# ZnO thin film as methane sensor

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**Abstract.** Methane ($CH_4$) sensitivity of zinc oxide (ZnO) thin film has been studied in the present work. The sensor element comprises of a chemically fabricated ZnO semiconducting layer and a layer of palladium (Pd) as catalyst. The catalyst layer was formed on the surface of semiconducting ZnO following a wet chemical process from palladium chloride ($PdCl_2$) solution. Fundamental features of a sensor element e.g. sensitivity, response time and recovery process has been studied. The effect of operating temperature on performance of the sensor material has been investigated and a choice of optimum temperature was made at around 200°C. The sensor element exhibited reasonable sensitivity of about 86% at this temperature in presence of 1 vol% methane ($CH_4$) in air.

**Key words:** thin film, palladium catalyst, ZnO, methane sensor.

## 1. Introduction

Since long it has been known that adsorption of reducing gas molecules results in decrease in electric resistance of oxide materials. Among oxide semiconductors, ZnO and $SnO_2$ are mostly studied and are known to have substantial gas sensitivity [1]. These oxides are non-stoichiometric independent of the preparation technique used. The materials are characteristically n-type semiconductors due to non-stoichiometry associated with oxygen vacancy and/or metal excess acting as donor states providing conduction electrons. However, the overall surface resistance of such films is greatly influenced by chemisorption (chemical absorption) of oxygen from air on the surface and at the grain boundaries. The chemisorbed oxygen traps conduction electrons and remains as negatively charged species ($O_2^-$, $O^-$ or $O^{2-}$ depending on temperature) on the surface [2]. The process results in an increase of surface resistance. In presence of a reducing gas, the trapped electrons are released due to reaction between the gas molecules and the negatively charged chemisorbed oxygen species resulting in a decrease in resistance of The material. The gas molecules are oxidized in this process. For example, the hydrocarbons are converted to $CO_2$ and $H_2O$ due to reaction with chemisorbed oxygen species. When the gas is removed from the sensor environment, the resistance again increases and the material recovers to original resistance.

In general, these materials are rarely used as a single phase for a gas sensor and their gas sensing characteristics are usually well modified by adding a small amount of catalysts. Platinum and palladium are well-know active catalysts, which enhance the sensitivity against reducing gases [3]. Gold (Au), silver (Ag) is also utilized to enhance sensitivity [4] of oxide materials. It is believed that the catalyst layer promotes chemisorption process and thus increases the density of chemisorbed oxygen species, which are the reaction centres for reducing gas molecules.

Both ZnO and $SnO_2$ have been tried by different workers to check sensitivity against $CH_4$ [5-10]. Apart from ZnO and $SnO_2$, $Al_2O_3$-based semiconducting ceramics and nanocrystalline zinc gallate ($ZnGa_2O_4$) has also been studied for methane sensing [11-12]. $CH_4$ is highly combustible and can form explosive mixture with ambient air. Thus it is important to monitor the low concentration of $CH_4$ (and in general lower hydrocarbons e.g. propane, butane etc.) escaping into the atmosphere for both industrial process control and reduction of environmental pollution [13].

The oxide sensing layer (ZnO or $SnO_2$) has been fabricated in different physical forms such as thin film, thick film, bulk pellets etc. However, the thin film form is expected to be most effective since sensing is basically a surface phenomenon. Various physical and chemical techniques have been utilized to obtain thin films of these semiconductors. The physical techniques includes thermal oxidation, reactive evaporation, electron beam evaporation, different forms of sputtering (eg. magnetron sputtering, rf sputtering) etc. On the other hand sol-gel and spray pyrolysis are the mostly used chemical techniques to fabricate gas sensitive layers of ZnO and $SnO_2$. Different techniques of catalyst loading have been employed by workers. These include spray technique [14], impregnation technique (this is particularly useful for bulk doping) [3], Chemical vapour deposition [9], photo deposition [15], sputtering and evaporation [2, 16-17].

In the present study, methane sensing characteristics of chemically deposited thin film ZnO with Pd catalyst has been examined. Compared to physical techniques, chemical techniques are much simpler and cheaper and thus can offer the desirable cheapness as far as the cost of the sensor material is concerned. The process being relatively cheap and less energy expensive can be easily transferred to industrial level also. The sensitization of the films with

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palladium (Pd) catalyst was also carried out following a novel wet chemical method. Earlier we have reported the results of LPG sensing characteristics of chemically deposited ZnO films sensitized with Pd following this technique [18]. The present results are of experiments on the sensing characteristic of resistive-type ZnO film sensor to $CH_4$. The role of construction of the sensor assembly along with the measuring set-up on the sensing properties has also been discussed.

## 2. Experimental

The details of zinc oxide film deposition following chemical dipping from sodium zincate or ammonium zincate bath have been reported elsewhere [19-20]. The process involves successive dipping of a substrate in the zincate bath and hot water. The film was deposited on precleaned glass substrates (microscope slides). The substrate was immersed first in the zincate bath and then in hot water (maintained near boiling point). The reaction leading to the formation of ZnO for ammonium zincate bath is as follows:

$$(NH_4)_2ZnO_2 + H_2O = ZnO + 2NH_4OH.$$
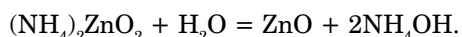
Subsequent heat treatment in air leads to phase pure ZnO. Films in the thickness range 1.0 – 5.0 mm can be prepared by varying the deposition parameters.

The surface sensitization of the films, also following a novel chemical dipping process from palladium chloride solution, has been reported earlier [18]. This involves multiple dipping of the film in a solution of palladium chloride ($PdCl_2$) in ethyl alcohol ($C_2H_5OH$) followed by heat treatment in air at 200°C. The sheet resistance of Pd loaded ZnO layer is of the order of few ohms before heat treatment since it is primarily controlled by the continuous palladium layer, which is metallic in nature [16]. Heat treatment resulted in agglomeration of the Pd layer and the ZnO layer controls the sheet resistance. It is of the order of $10^6 - 10^8$ ohm after heat treatment [16, 18]. Decrease in surface coverage after agglomeration process has been experimentally confirmed [1,16]. XRD results indicate the presence of palladium oxide (PdO) and palladium-zinc alloy phase after heat treatment [18].

The palladium sensitized ZnO film deposited on glass substrate was placed inside a quartz tube furnace (3.2 cm diameter and 30 cm length). The film thickness was approximately 5.0 mm. Approximately 20 mm long conducting silver (Ag) contacts, separated by 5 mm, were made on ZnO film having dimensions 3x2.5 cm². Prior to gas exposure, the sensor resistance was allowed to equilibrate at each operating temperature for a reasonable time (about 30 minutes) in order to avoid zero drift. The experimental setup for gas sensing measurement is shown in Fig. 1.

As the sensor is heated from a low operating temperature to a higher one, the resistance decreases sharply due to semiconducting nature of ZnO. This is followed by a slow decrease resulting from thermal
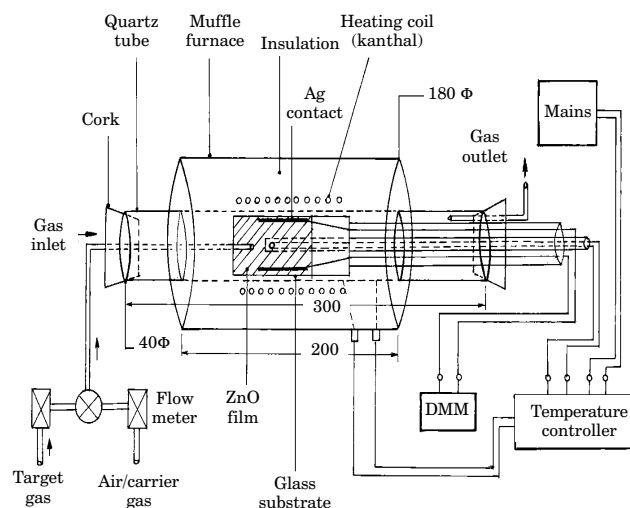


Fig. 1. Experimental set-up for the measurement of methane sensing characteristics (all dimensions in mm)

equilibration process of donor defects. Finally a stable value of surface resistance is obtained in air. This value of sensor resistance is defined as the initial equilibrium value in air ($R_{air}$). Subsequently, the target gas diluted with air was allowed to flow through the tube and the sensitivity was monitored through decrease in sensor resistance for an exposure time of 30 minutes. The gas concentration was fixed by adjusting the flow rates of the target gas ($CH_4$) and carrier gas (air). Finally, the gas flow was turned off and the sensor resistance was allowed to recover in air. The gas inlet-outlet facility is shown in the figure (Fig. 1). The recovery characteristic was also monitored as a function of time.

## 3. Results and discussions

Figure 2 shows the response and recovery characteristics of the Pd-sensitized ZnO film in presence of 1 vol% $CH_4$ in air at different operating temperatures. The exposure time to target gas (methane) was 30 minutes. The flow rate of the target gas was set to 100 ml/min.

The figure shows a reduction of sensor resistance ratio ($R_{gas}/R_{air}$) with time. The ratio of the sensor resistance in presence of the target gas (i.e. $R_{gas}$) to that in air (i.e. $R_{air}$) is a measure of the sensitivity (S) [21-22]:

$$S = R_{gas}/R_{air}.$$

Thus S is less than unity for reducing gases, since the sensor resistance decreases in a reducing atmosphere. The sensitivity is also often defined as $R_{air}/R_{gas}$ [12], in which case it is a quantity greater than 1 (one) for reducing gases.

On exposure to target gas, the sensor resistance decreases rapidly with time and thereafter reaches a stable value. This value of sensor resistance, which corresponds to the completion of sensing process, is called the equilibrium resistance value. From this value of equilibrium resistance [$(R_{gas})_{eq}$], percent sensitivity can be calculated. The percent sensitivity is also often referred to

as saturation sensitivity. The percent sensitivity i.e. the percent reduction of sensor resistance is given by [21]:

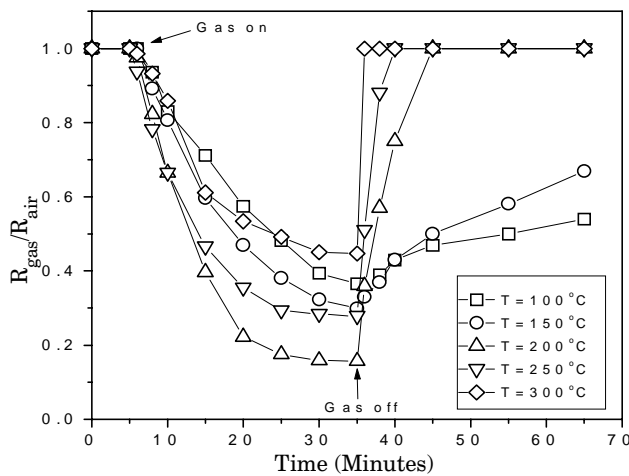$$S\% = [\{R_{air} - (R_{gas})_{eq}/R_{air}] \times 100.$$



Fig. 2. Sensing and recovery characteristics in presence of 1 vol% CH4 in air at different operating temperatures

It is seen from Fig. 2 that reasonable gas sensing action begins at a temperature of as low as 100°C. However, the attainment of equilibrium resistance in presence of target gas was unusually long. At lower operating temperatures (100°C and 150°C), the sensing process was incomplete even after 30 minutes of gas exposure. At 200°C, the resistance reduction continues for more than 20 minutes before it gets stabilized. For even higher temperatures, the resistance stabilizes approximately after 15 minutes.

The recovery process is also incomplete at low operating temperatures. It is incomplete at low temperatures (100°C and 150°C) even after 30 minutes. Both sensing and recovery characteristic curves becomes better with increasing operating temperatures. Figure 3 shows the variation of percent sensitivity (S%) with temperature. Table 1 shows the sensitivity (S%) and recovery property for different operating temperatures.
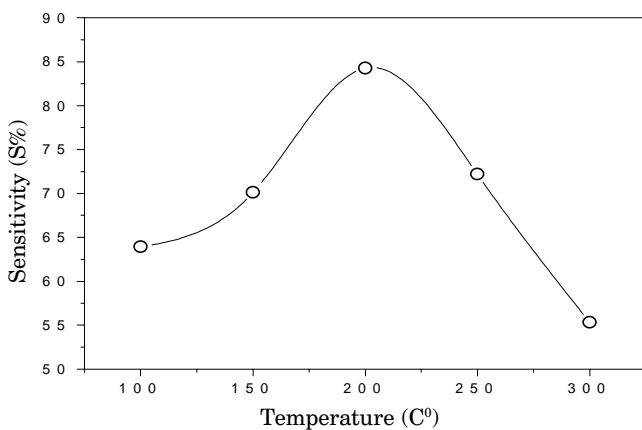


Fig. 3. Variation of sensitivity with temperature

Table 1
Sensor characteristics to 1 vol% CH$_4$ in air

| Operating Temperature | Sensitivity (S%) | Recovery Time (Minutes) |
|---|---|---|
| 100° C | 63.5 | Incomplete in 30 minutes |
| 150° C | 70.1 | Incomplete in 30 minutes |
| 200° C | 84.3 | 10 min (approx.) |
| 250° C | 72.2 | 3 min (approx.) |
| 300° C | 55.3 | Less than 1 min |

The maximum sensitivity is obtained at 200°C for the present films. This is comparable, in fact somewhat on the lower side, than those normally reported in literature [5, 12, 23].

It may be noted that in these experiments the equilibration time in both directions e.g. sensing and recovery were abnormally high. The results are not obviously intrinsic to the sensing device. On the other hand they are characteristics of the overall experimental set up including the furnace and its tubular chamber. As the volume of the chamber was unusually large, change of gas concentration was never instantaneous, which is a prerequisite for the accurate measurements of response and recovery times of a gas sensor. The response time is a very important parameter for commercial applications of sensor materials. It is generally defined as the time required for 90% of the total resistance reduction. Since the total resistance reduction is given by [$R_{air} - R_{gas(eq)}$]; response time is the time required for 90% of this change. It is not possible to measure the response time in the present setup since it took unusually long time to reach $R_{gas(eq)}$. The response and recovery times actually included equilibration time of the gas concentration inside the chamber and would obviously depend on the overall volume of the chamber as well as the flow rate. Therefore, it is essential that the chamber volume must be maintained at a minimum possible level for accurate measurements of response and recovery times. The present experimental set up is, however, good enough for the determination of sensitivity at different temperatures.

In the present set up, the attainment of a particular operating temperature also required a fairly long time as the heating is done externally and the volume of the chamber is large. Therefore, a different set up was used for accurate measurements with the objective of designing a sensor assembly with internal heating system so that the requisite operating temperature could be reached quickly.

For this purpose, as in conventional designs, a hollow tubular substrate was used to hold the film and the internal hole was used as the space for the resistive heating element. The substrate was a glass or alumina tube of 15 mm length, 6.52 mm external diameter and 3.3 mm internal diameter. The wall thickness was about 1.6 mm. A kanthal wire (30

SWG) was used in the form of a heating coil, placed inside the hollow tube, in order to operate the sensor element at the requisite temperature. Finally electrical contacts on the ZnO film were made at the two ends of the cylindrical sensor element, by using silver paste. The contacts were cured by heating to 200°C in air for 30 minutes. The solder connections were made on a 4-pin base.
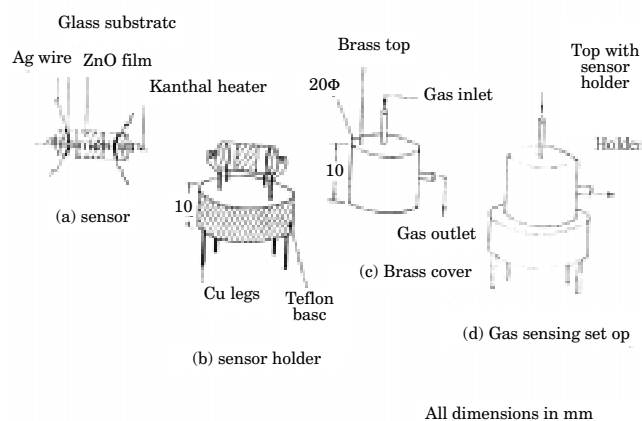


Fig. 4. Sensor element and sensor assembly for gas sensing measurements

Figure 4 shows the schematic diagram of the different components of the sensor element mounted on a Teflon base with copper (Cu) pins as electrodes. In order to make measurements of the sensor characteristics; the mounted sensor was covered with a small brass cover having gas inlet and outlet tubes that allowed the target gas to come in contact with the sensor element. The brass cover was of 20 mm inner diameter and 10 mm height.

A dc source was used to supply power to the heater coil. The temperature measurements were carried out on the surface of the cylindrical tube (substrate) using a Pt wire. The resistance measurement of the platinum wire having
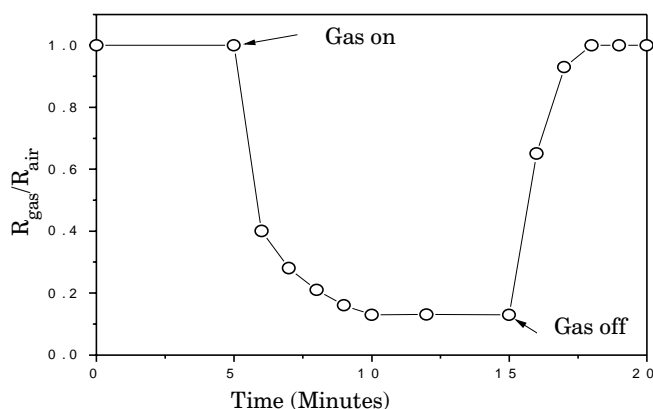


Fig. 5. Sensor response and recovery for 1 vol% CH4 at 200°C

known value of temperature coefficient of resistance indirectly provided the temperature of the sensor. The sensor element with internal heating system helps to attain the requisite operating temperature quickly.

Figure 5 shows the sensing and recovery characteristics of the sensor element at 200°C. The response time in this case is only one minute.

It is seen that the attainment of equilibrium resistance $[(R_g)_{eq}]$ is much faster with the miniaturized sensor assembly. It takes approximately 5 minutes compared to 20 minutes in tube furnace. The recovery process is also complete within 3 minutes whereas it took about 10 minutes in the furnace. This clearly demonstrates that the reaction of the sensor surface with the target gas is much faster in the miniaturized design. Also the recovery process is much faster as the gas molecules leave the sensor environment quite fast. The sensitivity of about 86% is almost similar to that obtained in the tube furnace.

## 4. Conclusions

It is seen from the Pd-sensitised ZnO obtained following a simple chemical technique responds to 1 vol% $CH_4$, which is on the lower side of the hazardous explosion range. It is also established that construction of the sensor influences some of the sensor properties such as response and recovery times. A reasonable sensitivity of approximately 86%, fast response time of less than one minute and a moderately fast recovery (approximately 3 minutes) is observed at 200°C. Although the operating temperature of 200°C is relatively on the lower side, the maximum sensitivity of 86% should be somewhat higher for application purpose. Reduction of film thickness and use of other catalysts (Pt, Au etc.) possibly can enhance sensitivity. Even further miniaturization of the sensor assembly can help to improve the response and recovery times, which are of immense importance for practical applications. Experiments in these directions are in progress. Also the selectivity and stability of the sensors are to be examined.

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