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# Optimization of Firing Temperature of PbO-doped $SnO_2$ Sensor for Detection of Acetone, Methanol, Propanol

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**Abstract:** In the present work, the response of a set of three PbO (1 %wt) doped thick film $SnO_2$ sensors fired at different firing temperatures ($650^0$ C, $750^0$ C, $850^0$ C) have been studied. The selection of appropriate firing temperature is necessary for the sensor fabrication in order to achieve the highest sensitivity for a particular species of gas. To achieve this, thick film PbO-doped sensor were fabricated on a 1″x1″ alumina substrate. The sensitivity of these sensors has been studied at different operating temperatures ($150^0$ C-$350^0$ C) upon exposure to acetone, methanol and propanol. The sensor fired at $850^0$ C besides having good adhesion yields maximum sensitivity at an operating temperature of $250^0$ C for all gases except acetone for which it gives maximum response at $200^0$ C. *Copyright © 2009 IFSA.*

**Keywords:** Thick film sensor, Tin oxide, Firing temperature, Gas sensing mechanism

## 1. Introduction

Semiconductor gas sensors are widely used in domestic and industrial applications due to favorable characteristics such as low cost and robustness. Metal oxide semiconductor gas sensors are, gas dependent resistors [1]. $SnO_2$ is one of the most widely used sensor material. The working principle is based on the change of conductivity that takes place after exposure to gases capable of reacting with chemisorbed oxygen. Since adsorbed oxygen immobilizes electrons near the surface of n-type semiconductors such as $SnO_2$, when a gas (e.g. hydrocarbon) reacts with and removes adsorbed oxygen, these electron are released and the electrical conductivity increases [2, 3]. These reactions

generally take place at temperature in the range $150^0$ C-$600^0$ C and therefore the sensor must be heated to obtain a suitable response. Despite a high sensitivity, repeatability and long term stability, the main drawback of such sensors is that they are operated at high temperature ($300^0$ C) upwards. Thus the applicability of these sensors remains limited [4]. Microstructure is an important factor that influences gas sensing properties. The properties of the microstructure can be controlled by controlling the properties of the sensor material itself [5]. Tin oxide serves as an important base material in a variety of conductance type gas sensing devices. The widespread applicability of this semi conducting oxide is related both to its range of conductance variability and to the fact that it responds to both oxidizing and reducing gases [6]. Such general responsiveness, however, leads to severe interference effects for pure $SnO_2$, so that in almost all practical cases it is used in a modified form. The modifying role may be either catalytic or electronic. Some dopants are added to it to obtain an enhanced response and improved selectivity [7]. In the present case, PbO has been used as a dopant for the sensors.

Yomazoe et al. [8] have demonstrated that the sensing characteristics of $SnO_2$ sensors can be improved by controlling the fundamental factor which effects its receptor and transducer functions. The transducer function depends upon the microstructure of the elements, i.e. the grain size of $SnO_2$ (D) and the depth of the surfaces charge layer (L) [9]. The sensitivity changes drastically if $D \leq 2L$ either by control of D for pure $SnO_2$ or by control of debye length (D/L) for impurity doped elements. Xu *et. al*. have pointed out that the gas sensitivity increases sharply as the diameter of tin oxide crystallites becomes smaller than twice of the depth of the space-charge layer(3nm) [10-12].

Several approaches have been studied for improving the sensing properties of gas sensors and decreasing the working temperature, including the addition of active catalysts, the reduction of grain size, and the use of special measurement techniques [10]. The firing is needed to develop the electrical properties and for the adhesion of paste to the substrate Also the grain size of $SnO_2$ is the function of sintering temperature [13]. The selection of appropriate firing temperature is necessary for the sensor fabrication in order to achieve the highest sensitivity for a particular species of gas. Thus keeping in view the response of sensor has been studied for three different PbO (1 % wt) doped $SnO_2$ sensors fired at three different temperatures ($650^0$ C, $750^0$ C, $850^0$ C).

## 2. Experimental

A set of three sensors were prepared by screen printing technique and fired at $650^0$ C, $750^0$ C and $850^0$ C respectively as shown in Fig. 1. It consists of gas sensing layer ($SnO_2$), a pair of electrodes underneath the gas sensing layer serving as a contact pad for sensors, and a heater element on the back side of the substrate. The gas sensing material, $SnO_2$ doped with 1 % PbO (by weight) was prepared in our laboratory. The active ingredients of the paste were tin oxide, glass frit (lead glass matrix) and a fluidizing agent [4]. The tin oxide powder was prepared by the process reported earlier [14]. For the preparation of doped paste dopant (PbO) was added to $SnO_2$ in calculated amount with cellulose based thinner. Firstly, PbO is weighed and mixed with tin oxide paste in a ball mill. The composition is thoroughly mixed by ball milling process for 8 to 10h. The thermistor pattern is screen printed first (paste NTC 2413 ESL), dried at a temperature of $100^0$ C and fired at $950^0$ C. In the second step, finger electrode pattern is screen printed using silver conductor paste (No. PD 6176, DuPont) and dried at a temperature of $100^0$ C. Subsequently, a heater element is screen printed on the back side of the substrate using silver palladium conductor paste (No. C1214, Heraeus, GmbH) which is dried at the same temperature. Now the dried screen printed films are fired at $850^0$ C. In the third step, PbO-doped tin oxide pastes was screen printed over the electrode pattern and the print was allowed to dry at a temperature $100^0$ C for 20 min. The dried film was then fired in a thick film furnace (DEK model 840). A set of three sensors fired at different temperatures i.e. $650^0$ C, $750^0$ C and $850^0$ C respectively were prepared and they were exposed to varying concentration of acetone, methanol, and propanol in a locally developed test chamber having volume 2047 $cm^3$ kept at metal base. The change in resistance

of sensors is measured using KEITHELY 195A multimeter. The testing was carried out in a test chamber with a provision to inject the test gas. The gases were injected into chamber one by one. After exposing one particular gas the chamber was left open for some time and the contents of the test chamber was flushed with clean air allowing the sensor to recover to its original state. After the sensor recovers to the original value, new gas is injected to get the effect of individual gas accurately. The schematic diagram of the measurement setup is shown in Fig. 2.

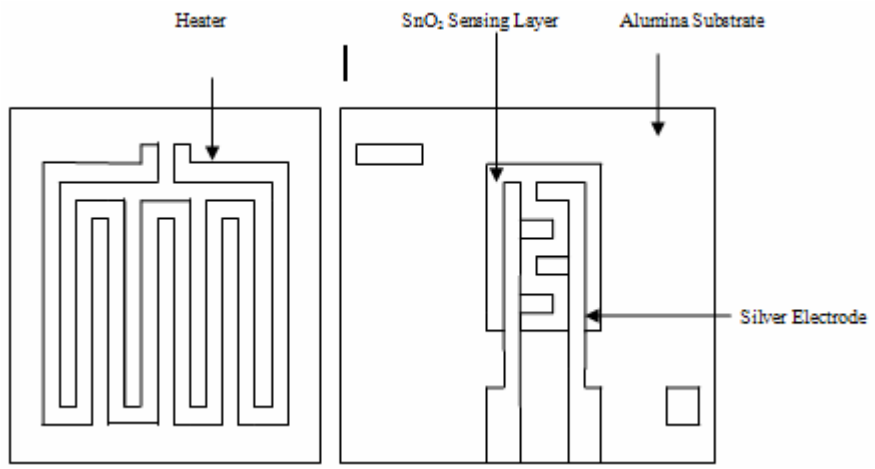


**Fig. 1.** Schematic of fabricated sensors.

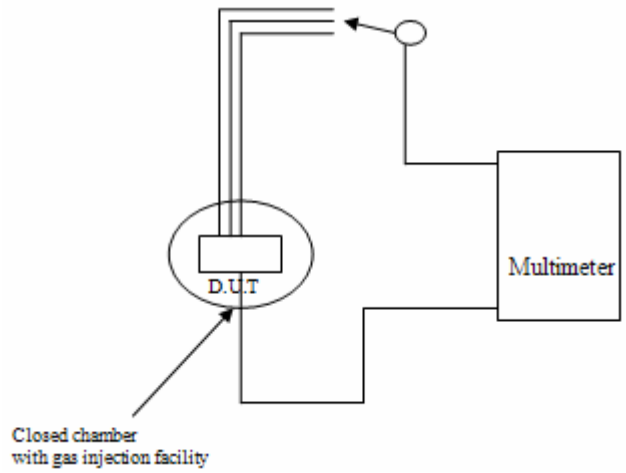


**Fig. 2.** Schematic diagram of measurement setup.

## 3. Results and Discussion

### 3.1. Performance Characteristics of the Sensor

The sensitivity of three fabricated sensors was studied at different fixed operating temperature with varying concentration of acetone, methanol and propanol (Figs. 3-5). It is clear from the Fig. 3 that sensitivity of sensor fired at $850^0$ C increases with the operating temperature beyond $150^0$ C (below this temperature the sensor has very poor sensitivity) and show a peak sensitivity at operating temperature $250^0$ C for methanol and propanol whereas peak sensitivity of acetone is found at

$200^0$ C. The sensitivity curves for acetone and methanol are very close to each other at this firing temperature.

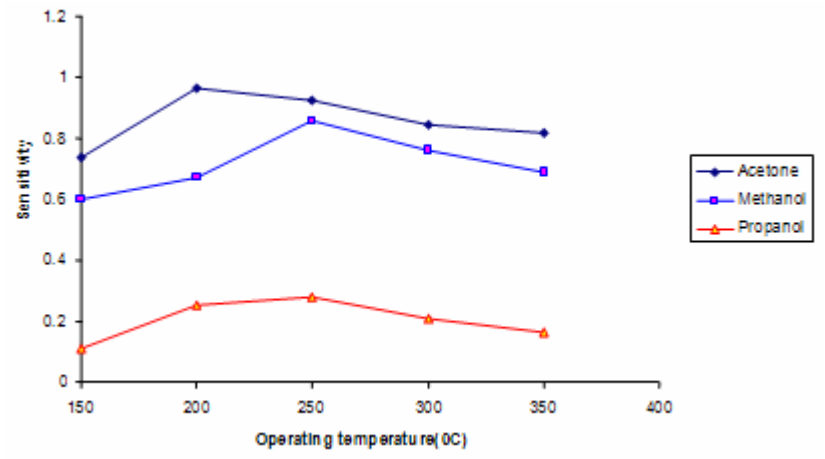


**Fig. 3.** Sensitivity response of sensor with variation in operating temperature fired at $850^0$ C.

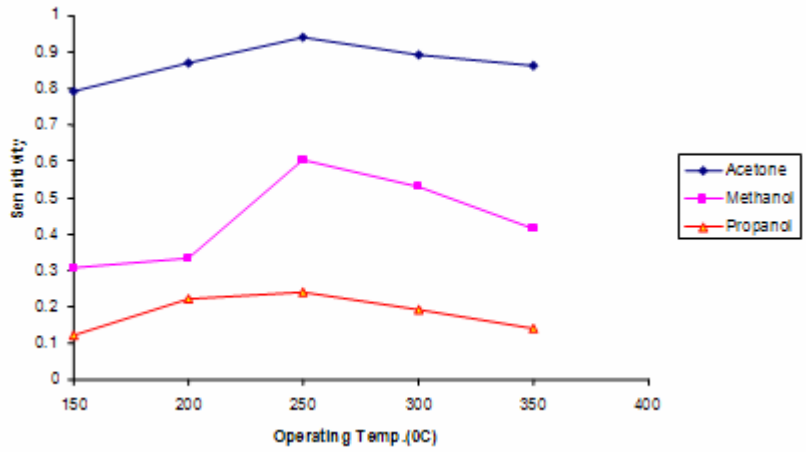


**Fig. 4.** Sensitivity response of sensor with variation in operating temperature fired at $750^0$ C.

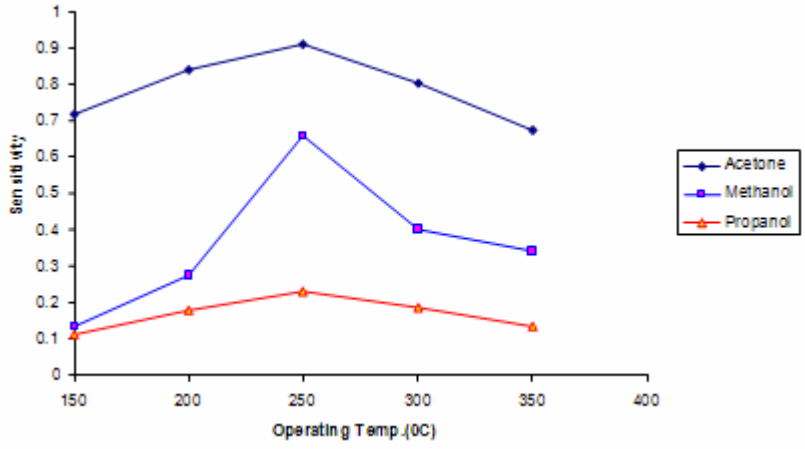


**Fig. 5.** Sensitivity response of sensor with variation in operating temperature fired at $650^0$ C.

The sensors fired at $650^0$ C and $750^0$ C (Figs. 4-5) show peak sensitivity at operating temperature $250^0$C for all the vapors. These Figs. (3-5) also show that all the three sensors possess highest sensitivity for acetone, followed by methanol and least for propanol. The variation of sensitivity of the sensors for acetone, methanol and propanol with firing temperature is shown in Fig. 6. It is evident from the figure that the sensor fired at $850^0$ C shows better sensitivity towards acetone than the sensor fired at $750^0$C and $650^0$C for an operating temperature of $250^0$ C. However at lower firing temperature i.e. at $650^0$ C, the sensitivity for all the selected organic compounds reduces significantly.

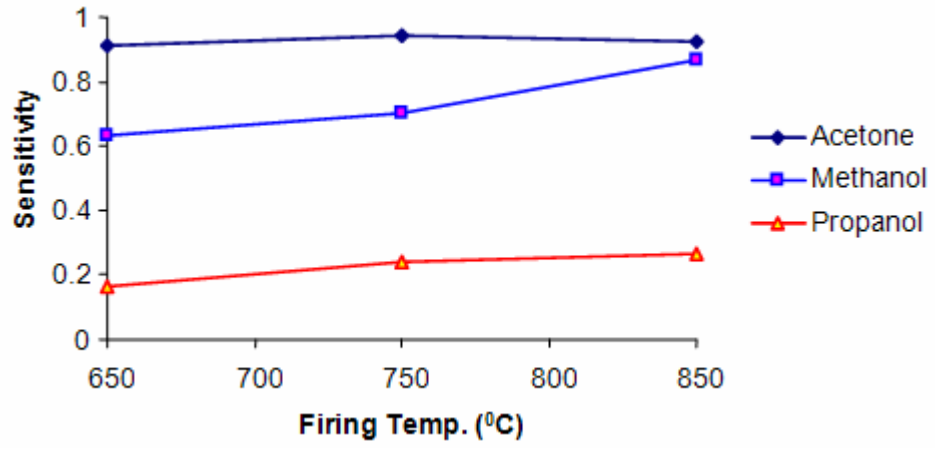


**Fig. 6.** Sensitivity variation of the sensor with firing temperature at operating temp. of $250^0$ C.

### 3.2. Gas Sensing Mechanism of PbO-doped $SnO_2$

It has been already proposed that on $SnO_2$ surface oxidative dehydrogenation of alcohols [15], causing the formation of intermediate products is mainly responsible for high sensitivity. In the operating temperature range ($150^0$ C-$300^0$ C) of the sensor, alcohols transform itself into a variety of intermediate products. G. Neri et. al. [16] have proposed that at the operating temperature ($300^0$ C-$600^0$ C) of sensors, adsorbed alcohols molecules are very reactive and easily oxidized to form $CO_2$. They concluded that methanol decomposition follows mainly the dehydrogenation pathway and gave the reaction scheme which is being reproduced for convenience:

1. $CH_3OH_{gas} \longrightarrow CH_3O_{ads} + H_{ads}$
2. $CH_3O_{ads} + O^-_{ads} \longrightarrow CH_2O_{ads} + ½\ H_2O + e^-$ or
   $CH_3OH_{ads} \longrightarrow CH_2O_{ads} + H_{ads}$
   $CH_2O_{ads} \longrightarrow CH_2O_{gas}$
3. (a) $CH_2O_{ads} + O^-_{ads} \longrightarrow HCOO^-_{ads} + H_{ads}$;
   (b) $HCOO^-_{ads} \longrightarrow CO_{2gas} + H_{ads} + e^-$
   (c) $H_{ads} + H_{ads} \longrightarrow H_{2gas}$

According to these reactions, on the exposure of methanol on oxide surface, first the methanol molecules decompose in methoxy group ($CH_3O_{ads}$), which further decomposes in adsorbed formaldehyde groups ($CH_2O_{ads}$), a part of $CH_2O$ also desorbs as $CH_2O_{gas}$. Finally the reaction of remaining $CH_2O$ with adsorbed oxygen $O^-_{ads}$ results in formation of unstable format like species $HCOO^-_{ads}$ which further decomposed in $CO_2$. Consequently, the electrons are then returned back to metal oxide, resulting in an increase of conductance that represents the response of the sensor. The hydrogen left in dehydrogenation process, combine to form molecular hydrogen $H_{2gas}$.

Various Ketones adsorbing with their carbonyl group on polycrystalline $SnO_2$ are attacked by OH groups at the double bond and also form carboxylate groups, e.g. Acetone reacts on hydroxylated $SnO_2$ to give acetate [17]. Acetate can decompose via following equations to give CO and $CO_2$ [17].

$$CH_3O_{lat}O_{lat} \longrightarrow CH_4\,(gas) + HCO_{lat}O_{lat}$$
$$HCO_{lat}O_{lat} \longrightarrow CO_2\,(gas) + H_{ads} + 2Vo$$
$$HCO_{lat}O_{lat} \longrightarrow CO\,(gas) + O_{lat}\,H + Vo$$

The reactions produce oxygen vacancies on the surface with a maximal rate between 700 and 740 K.

The gas sensing mechanism is based on the change in the conductance of the oxide in the sensing layers. The oxygen absorbed on the surface of the materials influences the conductance of the oxide-based sensor [18]. Another important issue is the particle size of the materials. The smaller the grain size, the larger the specific surface area, which results in greater oxygen adsorption and higher sensitivity [19]. The sensor operating temperature also affects the properties of the materials, leading to a difference in the sensitivity of the sensor.

The surface of $SnO_2$ can adsorb atmospheric oxygen so easily that their valence electrons will transfer to oxygen atom or molecule, and then the adsorbed oxygen becomes chemisorbed oxygen ion $O^-$ or $O_2^-$[20]. When the operating temperature increases in air, the state of oxygen adsorbed on the surface of $SnO_2$ will undergo the following reactions [21].

$$O_2\,(gas) \longleftrightarrow O_{2\,(ads),}$$
$$O_{2\,(ads)} + e^- \longleftrightarrow O_{2\,(ads)}^-\,,$$
$$O_{2\,(ads.)}^- + e^- \longleftrightarrow 2O_{(ads)}^-\,,$$
$$O_{(ads)}^- + e^- \longleftrightarrow O_{(ads)}^{2-}.$$

The reducing gas acting on the oxide's sensor surface can be explained by eqn.

$$R + O^-\,(ads) \longleftrightarrow RO + e^-$$ [18].

Where R is the reducing gas, $O^-$ is the oxygen adsorption $e^-$ are electrons. When reducing gas, such as alcohols vapor ( methanol, ethanol and propanol) and acetone, get in touch with $SnO_2$ , they will be partly adsorbed on the surface and then undergo the following reactions[20]:

$$2R\text{-}CH_2OH + O^{2-}\,(chem.) \longrightarrow 2\,R\text{-}CH_2O^- + H_2O + e^-$$

The electrons in the reducing gaseous molecules released onto the surface of the $SnO_2$ lead to the increase in electron concentration and the decrease in its resistance. The higher the concentration of the reducing gas, the lower the resistance, i.e. the sensitivity increases with the increase in the concentration of reducing gas [20].

## 4. Conclusion

It is concluded that the firing temperature and operating temperature has a strong influence on the sensitivity of PbO-doped $SnO_2$ sensors for acetone, methanol and propanol. The samples fired at $850^0$ C shows maximum sensitivity at an operating temperature of $250^0$ C for all gases except acetone for which it is found to be $200^0$ C. At lower firing temperatures, the sensitivity of the sensors show a reducing trend for acetone, methanol and propanol. Thus the firing temperature of $850^0$C is suitable for development of sensor to detect acetone, methanol and propanol. At this firing temperature, the

sensitivity of acetone and methanol is very close. In order to achieve better separation between the sensitivity for acetone and methanol firing temperature of $650^0$ C is suitable.

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