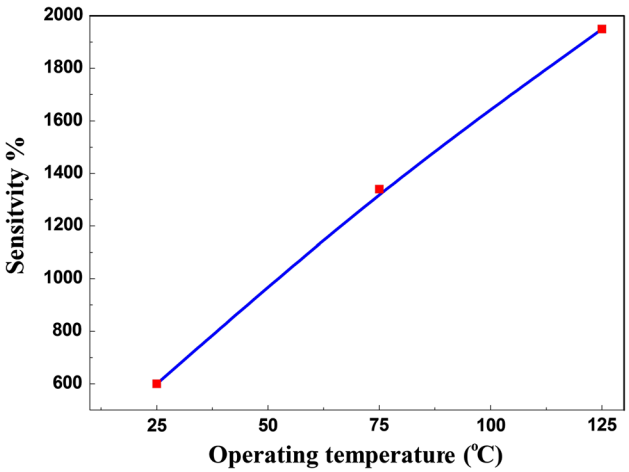

Fig. 7 The relationship between the sensitivity and operating temperatures for NC SnO_2 thin film sensor

Table 2 The comparison between the previous studies and the present work of the sensitivity, the response and recovery times for the NC SnO_2 thin film sensor at various operating temperatures

Temperature (°C)	Response/recovery time (s)	Sensitivity%/H_2 concentration (ppm)	Notice/references
RT	205/116	600/1000	This work
RT	220/–	60/20,000	Nanobelts SnO_2 [28]
75	192/55	1340/1000	This work
125	147/30	1950/1000	This work
100	6/40	1400/2000	SnO_2/Pt nanofilm [30]
125	–/–	1840/500	SnO_2-Ag_2O-PtO_x powder [29]

adsorption and desorption of gas molecules, where at higher operating temperatures various types of oxygen species are presence [15]. Consequently, the removal process of H_2 gas from the surface of NC SnO_2 thin film sensors is increased. Thereby, it can be observed that the sensitivity in Fig. 5c did not drift from the baseline. These high sensitivities for detecting H_2 gas at different operating temperatures were occurred by the high porosity for the NC SnO_2 thin film that was produced through adding glycerin to the sol solution [5]. This allowed easy working to adsorption/desorption of gas molecules [14], thus enhancing the sensitivity of the H_2 gas sensor [15].

The variation in the sensitivity values of NC SnO_2 thin film gas sensor in the presence of different concentrations of H_2 (150–1000 ppm) at different operating temperatures (RT to 125 °C) is shown in Fig. 6. The variation in sensitivity was observed for the H_2 gas sensor operated at a low temperature due to an insufficient adsorption and desorption processes of H_2 and O_2 molecules [13, 15]. A significant difference was observed in the sensitivity with increasing concentrations of H_2 at RT due to the low sensitivity values at lower concentrations of H_2. The variation in the sensitivity with increasing H_2 concentrations was decreases with increasing the sensor temperature. These findings are attributed to the considerably improved sensitivity with increasing operating temperatures [13, 15, 26]. Moreover, Fig. 7 displays the linear correlation between sensitivity and operating temperatures in the presence 1000 ppm of H_2, where the increase in the operating temperature from RT to 125 °C leads to increasing sensitivity. Response and recovery times are defined as the time needed for the target gas to access 90 % of the saturation state current and the time needed to recover 10 % of the initial value respectively [27]. Table 2 displays the response and recovery times of the NC SnO_2 thin film H_2 gas sensor and the relative sensitivities at different operating temperatures compared with previous studies.

4 Conclusions

High-quality NC SnO_2 thin film was grown on a SiO_2/Si substrate by sol–gel spin coating technique. Good structural properties were obtained by adding glycerin to the sol solution, which allowed the increase of surface porosity for the NC SnO_2 thin film. This results in improving the adsorption and desorption of the sensing gas on the NC SnO_2 thin film surface, leading to an increase in sensitivity. The NC SnO_2 thin film on SiO_2/Si displayed good sensitivity at RT; hence, it is considered as a promising portable H_2 gas sensor that can operate in a flammable environment. The repeatability of the NC SnO_2 thin film sensor upon exposure to H_2 gas for over 50 min showed good performance at RT and for different operating temperatures. The NC SnO_2 thin film sensor also showed a good capability of H_2 gas detection at different operating temperatures when exposed to different concentrations of H_2.

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