DEVELOPMENT OF HYDROGEN SULPHIDE MONITOR *

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Introduction

In many process controls, production centres, or in environmental monitoring, the measurement of concentration of one of the gases is often a key factor. In such a situation, a sensor provides the necessary interface between the gas under detection and the back up electronic instrumentation. In the past two decades, this field has been dominated by developments of sensors based on metal oxide semiconductor thin / thick films. A wide variety of materials like SnO₂, WO₃, MoO₃, TiO₂, ZnO, etc. have been investigated and a host of sensors have been developed for many toxic and hazardous gases including NOₓ, NH₃, CO, H₂, H₂S, halogen, PH₃, hydrocarbon, etc. However, the challenge of producing sensors that respond only to a specific gas - and to no other gas - as well as have quick response and long life in a hostile ambiance continues to attract the attention of scientists and technocrats. The present article describes the sensor development work carried out for Hydrogen Sulphide (H₂S) at Technical Physics & Prototype Engineering Division, BARC, to meet the condition of specificity of the sensors' response to H₂S.

(*The H₂S Monitor System developed by TPPED, BARC, was awarded the Best Prototype Presentation prize at the National Seminar on Physics & Technology of Sensors, held at University of Pune, during February 14-16, 2000.)

H₂S is a toxic gas and it is widely generated in nature, for example, in swamps and geothermal sources. This gas is used in large quantities in research laboratories for growing sulphide crystals and in heavy water plants as a process gas for producing D₂O. Hydrogen sulphide reacts vigorously with living tissues and causes several effects on health depending on the gas concentration. Although human nose can detect even 0.2 ppm H₂S - whereas the occupational exposure limit for H₂S is 10 ppm-8hr, our senses cannot readily distinguish different concentration levels. Also H₂S paralyses the olfactory system and, therefore, it is considered more dangerous than CO. Constant electronic monitoring of H₂S gas concentration in the ambient is the only means of protection against the ill effects of the gas. For this the gas must be detected in ppm levels in air by selective and sensitive sensors, especially when it is encountered in the presence of other gases in a wide variety of industrial and environmental situations.

Fig. 1 Schematic of sensor assembly highlighting the way film is laid on the alumina substrate, nichrome heater is attached on the alumina plate and the thermistor is located for temperature monitoring. Also shown is the top view indicating the gold contacts used for measuring film conductance.

Construction of H₂S Monitor

H₂S Monitor developed by TPPED consists of two parts; (i) Sensor Head, and (ii) Control cum Display Unit. The Sensor Head, which is the sensing element, consists of a
thin film of one of the metal oxides (e.g. SnO$_2$, WO$_3$, MoO$_3$, etc.) deposited on Al$_2$O$_3$ substrates. The film is suitably doped to enhance the sensitivity and also to impart specificity to H$_2$S. The sensor element is fixed to a tiny heater using a glass epoxy. The heater is made by winding nichrome wire on an Al$_2$O$_3$ plate which also has a small thermistor fixed to it on the reverse side. A low working temperature solder glass was specially developed for fixing various components of the sensor assembly. A schematic of the sensor assembly is shown in Fig.1. As the concentration of H$_2$S in the ambient picks up, the conductance of the sensor film changes.

By measuring this change, the concentration of H$_2$S is inferred. In order to ensure that this change in conductance is only due to H$_2$S, it is essential to keep the film temperature fixed. To achieve this, a controller unit is used, and the sensor assembly is connected to an electronic temperature controller circuit that ensures the sensor film operates at a constant temperature at a preset value in the range ~ 180° - 250° C with a control accuracy of ± 0.2° C. The sensor assembly and temperature controller circuit are sealed in a metal tube of 30 mm in diameter and 100 mm in length. The controller side is hermetically sealed while sensor compartment has a flame arrester consisting of a SS diaphragm which allows access of gases to the sensing element. Some further details of both the sensing element and control unit are given below.

Procedure for Deposition of Sensor Films

Three different techniques have been used to deposit thin films of metal oxide on semiconductor material, viz. (i) sequential evaporation of metals on Al$_2$O$_3$ substrate held at 250° C under high vacuum conditions and subsequent oxidation / sintering of the films at 800° C in flowing O$_2$, (ii) deposition of films on Al$_2$O$_3$ substrate from 40 mm dia target pellet using rf sputtering and subsequent sintering as described for (i), and (iii) laser ablation of composite target material and deposition on substrates held at 600° C under partial pressure of O$_2$. Prior to deposition of film by any of these techniques, two Pt wire electrodes are fixed on the substrates using gold paste with setting temperatures above 850° C. These electrodes ensure stable contact resistance on the sensor film when it is used at operating temperature of 200° C continuously over time periods of several months at a stretch.

The structure related characterization of the sensor films was also carried out using analytical techniques such as X-ray diffraction, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). Characterization of the sensor films for electrical conductance and other important properties included measurement of (i) Sensitivity, S = (s gas - s air)/s air, (ii) Calibration of the curve, S versus gas concentration, (iii) Response/Recovery times, (iv) Specificity, (v) Base line, (vi) Long term stability, and (vii) Operational life.

![Fig.2 Response of a typical sensor to 50 ppm H2S, ~100 ppm SO2 and 1000 ppm H2. Note the specificity of the sensor for H2S. The response time (T90) is ~1 min.](image-url)

The sensor characteristics are shown in Fig.2. It is seen that sensor response to SO$_2$...
and \( H_2 \) is negligible as compared to \( H_2S \). This shows the selectivity of the sensor. The response time (T90), time taken to reach 90% of the final value, is 1 min and recovery time (T10), time taken to reach 10% of starting value, is about 10 min. At the operating condition, the electrical resistance of different sensor films in air varies from 1 - 100 M ohm depending upon the composition of sensor film. The film resistance comes down to 10 K ohm at 50 ppm \( H_2S \). Sensors based on \( \text{SnO}_2(\text{CuO}), \text{SnO}_2(\text{ZrO}_2) \) and \( (\text{W}+\text{Mo})\text{O}_3 \) materials have been developed. It is observed that sensor response of \( \text{SnO}_2(\text{ZrO}_2) \) and \( (\text{W}+\text{Mo})\text{O}_3 \) remains constant over prolonged periods extending over several months of continuous use.

**Features of Control Unit and Full System**

*Control Unit:* In most of the cases, the response of the sensor to gas concentration was found to be non-linear.

Fig. 3 shows, for example, the variations of film conductance as a function \( H_2S \) concentration. There are different approaches to design an electronic circuit which could convert the non-linear response to linear output. In the present work, a piece-wise linearization approach is used employing voltage dependent amplifier circuits. The voltage signal from the sensor film showing nonlinear variation of conductance with \( H_2S \) gas concentration, as shown in Fig.3, is converted to a linear output and displayed as gas concentration in 0-50 ppm range. A linear output of 4-20 mA is also provided for data logging. For field measurement of \( H_2S \) gas concentration in air, the sensor head is connected to the control unit using a five core screened cable which can be extended up to 500 metres. Fig.4 shows the photograph of the monitor with a sensor head connected to it.

![Figure 4](image.png)

**Fig. 4 Photograph of \( H_2S \) monitor showing sensor head and control unit.**

The monitor has a preset alarm limit which can be adjusted over the entire range. A piezobuzzer gets activated when gas concentration near the sensor head exceeds the preset value and an LED provided on the front panel starts blinking. This monitor is also provided with a fault detection circuit. In this case, an LED will be ON whenever heater/thermistor malfunction. The fault indication would also appear if the supply voltage drops below a preset level. All outputs like alarm and fault are also used to energize relays which could be used to drive any other electronic devices. The monitor has a provision for easy calibration in 0-50 ppm range. Already some of TPPED...
made sensor systems that are currently installed in Heavy Water Plants for field trials have given rich experience to reach stable performance running over many months of continuous use. Experiments are now on to extend this life to over a year.

Conclusion

Solid state sensors based on metal-oxide semiconductor thin films are prepared for H2S monitoring. These sensors are compact, robust, reliable and economical which are suitable for use in industrial environment. Associated control system with linearization circuits and having provision for alarm, fault detection, data logging, etc. has also been developed for monitoring the gas in 0-50 ppm range.