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Improving Gas Sensing Properties of Tin Oxide Nanowires Palladium-Coated Using a Low Cost Technique

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Abstract

Thin films of SnO_2 nanowires were successfully prepared by using chemical vapor deposition (CVD) process on quartz substrates. Afterwards, a thin layer of palladium (Pd) as a catalyst was coated on top of nanowires. For the deposition of Pd, a simple and low cost technique of spray pyrolysis was employed, which caused an intensive enhancement on the sensing response of fabricated sensors. Prepared sensor devices were exposed to liquid petroleum gas (LPG) and vapor of ethanol (C_2H_5OH). Results indicate that SnO_2 nanowires sensors coated with Pd as a catalyst show decreasing in response time (~40s) to 1000ppm of LPG at a relatively low operating temperature (200^oC). SnO_2 /Pd nanowire devices show gas sensing response time and recovery time as short as 50s and 10s respectively with a high sensitivity value of ~120 for C_2H_5OH, that is remarkable in comparison with other reports.

1. Introduction

Applications of chemical gas sensors include environmental monitoring, automotive applications, emission monitoring, and aerospace vehicle health monitoring [1]. Semiconducting metal-oxides have been known for decades to be suitable for gas sensing purposes. There are many reports on applications of these materials as gas sensor devices due to their small dimensions, low cost, and high compatibility with microelectronic processing [2, 3]. Amongst all semiconducting metal-oxides, Tin oxide (SnO_2) is the most widely studied gas sensor material and the most commercially available chemical gas sensors exploit a SnO_2 element [4, 5]. Although these oxides themselves are catalytically active, they are rarely used in isolation as their gas sensing characteristics are usually enhanced by using a small amount of noble metal catalyst such as palladium (Pd) and platinum (Pt) [6]. It is widely accepted that the presence of noble metal elements (Pt, Pd, Au, Ag, etc.) on the surface of a metal

oxide enhances the interaction of reducing/oxidizing gases with the absorbed oxygen on the surface [3]. Besides improving the selectivity, catalysts also modulate the electron transport properties of the sensing SnO_2 layer and improved response characteristics are obtained. The introduction of catalysts influences grain size, the shape of crystallites, bulk and surface stoichiometry, properties of inter-crystalline barriers, and bulk electro-physical properties [7]. Table 1 has summarized maximum response in exposing to LPG in various SnO_2 based sensors at different temperatures.

Table 1. Maximum response to LPG in various SnO_2- based sensors at different temperatures.

Sensor type	LPG (in ppm)	Operating Temperatur	Response
SnO_2 Thick film	10,000	350	0.93 [8]
SnO_2 Thick film	200	300	0.7 [9]
SnO_2 Thick film	1000	350	3.68 [10]
SnO_2 Thick film	800	400	1.38 [11]
SnO_2 Thick film	1000	345	0.1 [12]
SnO_2 NWs	500	350	3.5 [5]
SnO_2 Hierarchica	500	350	8.1 [5]
TGS 2612 Figaro	1000	VH=5V	2.1 [13]

In this work, we have synthesized thin films devices comprising Pd-coated SnO_2 NWs using combination of CVD and spray pyrolysis techniques. Effects of Pd as a catalyst on the modification of gas sensing properties of SnO_2 NWs were studied using a home-made set-up for measuring sensing characteristics. The morphologies of the undoped and Pd-doped SnO_2 nanowires were observed by field emission scanning electron microscopy (FESEM; Hitachis-4160) and high resolution transmission electron microscopy (HR-TEM; JEOL2100F) techniques. Conductometric gas sensing measurements showed high sensitivity with fast response time at a relatively low sensor working temperature.

2. Experimental procedure

Thin films of SnO_2 NWs were deposited using CVD under a reactive ambient (100sccm of Ar and 15sccm of O_2) on top of quartz substrates. Precursor was composed of 0.5gr of SnO_2 powder and 0.5gr carbon powder. Alumina boat was used to heat the precursors up to 1050oC with the rate of 7.5oC/min. Afterwards, various concentrations of the solution of palladium chloride ($PdCl_2$) were deposited on the surface of SnO_2 nanowire thin films by spray pyrolysis to enhance gas sensing parameters. Briefly, 1gr $PdCl_2$ powder was solved in 100cc DI-water and ethanol (1:1 ratio), 0.1mL HCl was also added to the solution to get a transparent solution. To find the optimum amount of Pd on the surface of SnO_2 NWs film, a series of samples with different amounts of 0.02M solution of $PdCl_2$ (15, 25, 50, and 75cc) were sprayed at 450oC, as optimised substrate temperature. Finally, samples were annealed at 300oC for two hours on the flow of 100sccm Ar to get rid of any solvent traces. Moreover, annealing at 300^oC transforms the amorphous SnO_2 films into a poly-crystalline structure [4]. For the fabrication of sensor devices and to achieve good contact for the electrical measurements, pairs of Au electrodes were deposited onto on top of the SnO_2/Pd thin film samples (200nm thickness, 5mm distance. A sample area is 1cm×1cm (Fig. 4(a))), using vacuum thermal evaporation by molybdenum boat. Gas sensing measurements were taken by a testing apparatus consisting of a Teflon test chamber with a controllable heater, mass flow controllers, and a PC-based (PSIP 86D) multimeter. Finally, four kinds of samples with 15, 25, 50 and 75cc sprayed $PdCl_2$ were prepared which indexed as A, B, C and

D, respectively and their gas sensing properties were studied toward LPG and vapor of ethanol at different temperatures (50–300 ^{o}C).

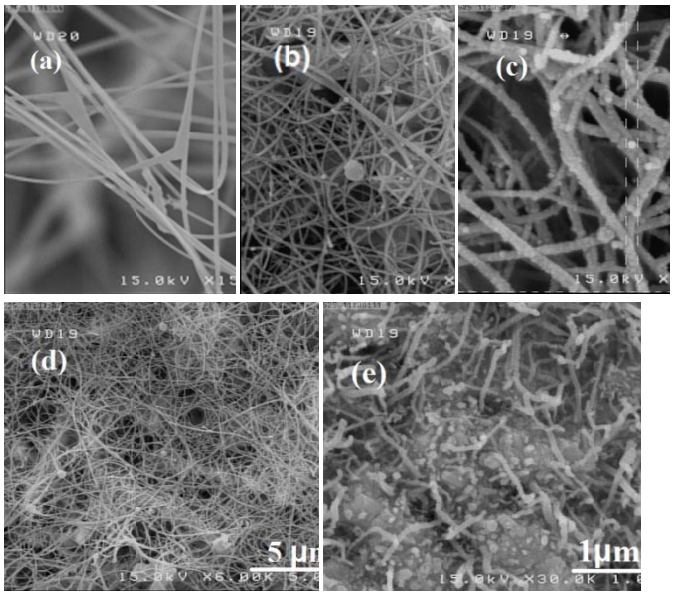

Fig.1. (a) Undoped SnO_2 nanowires grown by CVD on Quartz substrate. (b) SnO_2 NWs with deposition of 15cc Pd (sample A). (c) SnO_2 nanowires with deposition of 25cc Pd (sample B). (d) Top view of sample C with deposition of 50cc Pd. (e) Sample D with deposition of 75cc Pd on SnO_2 nanowires.

3. Results and discussion

Fig. 1(a) shows SEM image of SnO_2 nanowires deposited with about 80-100 nm diameter in average. Fig. 1(c) shows nanowires with Pd particles with mean size of about 50nm on nanowires surface. Fig. 2(f) shows a HR-TEM image of a single SnO_2 nanowire with Pd particles on its surface (sample B). The high-resolution TEM image confirms that the interplanar spacing of Pd particles attached to the SnO_2 nanowire is about 0.21 nm which is in agreement with other reports [14].

The sensing response characteristics of the SnO_2/Pd NWs sensor structures were studied over a temperature range of 50 to 300^{o}C for all fabricated sensors toward both LPG and vapor of ethanol. Responses of all sensors show a maximum value at a particular temperature which is called optimum temperature. Fig. 3(b) shows the gas response of un-doped and Pd-doped SnO_2 nanowire thin films as a function of operating temperature in the range from 50 to 300 ◦C. The testing gases were 1000ppm LPG, in N_2 with a total flow rate of 500 sccm. Fig. 4 shows dynamic response of prepared sensors towards different concentration of C_2H_5OH vapor at 100^{o}C. Here, we use the definition of sensor response as Sensor Signal = R_g/R_N where R_N and R_g are the resistance of the nanowire exposed to nitrogen and the target gases respectively [3]. A relatively poor response for sensor A was obtained at 100^{o}C to ethanol vapor (Sensor signal =2.75). The highest response ~120 was also observed for sensor B to 4000ppm ethanol vapor (at 100^{o}C). With sensor performance comparison of SnO_2-Pd doped with pure SnO_2 NWs, it can be observed that there is an optimum concentration. In this case, optimum concentration was occurred in 25cc Pd, which result in remarkable sensor response and sensitivity increase (Fig 4.). As it depicted in Figs 4(a) and 4(c), it can be easily seen that sensor signal of SnO_2-Pd doped NWs has been increased by factors of 24 and 4 in exposure to 4000 and 8000ppm ethanol vapor, respectively.

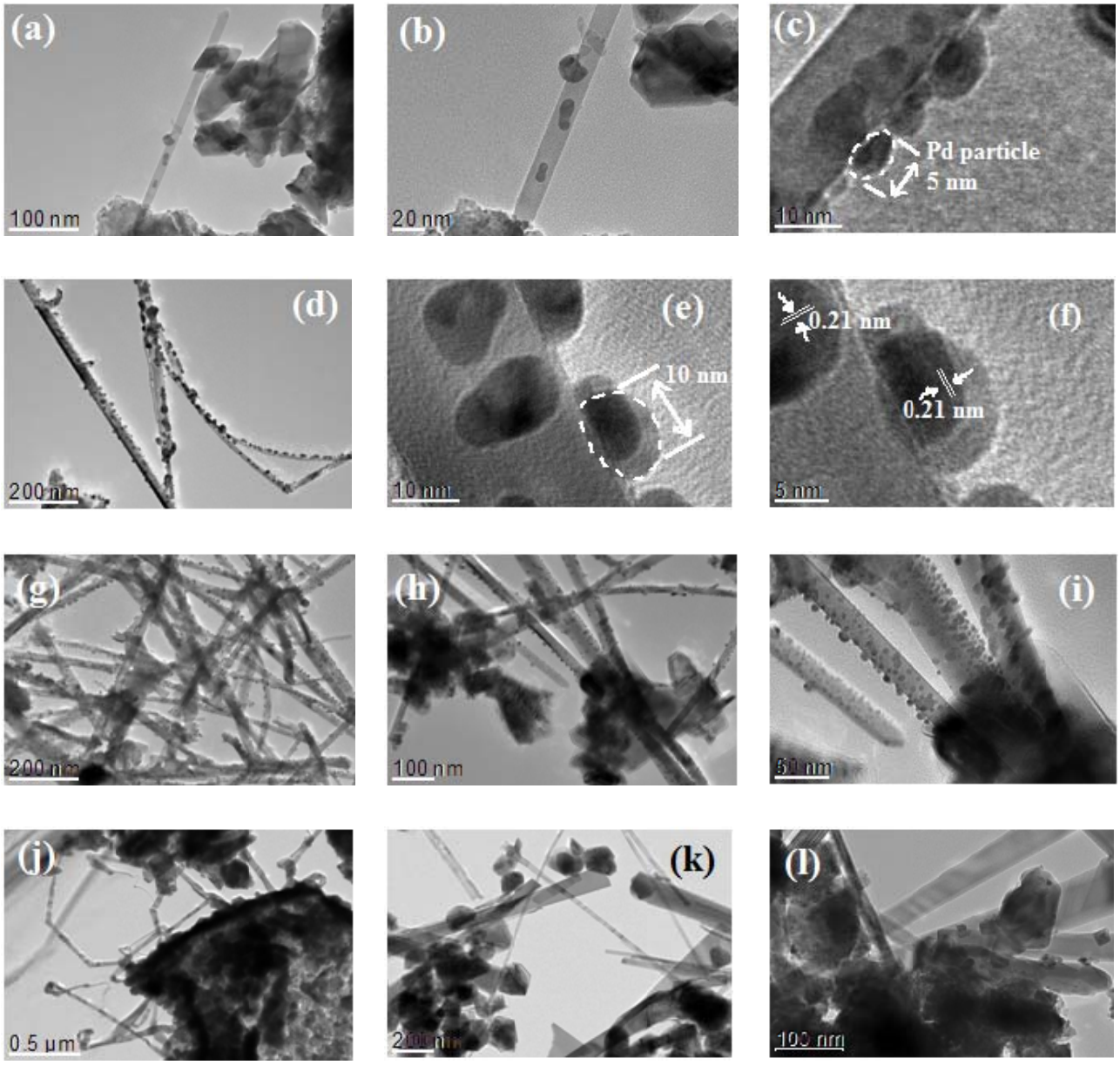

Fig. 2. HR-TEM images of (a) - (c) 15cc Pd deposition on SnO_2 nanowires, (d) – (f) 25cc Pd deposition, (g) – (i) 5 deposition and (j) – (l) 75cc Pd deposition.

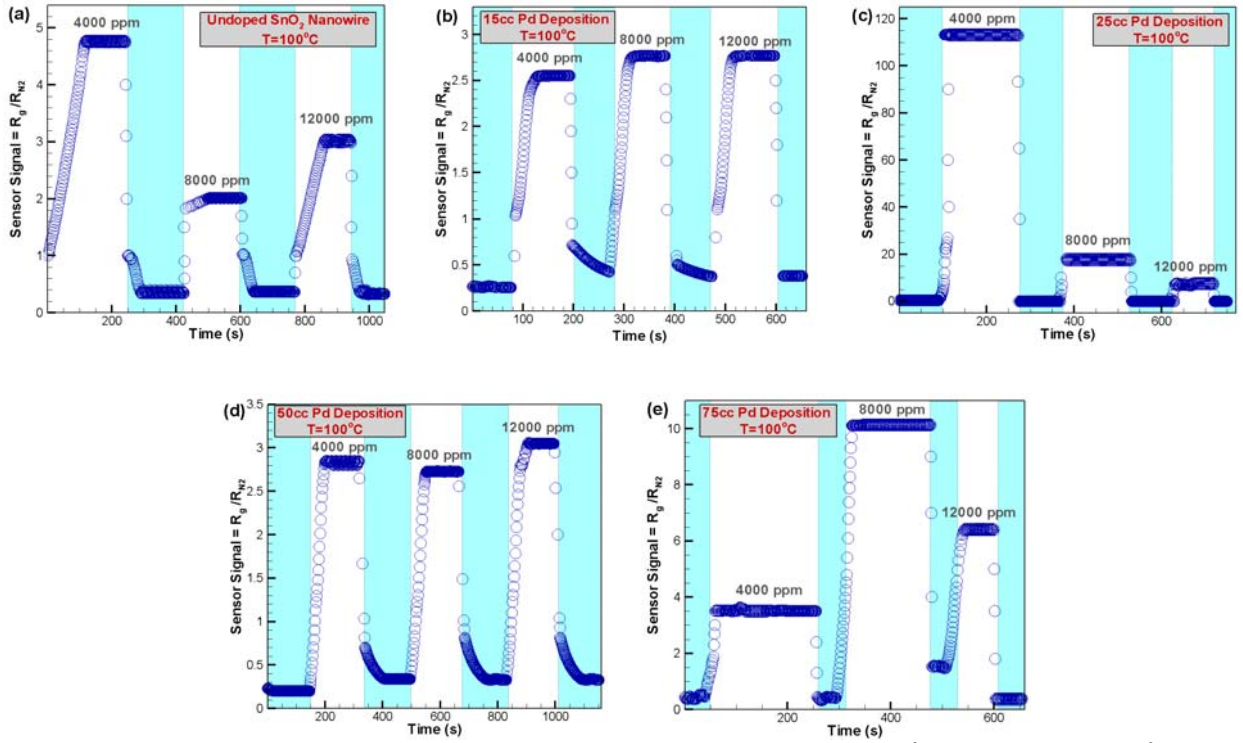

Fig.4. Gas sensing response of fabricated sensors toward ethanol vapor (a) Sensor A at 100°C, (b) Sensor B at 100°C, (c) Sen 100°C and (d) Sensor D at 100°C.

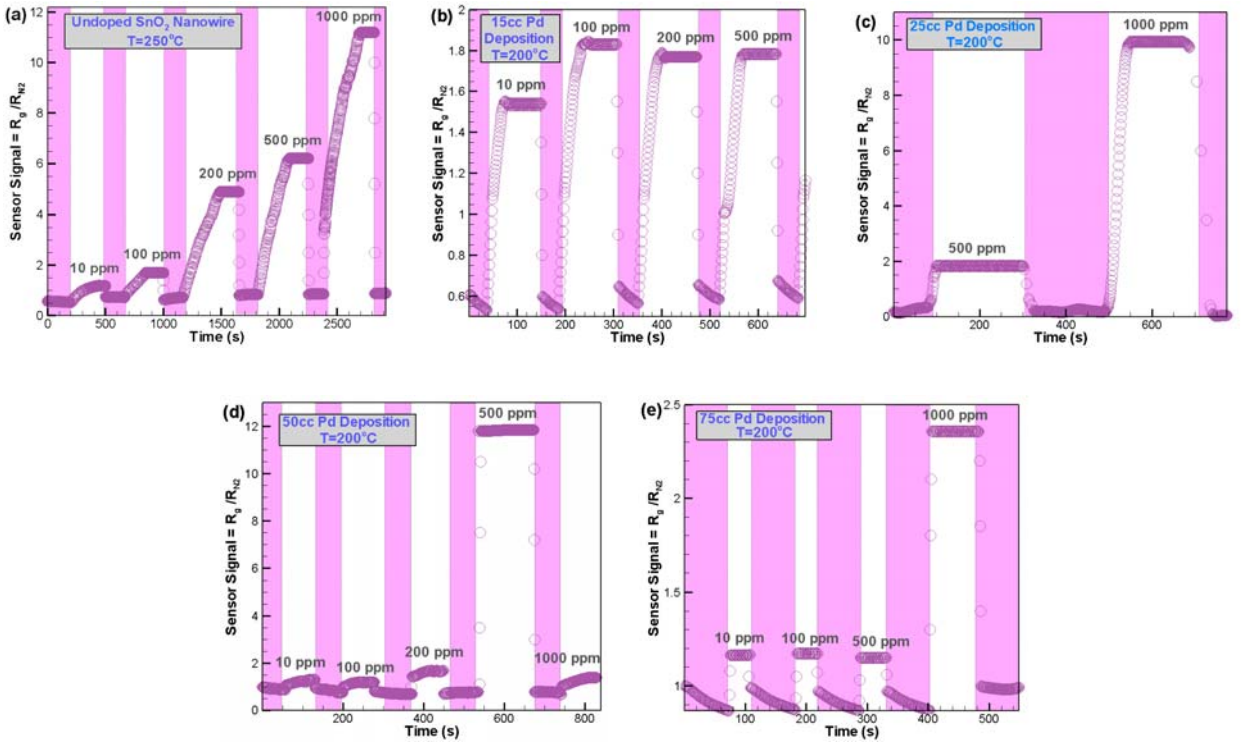

Fig. 5. Gas sensing response of fabricated sensors for LPG sensing response: (a) Undoped SnO_2 nanowires at 250°C, (b) Sens 200°C, (c) Sensor B 200°C, (d) Sensor C 200°C and (e) Sensor D 200°C.

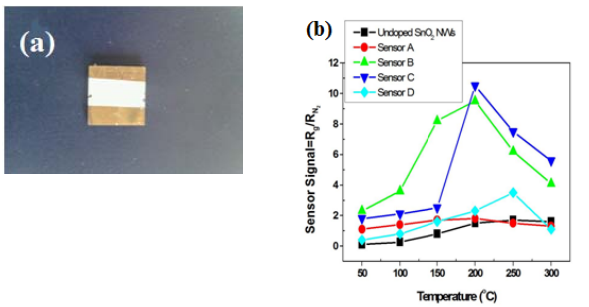

Fig. 3. (a) SnO_2 nanowires with two gold electrodes on quartz substrate. (b) The gas response of un-doped and Pd-doped SnO_2 nanowire thin films as a function of operating temperature towards 1000ppm LPG.

Fig 5(a) - (e) indicates gas sensing response of sensors to LPG at different concentrations. It can be seen that sensor B is more sensitive to 1000ppm LPG at a relatively low temperature about 200°C than other sensors with a response value of about11. SnO_2-Pd doped sensors performances in the presence of LPG show that there is not a significant increase in sensor signal compared to pure SnO_2 NWs sensor and only in the 50cc Pd concentration, the sensitivity of the sensor relative to reference sensor has increased from 10 to 12.

Accordingly, sensor B was demonstrated better gas response toward both target gases in comparison with other fabricated sensors. It is observed that Pd particles have decreased the working temperature of the device in comparison with uncoated SnO_2 nanowires (Fig 5(a) and (c)) which has been confirmed by other authors [6]. In the C_2H_5OH vapor and LPG atmosphere, the better sensing response of sensor B can be attributed to the small size of Pd particles coated on top of SnO_2 nanowire films.

Here the response time (recovery time) is defined as the time period needed for the device to undergo resistance changing from 10% (90%) to 90% (10%) of the value in equilibrium upon exposure to the target gas [3]. Response and recovery time of fabricated sensors to both target gases can be obtained from Fig. 6. Sensor B shows C_2H_5OH vapor gas sensing response time and recovery time 50s and 10s respectively with sensitivity value about 120 which is remarkable regarding to previous reports [9]. The response and recovery time were estimated to be about 40s and about 90s, respectively for sensor B toward LPG.

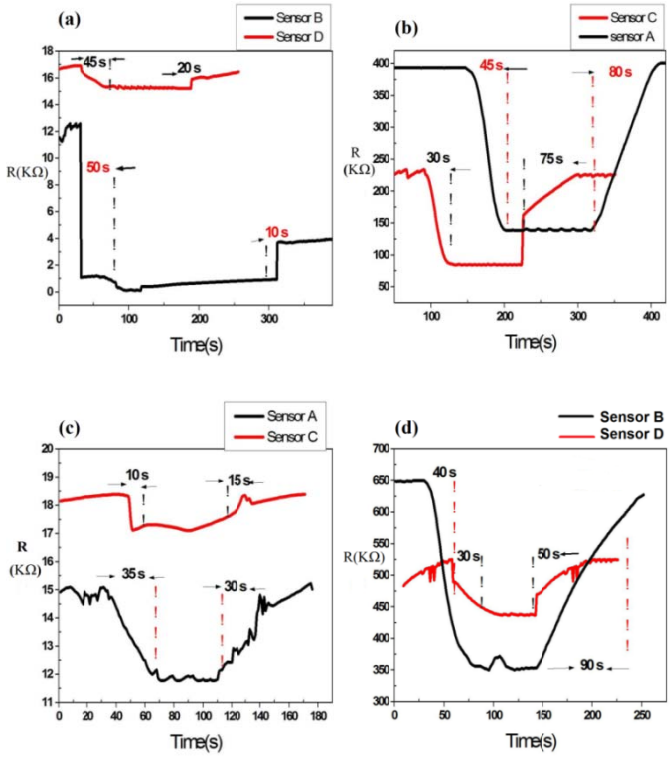

Fig. 6. Response and recovery behavior of fabricated sensors to target gases. (a) Sensor B to 4000ppm ethanol vapor and Sensor D to 8000ppm at operating temperature 100°C and (b) Sensor A to 8000ppm ethanol vapor and Sensor C to 4000ppm at 100°C (c) LPG response of Sensor A to 1000ppm and Sensor C to 500ppm at an elevated temperature 200°C and (d) Sensor B to 1000ppm LPG and Sensor D to 1000ppm at operating temperature 200°C.

In order to investigate the sensing mechanism, since SnO_2 typically is an n-type wide band gap semiconductor, the electron transfer resulted from oxygen vacancies and the adsorbed gas molecules at the active site on the surface of SnO_2 sensors,

acting as donator or acceptor sites. At working temperature of the device in air, SnO_2 sensor adsorbs oxygen (O^{2-}) and moisture (OH^-), which traps electrons from the conduction band of SnO_2. In the presence of target gases, two typical interactions cause a decrease in resistance of SnO_2. First, the target gas chemisorbed at the active site on SnO_2 surface. Second, the adsorbed oxidizing agent (O^{2-}) oxidized the target gases, resulting in electron transferring from target gases to O^{2-}. Most of electrons which have been trapped by O^{2-} transfer to the SnO_2 surface, which increased electronic conductivity of SnO_2 sensors [15]. Upon removal of reducing species or introduction of air or oxygen, the mechanism is reversed and the conductivity returns to its original state. The adsorption of atmospheric oxygen on the sensor surface forms ionic species such as O^{-2} and O^- which acquire electron from the conduction band. The reaction kinetics is as follows [16]:

$$O_2\ (gas) \rightarrow O_2\ (ads) \quad (1)$$

$$O_2\ (ads) + e^- \rightarrow O^{-2}\ (ads) \quad (2)$$

$$O^-\ (ads) + e^- \rightarrow 2O^-\ (ads) \quad (3)$$

The oxygen species react with ethanol [17] and LPG [18, 19] through complex series of reactions as follows:

$$C_2H_5OH + 6O^- \rightarrow 3H_2O + 2CO_2 + 6e^- \quad (4)$$

$$C_4H_{10} + 13O^- \rightarrow 5H_2O + 4CO_2 + 13e^- \quad (5)$$

The above reactions take place only if gases are completely oxidized on the sensor surface. By looking at these reactions, it seems that LPG does not oxidize completely and may be following the reaction scheme given below [20]:

$$C_4H_{10} + 2O^- \rightarrow C_4H_8 - O + H_2O + 2e^- \quad (6)$$

Partially oxidized gases may not change the conductivity of sensor element drastically, which might have happened in present study of LPG sensing. The observed enhanced response characteristics for ethanol vapor may be attributed to the activation of spill-over of sensing gas molecules by the presence of Pd catalyst particles on to the surface of sensing SnO_2 layer. In the C_2H_5OHvapor and LPG atmosphere, the sensing response of sensor B was much better than those of other sensors. This can be attributed to the smaller size of Pd particles coated on top of SnO_2 nanowire films.

4. Conclusion

Palladium nanoparticles were deposited on the surface of SnO_2 NWs films by spray pyrolysis to enhance gas sensing performances. The undoped and Pd-doped SnO_2 hollow nanofibers showed significantly different responses to C_2H_5OH and LPG according to the sensor temperature and Pd doping concentration. The sensing response characteristics of the SnO_2/Pd NWs sensor were studied over a temperature range of 50 to 300^oC. The response and recovery time were estimated to be about 40s and about 90s, respectively for LPG. Sensor B with 25cc Pd shows C_2H_5OH vapor gas sensing response time and recovery time as short as 50s and 10s respectively with high response of about 120 which is remarkable in comparison with other reports in this area. The capability of the selective gas sensors was explained in terms of the analyte gases as a function of sensor temperature and Pd doping concentration.

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