Integrated Hydrogen gas sensing device Based on sputter-deposited Pd thin films

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Abstract

Pd thin film based hydrogen (H_2) gas sensor device working on Pellister-type principle has been developed. The sensor consists of Pt-100 heater coated with RF sputtered Pd thin film (100 nm). The device operates at 150°C in sensor-compensator configuration in a Wheatstone bridge that makes it sensitive to small temperature increments caused due to the presence of H_2 gas. The response of the sensor is integrated with a digital monitor displaying the calibrated values of H_2 gas concentration (independently confirmed using ultrasonic transducer). The sensor device exhibits a minimum detection limit of 0.3% with linear response (0-3.5% H_2), tested in an in-house made dynamic gas sensing set up. The indigenously developed sensor device exhibits reliability, precision, long term stability and consequently a long lifespan > 3 years and is currently being utilized by various users within and outside DAE.

Keywords: RF sputtered Pd thin film, Catalytic, H_2 sensor, Lower explosive limit

Introduction

Environmental sustainability of the energy sources has been the defining foundation of many recent scientific and technology development activities. Consequently, several research groups are rigorously trying to find out alternate solutions to this crisis-like-situation through techniques, which are by and large green and do not add to the existing carbon footprint. In this context, it is probably worth mentioning that Hydrogen (H_2) based energy generation has been a globally accepted practice for obtaining clean energy. Being a clean source of energy, H_2 gas is in high demand in various industrial and commercial applications. However, H_2 is an explosive gas and it is colorless and odorless. The flammability of H_2 is in the range of 4 – 75 % in air. In presence of an oxidizer, hydrogen catches fire explosively. Its 4% (v/v) mixture in air forms lower explosive limit (LEL) and 75% (v/v) is the upper explosive limit (UEL). H_2 gas is used for various sorts of industrial applications such as hydro-desulferization and hydrocracking operation in refineries, ammonia production, metallic ore reduction, rotor coolant in large electrical generator etc. Further, the small sized gas molecules of H_2 are prone to leak through the smallest possible holes and cracks. Hence, the detection of H_2 gas becomes essential even at trace levels in nuclear reactors, power plants, battery house, terminal ballistic research laboratories etc. The production, uses, storage and transportation of hydrogen gas are very risky without sensor. Hence, the H_2 gas monitoring is highly essential in various applications to ensure safety of national property and human life.

There are many methods for detection of H_2 gas as schematically shown in Figure 1. Most of the methods show good response; however they suffer from shortcomings like large size and weight, high cost, time consuming process, requirement of trained personnel to operate them, maintenance and portability

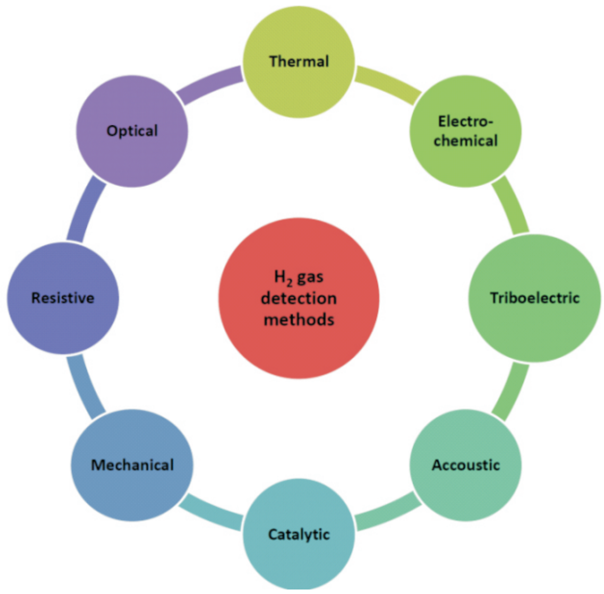

Fig. 1: Schematic diagram representing the methods for H_2 detection.

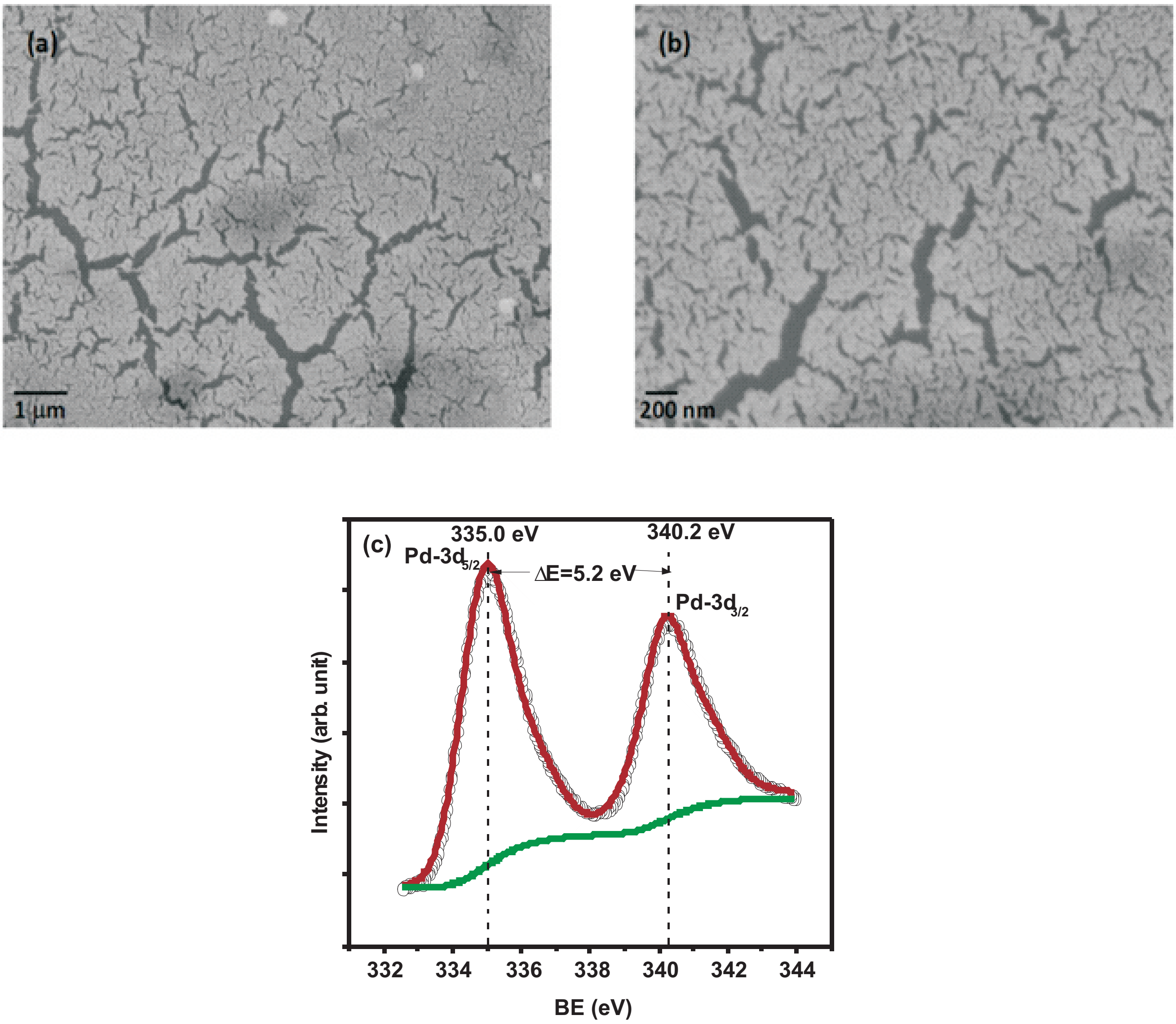

Fig.2: SEM image of as-deposited Pd films on Pt-100 heater at (a) m scale, (b) nano scale (c) XPS spectrum of Pd-3d peak.

issues etc. The above mentioned limitations restrict the continuous operation of such instruments. Both resistive and optical sensors are based on the principle of formation of PdH, leading to surface deformation of the sensor film that may pose repeatability and reliability issues. Although electrochemical type sensors are very sensitive but this type of sensors have short lifespan and narrow range of operating temperature i.e. calibration is highly susceptible to the variation of ambient temperature. Also, triboelectric and mechanical methods of detection are more suitable for lower concentrations. On the contrary, catalytic type sensor operated at an elevated temperature has many advantages such as long lifespan, robustness, simple to operate, easy to install, calibrate and operational in the range of 0-4% H_2 concentration. Catalytic type sensor by Figaro is commercially available with detection range of 30-1000 ppm exhibiting a power consumption of 660mW. Pellistor type Pt/Pd based catalytic sensors are well known to be suitable for hydrogen detection. In this report, we discuss the device development of Pd thin films based H_2 sensor at Technical Physics Division, in collaboration with Electromagnetic Application & Instrumentation Division.

Deposition of Pd films

Standard Pt-100 heaters (10 mm x 2 mm) were used as substrates to fabricate sensor elements. Pd layer of 100 nm (confirmed using a profilometer for thickness measurement) thickness was deposited on both sides of Pt-100 using rf sputtering (photograph shown in Fig. 4(c)). The deposition was carried out at 20W for 8 min under Ar pressure of 0.08 mbar. Fig. 2(a) and (b) shows the scanning electron microscopy (SEM) images of as-deposited Pd-films on Pt-100 heater surface. As clearly seen, the film is very smooth with visible nano cracks which may be attributed to interfacial stress due to lattice mismatch and which may be responsible for better gas diffusion and excellent sensor response towards H_2 gas owing to enhanced surface area to volume ratio. The metallic nature of Pd film was confirmed by X-ray photoelectron spectroscopy (XPS). The Pd-3d$_{5/2}$ peak (Fig. 2(c)) position at 335.0 eV and E ~ 5.2 eV confirm the zero valence state of Pd i.e metallic nature.

Working Principle and Device Configuration

The sensor element (Pd coated Pt-100) and a compensator element (Pt-100)

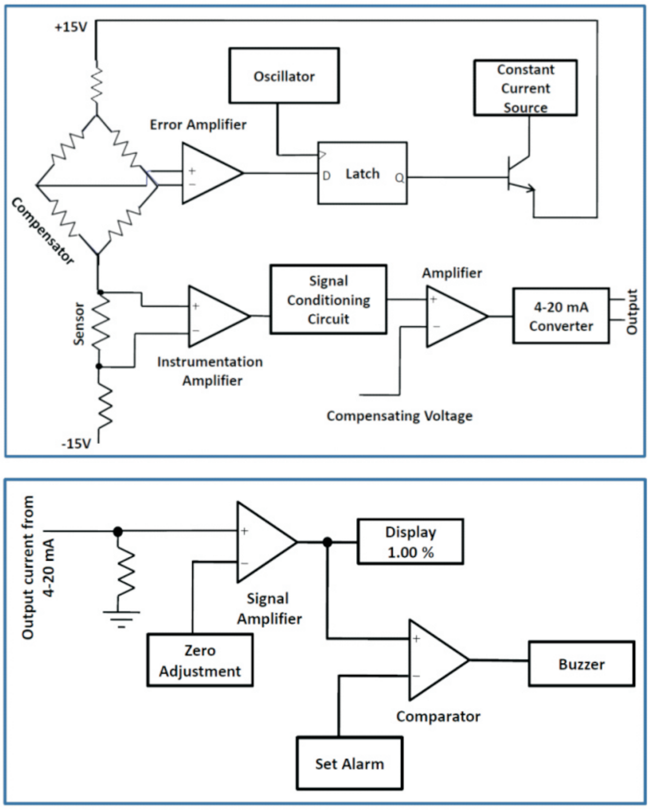

Fig. 3: Block diagram of in-house designed sensor device, (a) sensor unit, and (b) Monitor unit.

are connected in the Wheatstone bridge of an in-house designed temperature controller circuit, whose block diagram is shown in Fig.3(a). The oscillator to yield forced oscillation time that curbs constant current mode. The exothermic reaction of H_2 with O_2, $2H_2 + O_2 \rightarrow 2H_2O$ + 285 kJ/mol, on the sensing element (containing Pd as catalyst, facilitating low heat of adsorption of oxygen on their surface) causes rise in temperature w.r.t the compensator. The circuit transforms the change in temperature of the sensor element into voltage developed between sensor and compensator that is calibrated against H_2 concentration and displayed through an integrated monitor, depicted in Fig. 3(b).

The output voltage is then converted into 4-20 mA using a monolithic current transmitter (AD694 IC). The 4-20 mA current loop helps to keep the sensor away from the control room (< 300 m) where H_2 concentration can be monitored remotely. This facilitates customization of the sensor device unit as per the requirement of different monitoring conditions of users.

The 4-20 mA current is converted into 0-5V with a single terminating resistance, and this voltage is attenuated and displayed as a sensor response directly related to vol. % of H_2 concentration in an integrated monitor unit. With the help of zero potentiometer on the front panel, the zero on the display is adjusted in the absence of hydrogen. The integrated monitor unit also has the provision for alarm setting that can be set as per the user requirement. The actual photographs of the sensor device are shown in Fig. 4. The sensor device consists of a sensor unit (Fig. 4(a) & (b)) in which sensing element (Fig. 4(c)) and compensator along with temperature controller circuit are concealed. This unit is mounted at the location of H_2 gas leakage. The other part is an integrated digital monitor (Fig. 4(a) below the sensor unit) displaying output voltage (calibrated as actual H_2 gas conc.) to be placed at the location of monitoring with provisions of alarm and zero set.

Sensor Calibration

The hydrogen sensing was studied in a dynamical gas sensing set up shown in Fig.5. The H_2 gas was used from a hydrogen generator (Model CIC-PW-SPE500HC) based on the principle of electrolytic splitting of water, and air was used from an oil free air compressor. The H_2 and air were mixed in the desired ratio, to generate various H_2 concentrations (0-3.5 %), and made to flow through the sensor housing mounted in the setup and directed to the exhaust after sensor exposure. To ensure safety measures we did not cross 3.5 % H_2 during calibration in the laboratory. The mass flow controllers (MFC's) and rotameters were used to set the H_2 flow in the 0-30 cm^3 range and air flow in 0-400 cm^3 range. The sensors were calibrated against an ultrasonic transducer which can measure time of flight with resolution of 10 ns. It is a pulse receiver model 4400 MX from Roop Telesonic Ultrasonix Ltd. Mumbai.

It works on the principle of time of flight measurement. The transducer is excited at a frequency of 500 kHz in pulse

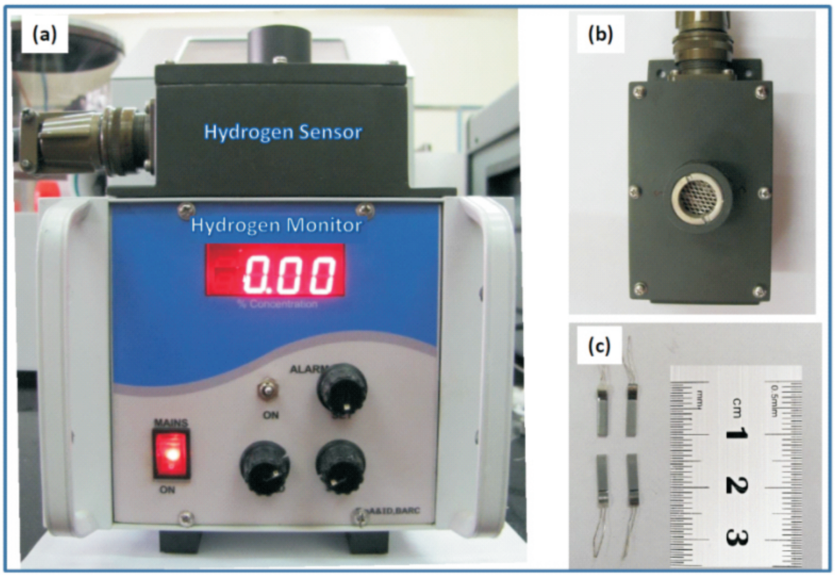

Fig. 4: (a) The complete sensor device with sensor mount on top of monitor and monitor displaying output voltage (corresponding to H_2 % conc.), (b) top-view of the sensor mount to be installed at the location of H_2 leakage and (c) Pd films deposited on Pt-100 heaters.

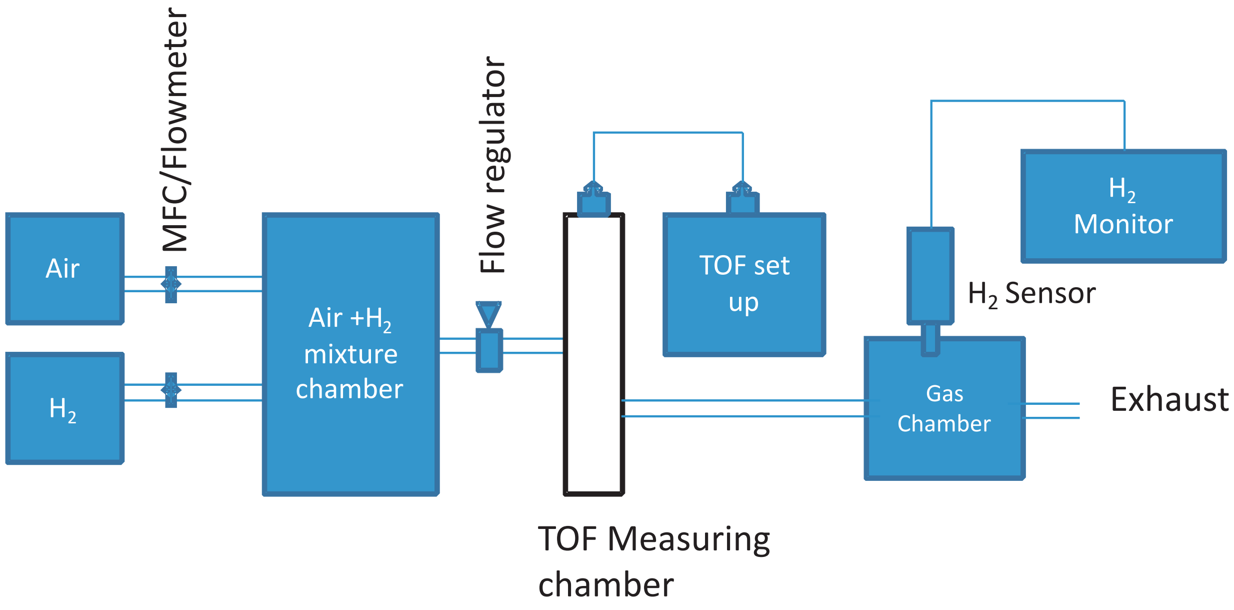

Fig. 5: : Schematic of dynamic H_2 gas sensing set-up.

mode and it detects the echo of the reflected signal at the piezoelectric crystal. The velocity of ultrasonic sound in gas mixtures is dependent on the concentration or the volume percentage of hydrogen (H_2) in the mixture, which is governed by the formula of classical sound velocity as indicated in the following equation:

$$v = \sqrt{\frac{\gamma RT}{M}}$$

where (~1.41 for H_2 and air), R, T, and M are the heat capacity ratio (C_p/C_v), gas constant, temperature, and the molecular weight of gas, respectively. In practical experiment, air is commonly used as background gas, and Eq. (1) can be rewritten as:

$$v = \sqrt{\frac{\gamma RT}{M_{air}.(1-\rho) + MH_2.\rho}}$$

where the molecular weight of nitrogen M_{air} is 28.97, the molecular weight of hydrogen $M_{Hydrogen\ gas}$ is 2.02, and the volume ratio of H_2 is (0%, 1%, etc.). The velocity of sound in air ~ 350 m/sec and in in H_2 ~ 1270 m/sec. The calculated value for air (H_2 = 0%) is 669.125 s. The time allowing the propagation of an ultrasonic wave from emitter to receiver in the cavity (t) was calculated for different vol. % of H_2. For H_2 = 0%, the value obtained is 669.125 s which reduces by 3.12 s with every 1% vol. % increase of H_2 w.r.t air.

For calibrating the sensor device, a fixed H_2 concentration (2%) (verified by ultrasonic transducer) was made to flow into the testing set-up and the voltage on the monitor was adjusted to ensure 1:1 relation with the gas concentration. The sensor response was then recorded for the entire range of H_2 conc. from 0-3.5% at an interval of 0.5%. Fig. 6(a) depicts the sensor response (black) in volts at various time of flight values. The data is superimposed with actual calculated H_2 conc. (red) flowing in the dynamic set up. As clearly shown, sensor response agrees well with the calculated values with displayed voltage values (y-axis) directly related to H_2 conc. The same can be transformed into a calibration curve.

As seen in Fig. 6(b), the sensor response varies linearly as a function of H_2

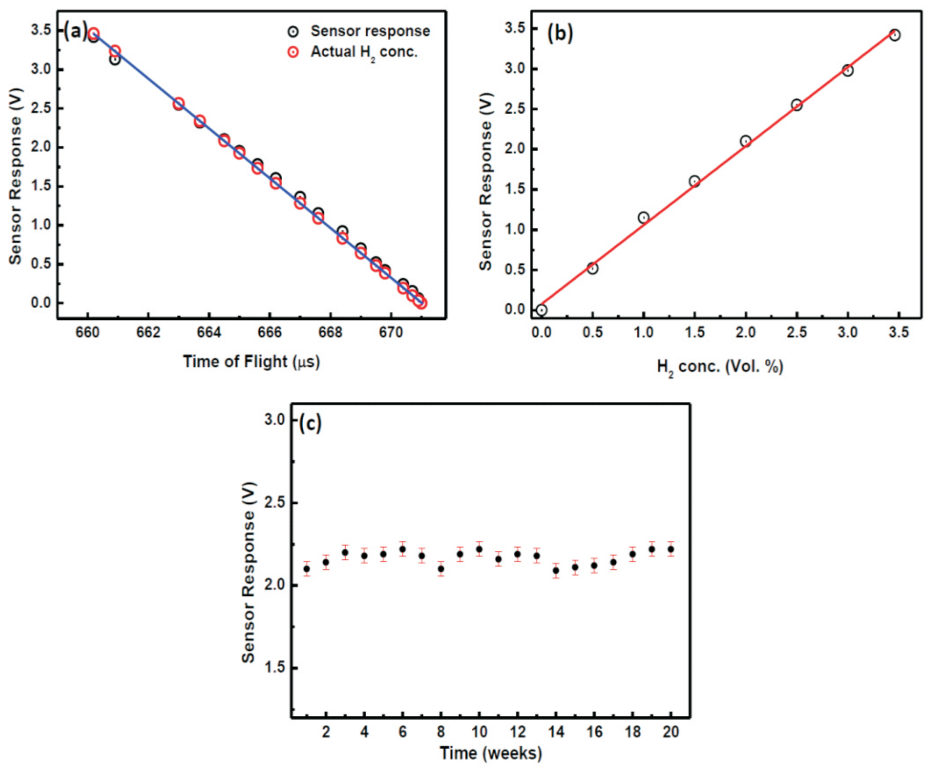

Fig. 6: (a) sensor response as a function of time of flight in ultrasonic transducer, superimposed on calculated H_2 concentration values, (b) Calibration curve derived from time of flight data, and (c) Sensor response at fixed H_2 concentration of 2% as a function time.

Measuring Range	0.3 – 4.0% in air
Operating Temperature	150 °C
Response Time	2 - 5 sec
Recovery Time	2 - 3 min
Sensitivity	0 .3 %
Working Lifespan	> 3 year
Noise Level	± 100 mV

Table 1. Technical Specifications of H_2 sensor

concentration tested up to 3.5%. Fig. 6(c) shows the repeatability/stability data recorded for subsequent weeks for 2% H_2 concentration with error bars as a measure of standard deviation. The technical specifications of the sensor device are listed in Table 1.

Conclusion

We have successfully developed Pd-thin film based Pellister type H_2 sensor at Technical Physics Division, BARC. The sensor device has been designed in-house, fabricated, tested using an in-house made dynamic gas sensing set up. The sensor device exhibits linear sensor response in presence of H_2 gas (0-3.5% conc.) with a minimum detection limit of 0.3%. The calibration of sensors is carried out using ultrasonic transducer to ensure high precision. 90% of the sensor films exhibit a life-time > 3 years. Till date we supplied 16 sensor devices to various users within and outside DAE.

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References

[1] A. K. Basu, S. Tatiya, G. Bhatt, S. Bhattacharya. “Fabrication processes for sensors for automotive applications: a review”. Sensors Automot Aerosp Appl, Singapore, Springer, 2019.

[2] M.N. Carcassi, F. Fineschi. “Deflagrations of H_2–air and CH_4–air lean mixtures in a vented multi-compartment environment”. Energy, 30 (2005): **1439-1451**.

[3] Sadullah Oztürk, Necmettin Kılınç. “Pd thin films on flexible substrate for hydrogen sensor”. Journal of Alloys and Compounds, 674 (2016): **179-184**.

[4] Xiaoyi She, Yang Shen, Jianfang Wang and Chongjun Jin. “Pd films on soft substrates: a visual, high-contrast and low-cost optical hydrogen sensor”. Light: Science & Applications, 8 (2019): **4**.

[5] D.W. Dabill, S.J. Gentry, P.T. Walsh. “A fast-response catalytic sensor for flammable gases”. Sensors & Actuators, 11 (1987): **135-143**.

[6] P.T. Moseley, B.C. Tofield (Eds). Solid State Gas Sensors. Bristol, UK, IOP Publishing Ltd., Adam Hilger, 1987.

[7] Young Tack Lee, Jun Min Lee, Yeon Ju Kim, Jin Hyoun Joe and Wooyoung Lee. “Hydrogen gas sensing properties of PdO thin films with nano-sized cracks”. Nanotechnology, 21(2010): **165503**.

[8] Sylwia Owczarek, Sten V. Lambeets, Robert Bryl, Cédric Barroo, Olivier Croquet, Leszek Markowski & Thierry Visart de Bocarmé. “Oxygen Adsorption, Subsurface Oxygen Layer Formation and Reaction with Hydrogen on Surfaces of a Pt–Rh Alloy Nanocrystal”. Topics in Catalysis, 63 (2020):**1522–1531**.