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Effect of Annealing and Operating Substrate Temperature on Methanol Gas Sensing Properties of SnO_2 Thin Films

[1, *] Priyanka Kakoty, [1] Manabendra Bhuyan and [2] Karen Das

[1] Tezpur University, Tezpur, Assam, India
[2] Assam Don Bosco University, Guwahati, Assam, India
[*] E-mail: priyankak@tezu.ernet.in

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Abstract: SnO_2 based sensing nano-material have been synthesized by simple chemical route using Stannic (IV) chloride-pentahydrate ($SnCl_4.5H_2O$) as precursor. The structural properties of the prepared SnO_2 nano-particles annealed at different temperatures have been characterized by X-ray diffraction (XRD) analysis. The XRD patterns showed pure bulk SnO_2 with a tetragonal rutile structure in the nano-powders. By increasing the annealing temperatures, the size of crystals were seen to increase, the diffraction peaks were found narrower and the intensity was higher. SnO_2 films prepared by spin coating the prepared nano-material solution was tested at different temperatures for methanol vapour and it showed that the film prepared from SnO_2 powder annealed at 500 °C shows the higher sensitivity to methanol vapour at 150 °C substrate temperature with significantly low response and recovery time.

Keywords: SnO_2 sensing material, Annealing, Methanol, Gas sensor.

1. Introduction

Methanol is an extremely lethal organic solvent and is often fatal to living beings. It is highly carcinogenic and may cause serious adverse effect on health and environment. Significant exposure of methanol can cause bronchial constriction, narrowing of airways, increased pulmonary resistance, changes in metabolism and even irritation to mucus membrane in eyes [1]. But in the field of manufacturing of drugs, perfumes, dyes, power sources, etc., methanol has extensive applications [2]. So although methanol is harmful, use of this solvent is almost unavoidable. Therefore, a methanol sensor is in huge demand which has reliability in detection. Detection of methanol at low concentration levels would be even more important as small amount of leakage to the environment could be detected and necessary measures could be taken to save the living beings as well as the environment from any danger from methanol.

Researchers have reported the use of many metal oxides for methanol sensing in many different forms like nanorods, nanosheets, nanoribbons, nanobelts, thick film, thin film, etc., among which SnO_2 is established as a popular choice owing to its various physical characteristics [3]. It is an n-type wide bandgap (3.6 eV) semiconductor that shows high sensitivity to volatile gases, stability, non-toxicity an abundancy. SnO_2 shows sensitivity to various oxidizing and reducing gases and has superior reproducibility. SnO_2 is a low cost material and has been developed as different structures for sensing various oxidizing and reducing gases. SnO_2 have been studied for alcohol gas sensors [4], H_2S gas sensor [5], ammonia sensor [6], CO_2 gas sensor [7], NO_2 sensors [8]. Gases which are a subject of risk to the environment like combustible gases, organic vapours,

toxic gases needs to be controlled and SnO_2 have been extensively exploited for the purpose.

While preparing SnO_2 material for gas sensing applications, annealing is an important process that activates the material for the purpose of gas sensing. Annealing process confiscates the surface oxygen anions and leads to surface made of tin cations in various bonding arrangements and oxidation states with delocalized electronic structure [13]. Adsorption of various gases onto the surface of the treated SnO_2 by annealing process alters the surface electronic properties and allows detection of gas through conductance measurements.

Herein, preparation of SnO_2 based gas sensor is presented which is developed using a simple wet chemical process for methanol sensing. In this paper, analysis of variations seen in the characteristics of the prepared SnO_2 material at different annealing temperatures is presented. This work brings forward the importance of selection of a proper annealing temperature for preparing SnO_2 for methanol sensing. This paper includes the description of chemisorption sensing reaction scheme of the gas sensor on exposure to methanol, the preparation of the sensing material, its structural as well as electrical characterization.

2. The Chemisorption Mechanism of the Sensor Towards Methanol

An adsorption/desorption process of oxygen and the gas molecules at the sensor surface governs the SnO_2 sensing mechanism. The chemical reaction mechanism is therefore very essential for portraying a clear view of the sensing operation.

During chemisorption reaction, when the SnO_2 film is heated in air, the atmospheric oxygen is converted to different ionic form such as O_2^-, O^-, O^{2-} by acquiring the trapped electrons from the conduction band. The oxidation reaction (which is temperature dependent) that takes place is as follows [9]

$O_2 + e^- \rightarrow O_2^-$ (T < 100 °C)

$O_2^- + e^- \rightarrow 2O^-$ (100 °C <T <300 °C)

$O^- + e^- \rightarrow O^{2-}$ (T >300 °C)

This oxidation reaction results in an energy band bending as the trapped oxygen gets reduced in number from the surface and oxygen in ionic form gets adsorbed on the SnO_2 surface which leads to an increase in resistance of the sensor film.

It was proposed in [10-13] that at an operating temperature between 100 °C - 300 °C, the sensitivity of pure SnO_2 film is maximized to reducing gases. For methanol, the absorbed alcohol molecules are very reactive and easily oxidize to form CO_2. At this temperature range, the O^- is highly active and acts as the dominating ionic species of oxygen present in the surface of the sensing layer. This ionic species thus turn as major adsorbed species that influence sensitivity of sensor element. On the other hand, O_2^- is categorized as 'electrophilic' agent and O^{2-} as 'nucleophilic' agent connected with the lattice at the surface and are highly unstable and do not take significant role in inducing sensitivity. While O^- dominates the decomposition reaction of methanol when exposed to the sensing surface layer. Methanol is initially adsorbed on the surface of SnO_2 as a form of methoxide (OCH_3) and then reacts with adsorbed oxygen ions at the surface of SnO_2.

Methanol mainly decomposes following the dehydrogenation path into formaldehyde and consequently into formic acid following the reaction steps releasing electrons into the conduction band as given below [1]:

$$CH_3OH_{gas} \rightarrow CH_3O_{ads} + H_{ads} \quad (1)$$

$$\begin{gathered} CH_3O_{ads} + O^-_{ads} \rightarrow CH_2O_{ads} + \frac{1}{2}H_2O + e^- \\ CH_3O_{ads} \rightarrow CH_2O_{ads} + H_{ads} \\ CH_2O_{ads} \rightarrow CH_2O_{gas} \end{gathered} \quad (2)$$

$$\begin{gathered} CH_2O_{ads} + O^-_{ads} \rightarrow HCOO^-_{ads} + H_{ads} \\ HCOO^-_{ads} \rightarrow CO_{2gas} + H_{ads} + e^- \\ H_{ads} + H_{ads} \rightarrow H_{2gas} \end{gathered} \quad (3)$$

As shown in Equation (1), (2) and (3), methanol first decomposes into methoxy group (CH_3O (ads)) which again decomposes into formaldehyde groups (CH_2O (ads)). A part of this group also desorbs as CH_2O (gas). The remaining CH_2O reacts with adsorbed oxygen O^-_{ads} resulting in species like $HCOO^-$ (ads) which is very unstable and so further decompose to CO_2. Subsequently, the electrons are returned back to the metal oxide, which results in an increase of conductance. The hydrogen atoms combine to form molecular hydrogen gas. The increase in conductivity due to liberation of electrons back into the conduction band represents the response of the sensor.

3. Experimental

3.1. Sensing Material Preparation

The sample preparation procedure involves a low cost wet chemical method. Stannic (IV) chloride-pentahydrate ($SnCl_4.5H_2O$) (from Sigma Aldrich) is dissolved in distilled water to prepare 0.1 M solution to which NH_4OH aquous solution (1 mol/L) was added dropwise under constant stirring for 1hr to get white precipitate of pure SnO_2. The pH of the solution was maintained at 10. The precipitate was further washed with ethanol and DI water to remove NH^{4+} and Cl^- ions. $AgNO_3$ test was done to ensure removal of chloride ions from the precipitate. The samples were then preheated at 100 °C for 10 minute to remove organic residuals. Equations (4) and (5) shows the formation of SnO_2 through the chemical process steps.

$$[SnCl_4 + 4NH_4OH \rightarrow Sn(OH)_4 + 4NH_4Cl], \quad (4)$$

$$[Sn(OH)_4 \rightarrow SnO_2 + 2H_2O] \quad (5)$$

3.2. Deposition of the Prepared Sensing Material on Si/SiO2 Substrate:

A 3" Si wafer of <100> orientation was cleaned and then oxidized to form SiO_2 layer by PECVD deposition technique at pressure 0.8 torque at 250 °C for 150 sec. The prepared SnO_2 solution was then spin coated onto the substrate at 3000 r.p.m. for 60 sec after which the substrate was cut into five samples of 1.5 cm×1.5 cm and dried in an oven for 50-60 minutes maintaining the temperature within 90 °C to 100 °C. Then all the samples were annealed in a muffle furnace for 1hr to improve crystallinity of the sensing layer at five different temperatures of 200 °C, 300 °C, 400 °C, 500 °C and 600 °C.

The sensors were designed to operate in resistive mode for which wire bonding for electrical characterization was required. Thereby, metallization process was carried out in a vacuum coater at a pressure of 10-9 mbar and 80A current. The active sensing layer was protected by an aluminium foil and the space for metallization was exposed to Pd vapours in the metallization chamber which resulted in formation of Pd film of 266 nm thickness over the exposed region. The model used for vacuum coating is "HINDHIVAC" Vacuum coating Unit Model (HHV BC-300). The contact pad dimension was 3 mm × 3 mm and the average distance between two lateral pads was 5 mm. Thin copper wires were used for wire connections using silver paste. The sample was then mounted on a glass slide and was kept in oven at 150 °C for 1hr so that the paste dries up and a proper contact is made and then it was allowed to cool. The schematic diagram of the prepared sensor with its dimensions is shown in Fig. 1.

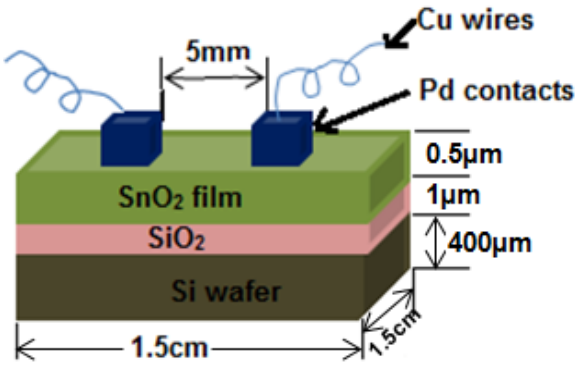

Fig. 1. The prepared sensor structure.

4. XRD Analysis

The crystalline structure analysis of the samples annealed at five different temperatures was carried out using X-ray Diffractometer (Bruker AXS, D8 focus) with CuKα radiation as an X-ray source at 40 kV and 30 mA in the scanning angle (2θ) from 10^0 to 70^0 with a scan speed of 0.02^0/s. The samples shows major reflections at (110), (101), (200), (211), (220), (002), (310), (112) and (301) crystal planes. Fig. 2 shows the XRD of the five samples and their variations in crystalline structure.

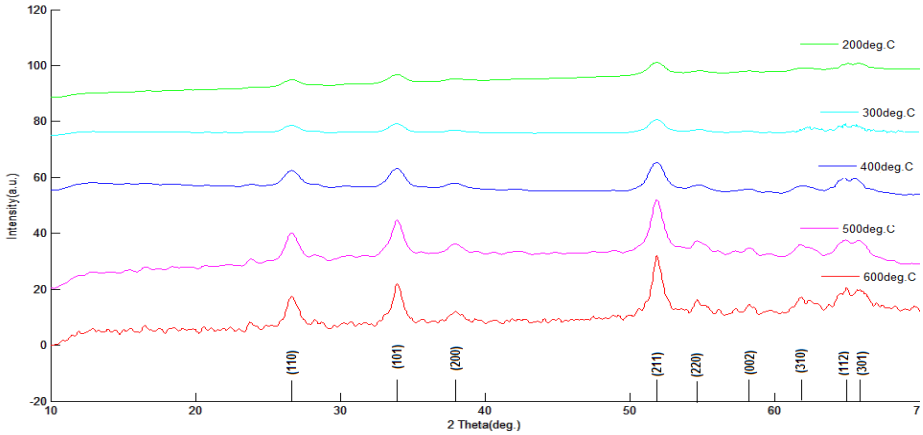

Fig. 2. XRD pattern of the prepared materials at different annealing temperatures.

These reflections shown in Fig. 2 correspond to the standard card (JCPDS card No. 041-1445) that can be indexed to standard pure bulk SnO_2 with a tetragonal rutile structure [14-15]. No impurities were observed. It is seen that as the temperature increases, the prepared SnO_2 nanomaterial becomes more crystalline. It is also observed that with the increase in temperature the diffraction peaks become narrower and exhibits a higher intensity. This can be ascribed to the change in crystal size.

The first major peaks were then used to estimate the SnO_2 crystallite size according to Debye-Sherrer formula [16]:

$$D = \frac{0.9\lambda}{\beta Cos\theta},$$

where λ is the wavelength of the incident X-ray (1.54Å), β is the full width at half maximum intensity of the distinctive peak, and θ is the Bragg's angle.

The crystallite sizes were found to be increasing with increasing temperature shown in Table 1. So we can tune the material crystal size by varying the annealing temperature.

Table 1. Variation of crystallite size with annealing temperature.

Annealing temperature	Crystallite size(nm)
200	7.08
300	7.55
400	7.57
500	8.2
600	8.98

5. Electrical Characterization

A custom made sensor characterization set up as shown in Fig. 3 was used for measurement of the gas sensing properties based on two probe measurement technique. The prepared sensor was placed inside an air tight enclosed test chamber where an arrangement of heating the substrate to an optimum operating temperature was provided. All the five samples were tested to analyze the resistance variation with change in substrate temperature.

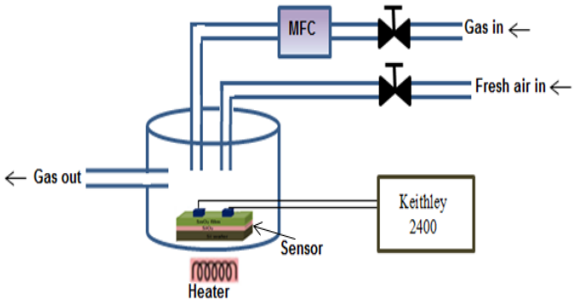

Fig. 3. The sensing set up.

Fig. 4 shows the resistances offered by the samples with change in substrate temperature starting from room temperature (27 °C) to 200 °C. An electrometer (Keithley 2400) was used to monitor the sensor resistances. It is observed that the samples annealed at 200 °C and 300 °C showed very little change in resistances even when substrate temperature was increased up to 200 °C from room temperature. Although a change in resistance is seen for the sample annealed at 400 °C, but it become prominent with the sample annealed at 500 °C. For the sample annealed at 600 °C, it is seen that the change in resistance with substrate temperature becomes insignificant. So, from this experiment it can be stated that among the prepared sensors, the one annealed at 500 °C exhibits a good amount of change in resistance with increase in substrate temperature and this characteristics is desirable for a sensing material to work efficiently as a gas sensor.

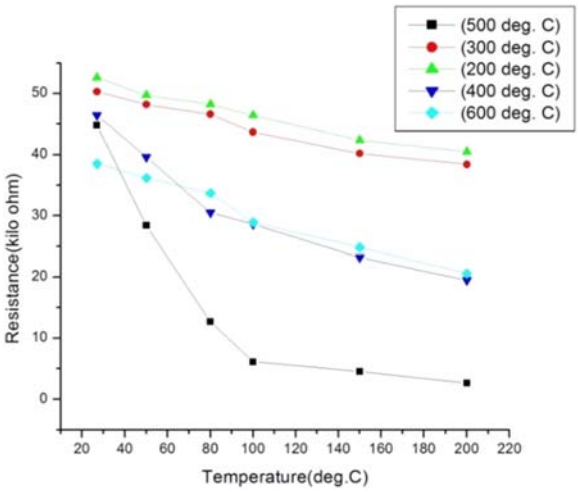

Fig. 4. Resistance vs temperature of SnO_2 samples synthesized at different annealing temperatures.

With all the five prepared sensors, I-V characterization was performed (Fig. 5) to see the variation of current in the sensors with application of voltage from 1 V to 10 V.

It is seen that for all the samples, the current increases as the substrate temperature rises on application of a certain voltage. Nevertheless, amongst all the samples, the current vs voltage variation was highest with the sample annealed at 500 °C, which indicates formation of better crystalline structures and grain boundaries on its surface, making it the most suitable sample for gas sensing operation.

6. Response on Exposure to Methanol

6.1. I-V Characterization

Since the sample annealed at 500 °C exhibited a good amount of change in resistance with temperature variation, 500 °C can be inferred to be the optimum annealing temperature for SnO_2 based sensing material to work as a gas senor. This sample was then further characterized with gas exposure.

The sensor was experimented with methanol vapour at different operating temperatures and change in current through the sensor with varied applied voltages across the sensor was analyzed (Fig. 6). The operating temperature to the sensor was provided though a heater via a hot-plate as shown in Fig. 3. The flow of methanol vapour to the gas sensor chamber was controlled using a mass flow controller at 0.8slpm (model: Alicat MC-05slpm-D). By keeping the voltage fixed at a certain value, the gas was allowed to enter to the chamber and current readings were recorded. In all the samples, it is seen that after a certain period of time, the current became almost constant on a certain value. Nevertheless, it is found that rise in current level is highest when the operating temperature was maintained at 150 °C.

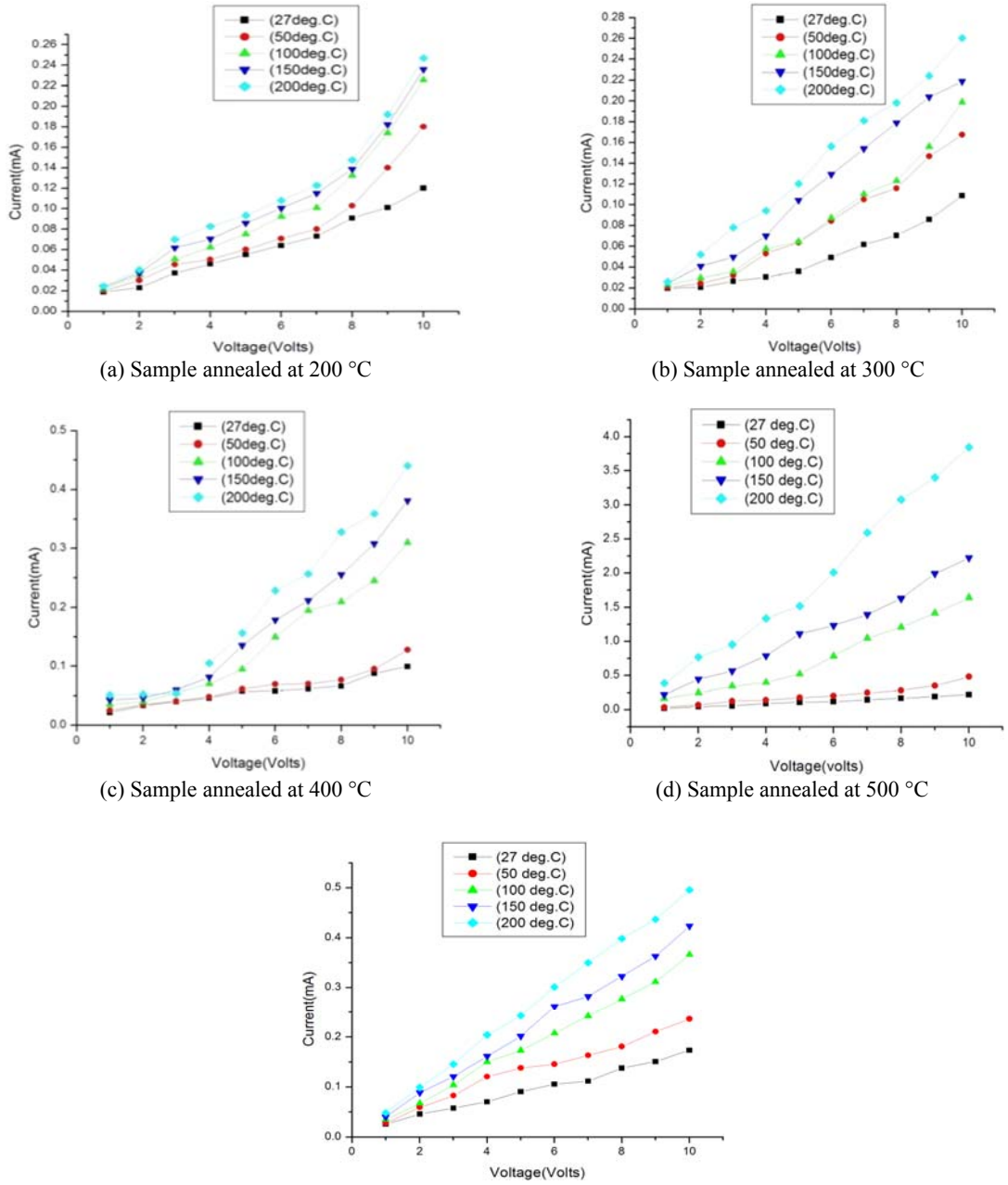

Fig. 5. I-V characterization of the prepared sensors at different operating temperatures without gas exposure.

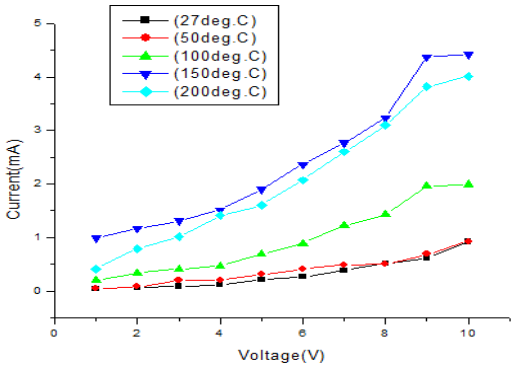

Fig. 6. I-V characteristics of the gas sensor (annealed at 500 °C) at different operating temperatures on exposure to methanol.

6.2. Response and Recovery Time

It is seen that the resistance exhibited by the samples decreases with time when exposed to methanol vapour and it increases during the recovery time. It is observed that at operating temperature of 150 °C, the response and recovery time is lower than that of the other operating temperatures. At operating temperature of 150 °C the sensor's response reached a stable value after 105 s upon exposure to methanol. After the sensor was refreshed with fresh air by opening the fresh air inlet and the gas outlet, it was seen that after 122 s, the sensor resistance returned to its baseline value as shown in Fig. 7. Response and recovery time at 150 °C operating temperature was

relatively lower amongst all other operating temperatures. The response and recovery times of the sensor at different operating temperatures is shown in the histogram in Fig. 8.

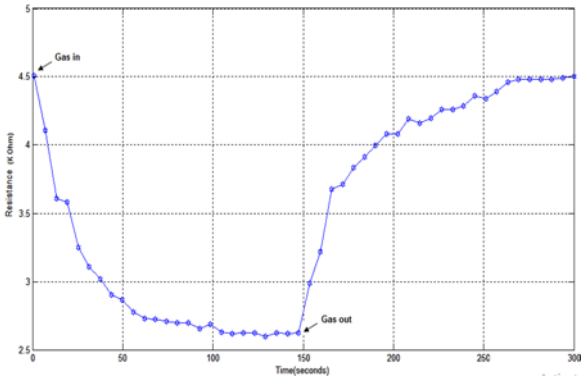

Fig. 7. Gas sensor response at 150 °C operating temperature (Variation of resistance with time).

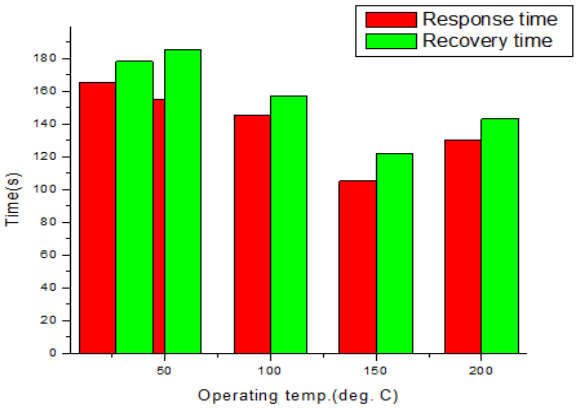

Fig. 8. Response and recovery time of the sensor (annealed at 500 °C) at different operating temperatures.

7. Conclusions

Fabrication and characterization of SnO_2 based methanol sensor is presented in this paper. SnO_2 was prepared using a low cost wet chemical process and deposited on Si/SiO_2 substrate by spin coating process. The deposited films was then annealed at five different temperatures of 200 °C, 300 °C, 400 °C, 500 °C, 600 °C. XRD based characterization was carried out and it is found that with increase in temperature the crystallite size were increasing. Change in resistance of the sensing film was studied by varying the substrate temperature and it is found that the sample annealed at 500 °C showed prominent change in resistance with increase in substrate temperature as compared to the other samples which makes the sample annealed at 500 °C better choice for gas sensing. So, the sensors annealed at 500 °C was further characterized with exposure to methanol with various operating temperature and it is found that the prepared sensor works better at an operating temperature of 150 °C. The response and recovery time was also studied. It is seen that the sensor's response reached a stable value after 105 s upon exposure to methanol and it takes 122 s to reach the stable value while flashing the methanol from gas chamber. The response and recovery time of the fabricated sensor was studied for different operating temperature and it is found that at 150 °C response and recovery time is lower as compared to other operating temperatures. In this work it is found that SnO_2 as gas sensor for methanol sensing, 500 °C is optimum temperature for annealing and at 150 °C operating temperature better response is obtained.

References

[1]. Amit Gupta, J. K. Srivastava, Anand A. Bhaskar, Pd-doped SnO_2 based Thick Film gas sensor for detection of Methanol, *International Journal of Innovative Research in Engineering & Science*, Vol. 5, Issue 3, May 2014, pp. 49-55.

[2]. P. Siciliano, Preparation, characterization and applications of thin films for gas sensors prepared by cheap chemical method, *Sensors and Actuators B: Chemical*, Vol. 70, No.1-3, 2000, pp. 153-164.

[3]. P. Kakoty, M. Bhuyan, SnO_2 based Gas Sensors: Why it is so popular?, in *Proceedings of the IEEE International Conference on Electrical, Computer and Communication Technologies (ICECCT)*, 2015, pp. 1-5.

[4]. Chen Y. J., *et al.*, Synthesis and ethanol sensing characteristics of single crystalline SnO_2 nanorods, *Applied Physics Letters*, Vol. 87, 2005, pp. 233503-1–233503-3.

[5]. Maekawa Tomoki, *et al.*, Sensing behavior of CuO-loaded SnO_2 element for H_2S detection, *Chemistry Letters*, Vol. 25, No. 4, 1991, pp. 575-578.

[6]. Zhang Jun, *et al.*, Polypyrrole-coated SnO_2 hollow spheres and their application for ammonia sensor, *The Journal of Physical Chemistry C*, Vol. 113, No. 5, 2009, pp. 1662-1665.

[7]. Mizuno Noritaka, *et al.*, CO_2-sensing characteristics of SnO_2 element modified by La_2O_3, *Sensors and Actuators B: Chemical*, Vol. 13, No. 1-3, 1993, pp. 473-475.

[8]. Maiti Amitesh, *et al.*, SnO_2 nanoribbons as NO_2 sensors: insights from first principles calculations, *Nano Letters*, Vol. 3, No. 8, 2003, pp. 1025-1028.

[9]. J. Gonzalez-Chavarri, C. Hurtado, G. G. Mandayo, E. Castano, Design and fabrication of sensor structures for the measurement of toxic gases, in *Proceedings of the Spanish Conference on Electron Devices (CDE)*, 2013, pp. 107-110.

[10]. Jayaraman V., *et al.*, A low temperature H_2 sensor based on intermediate hydroxy tin oxide, *Sensors and Actuators B: Chemical*, Vol. 55, No. 2, 1999, pp. 147-153.

[11]. Zhang Gong, Meilin Liu, Effect of particle size and dopant on properties of SnO_2-based gas sensors, *Sensors and Actuators B: Chemical*, Vol. 69, 2000, pp. 144-152.

[12]. Cabot A., Arbiol J., Morante J. R., Weimar U., Barsan N., Göpel W., Analysis of the noble metal catalytic additives introduced by impregnation of as

obtained SnO_2 sol–gel nanocrystals for gas sensors, *Sensors and Actuators B: Chemical*, Vol. 70, No. 1, 2000, pp. 87-100.
[13]. Park Sung-Soon, J. D. Mackenzie, Thickness and microstructure effects on alcohol sensing of tin oxide thin films, *Thin Solid Films*, Vol. 274, No. 1-2, 1996, pp. 154-159.
[14]. M. Aziz, S. Abbas, W. Baharom, Size-controlled synthesis of SnO_2 nanoparticles by sol-gel method, *Materials Letters,* Vol. 91, 2013, pp. 31-34.
[15]. Y. Li, W. Yin, R. Deng, R. Chen, J. Chen, *et al*., Realizing a SnO_2-based ultraviolet light-emitting diode via breaking the dipole-forbidden rule, *NPG Asia Materials*, Vol. 4, Issue 11, 2012, p. e30.
[16]. I. H. Kadhim, H. A. Hassan, Effects of glycerin volume ratios and annealing temperature on the characteristics of nanocrystalline tin dioxide thin films, *Journal of Materials Science: Materials in Electronics*, Vol. 26, Issue 6, 2015, pp. 1–10.