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Digital sensors for detecting toxic gas leaks

N. Malathi,[1*] Arun. A.D.,[1,2] S. Chithrakkumar,[1] M. Sivaramakrishna,[1] Arindam Das,[2,3] G. Mangamma,[2,3] Arun K Prasad,[2,3] S. Dhara[2,3]

[1]Innovative Sensors Section, Electronics and Instrumentation Group, Indira Gandhi Center for Atomic Research, Kalpakkam 603102, Tamil Nadu, India. [2]Homi Bhabha National Institute, Indira Gandhi Center for Atomic Research, Kalpakkam, 603102, Tamil Nadu, India. [3]Surface and Nanoscience Division, Materials Science Group, Indira Gandhi Center for Atomic Research, Kalpakkam 603102, Tamil Nadu, India.

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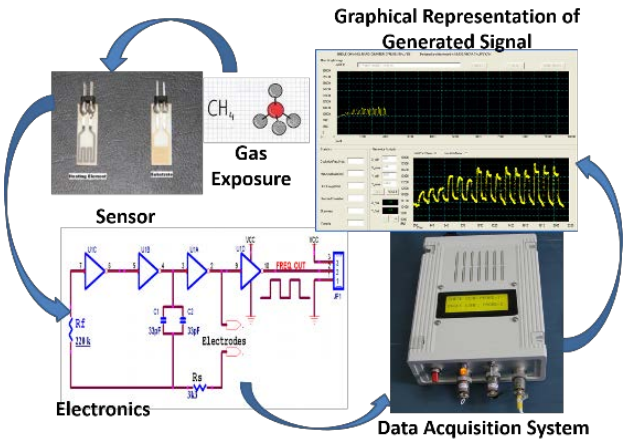
Article

ABSTRACT Design of an innovative gas sensor with direct digital signal output is presented in this paper. These sensors are suitable for diverse field applications envisaging detection of leaks of gases such as methane, hydrogen, ammonia and other toxic gases. They are also used in stand-alone gas monitoring systems in chemical industries. The sensor probe consists of gold inter-digitated electrodes sputtered on insulating substrate. A heater element made up of platinum meander structure is on the other side of the substrate, which is used to assess the performance of the sensor at different temperatures. The gold electrode is connected with a fixed value capacitor as timing circuit of a logic gate oscillator (LGO). In presence of the gas, the resistance change across the sensing electrodes at constant temperature is measured as frequency change of digital pulse output from the LGO circuit. This transduction method works with 5V DC voltage and generates Transistor-Transistor Logic (TTL) compatible digital pulse output. Hence it reduces complexity of signal generation hardware by eliminating use of amplifier and filter circuits. The frequency of TTL pulse signal output in response to the change in resistance induced by gas is calibrated for different concentrations and heater voltages. The performance of the gas sensor was studied at various temperatures and the optimum temperature for maximum sensitivity was found to be around 100°C. The precision, sensitivity and the lowest detection limit in measurement of methane gas using this method are <100 ppm, ~10 Hz/ppm and ~100 ppm, respectively.



Keywords: Toxic gas leaks, Gas sensors, pulsating sensor, transduction technique, logic gate oscillator

INTRODUCTION

Gas sensors are extensively used in industries and research laboratories to measure concentration of gaseous species present in the ambient atmosphere and experimental conditions. This helps to prevent the accidents by issuing early warning about presence of toxic gases. Solid state gas sensors have gained popularity over the last three decades for use in domestic as well as industrial applications.[1] The suitability of a chemical sensor for portable applications requires the sensor to possess high sensitivity, selectivity, ability to operate at low-power, low cost fabrication, small size among other attributes.[2] Metal oxide semiconductor-based sensors respond to change in concentrations of analyte gases. After a reactive molecule chemisorbs on the metal-oxide surface, a charge transfer takes place. When a metal-oxide such as SnO_2 is heated at a certain high temperature in air, oxygen is adsorbed on the surface, and a surface potential is formed that inhibits electron flow. When the surface is exposed to reducing gases such as hydrogen, methane, ammonia and carbon monoxide, the surface potential lowers and conductivity measurably increases. As the concentration of the target chemical increases, so does the magnitude of the change in resistance.

Conventionally the change in resistance is measured using V-I or I-V converters and ADC which involves analog signal processing circuits.[3] In addition to this, filters and amplifiers are used in primary signal processing for noise reduction and improved resolution. These analog circuits are sensitive to noise and require a lot of effort to generate a linear output generation corresponding to sensing parameter. The motivation of this work

*Corresponding Author: N. Malathi, Scientific Officer/F, Innovative Sensors Section, Indira Gandhi Center for Atomic Research Kalpakkam
Tel: 044 27480500 22686
Email: nmalathi@igcar.gov.in

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is to demonstrate the pulsating sensor-based approach for direct digital signal generation from semiconductor-based sensors. This method offers flexible design features such as accurate measurement, easy signal transmission and excellent noise immunity for semiconductor-based gas sensors which is the prime novelty in this work.

SENSING METHODOLOGY

Pulsating sensors are indigenously designed novel devices that produce direct digital pulse output whose frequency is encoded with parameter being measured. Any physical or chemical parameter that causes a change in electrical properties viz. resistance, capacitance and inductance is measurable using pulsating sensors. High performing conductivity monitoring instrument,[4] high performance differential pressure monitoring device,[5] liquid level sensors[6,7] and radiation dosimeters[8] have already been developed and deployed in various applications. This digital transduction method offers simple yet powerful solutions for industrial measurement systems. The gas sensor probe contributes change in resistance when exposed to varying concentration of gas and hence is measurable using pulsating sensor measurement technique.

GAS SENSING PROBE CONSTRUCTION

The gas sensor probe comprises of two parts; namely gold inter-digitated electrodes (IDE) sputtered on one side of an insulating substrate and a heater element made up of platinum meander structure on the other side of the substrate (Figure 1). The physical dimensions of the substrate are 22.8 mm × 7.6 mm × 1 mm with active area of 6.5 × 6.5 sq.mm.

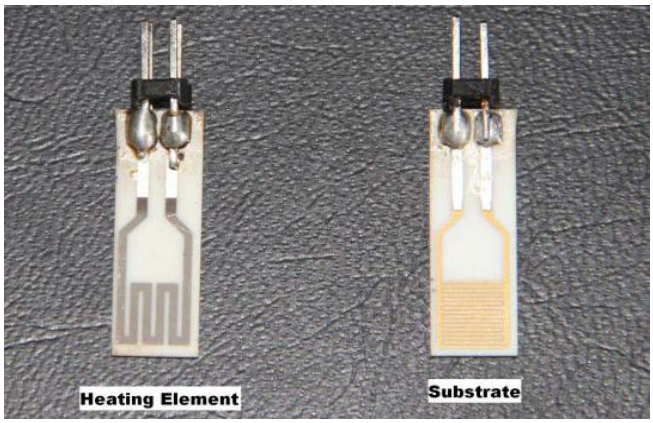

Figure 1 Photograph of heater element and gas sensing electrode.

The heater element beneath the gas sensing electrodes is powered using variable DC power supply unit. The gold electrode structure forms the resistor part and is connected with a fixed value capacitor as timing circuit of a logic gate oscillator (LGO). The sensing probe is connected to the LGO through an appropriate four lead connection, so as to remove and change the sensing probe substrates for different studies.

INSTRUMENTATION

ELECTRONIC CIRCUIT OF SENSOR

The pulsating sensor is a logic gate oscillator (LGO) with its timing circuit, a combination of resistor and capacitor as shown in Figure 2. The logic gate oscillator circuit works with 5V DC supply, hence generating signal in digital domain. The sensor probe which is a variable resistor (R), in series with a fixed resistor (Rs) in combination with a fixed capacitor forms the timing circuit of LGO and this timing circuit combination dictates the output pulse frequency of the LGO (Eq.(1)). This digital pulse frequency output carries the information of the parameter being measured. Any physical or chemical parameter which is a function of R/L/C is measurable using this technique.[6,9] The relation between the pulse frequency and the timing circuit components; resistance and capacitance is given by the following equation:

$$f \alpha 1/(RC), \qquad \text{-------} \qquad \text{Eq.(1)}$$

Where, f = frequency in kHz, R = Resistance in kΩ, C = Capacitance in pF.

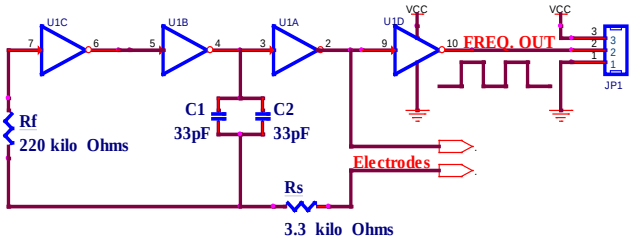

Figure 2 Logic gate oscillator circuit diagram with variable R.

DATA ACQUISITION SYSTEM

The measurement system includes a single channel digital pulse counter with dual 5V DC power supply unit. The pulse output frequency of gas sensor is measured using this counter unit. The gate time for frequency measurement is configurable (1-1000 ms) depending upon the sensor response time. The frequency value is transmitted to the interface PC via serial port. This frequency value is converted into gas concentration using calibration equation and saved onto computer. The field signal from sensor is optically isolated from instrument ground using an optical isolator circuit. The counter unit is designed using an 8-bit microcontroller ATMEL 89C4051.The unit communicates with PC through RS-232 serial port interface. The 16-bit timer inside the microcontroller is configured as a counter. A built-in reference clock of 10 kHz within the unit is used to generate the strobe pulse for counting. The frequency value is calculated as [number of pulses/ gate time] and then it is sent through serial port to the interface PC.

APPLICATION SOFTWARE FOR DATA PROCESSING

An application software developed using VB 6.0 installed in the PC receives data from counter unit through its RS-232 port. The GUI of application software plots the frequency value or gas concentration (user selectable) in online and records for offline

analysis.[10] User can set the options for recording time, parameter unit, calibration coefficients and path for the data logging file via GUI.

Experiment

Heater element studies

The heater is used to identify the optimum operating temperature and the performance of the sensor. The heater element is a platinum meander structure (Figure 1) which is on the rear side of the insulating substrate of sensor probe. The heater is calibrated for a range of applied voltage varying from 1 to 6V. The sensitivity of the heater was measured by varying voltage insteps of 1V and was measured as 25°C/1V. The response time of the heater element is <1s. Figure 3 depicts the heater response on heater and substrate side with respect to applied voltage.

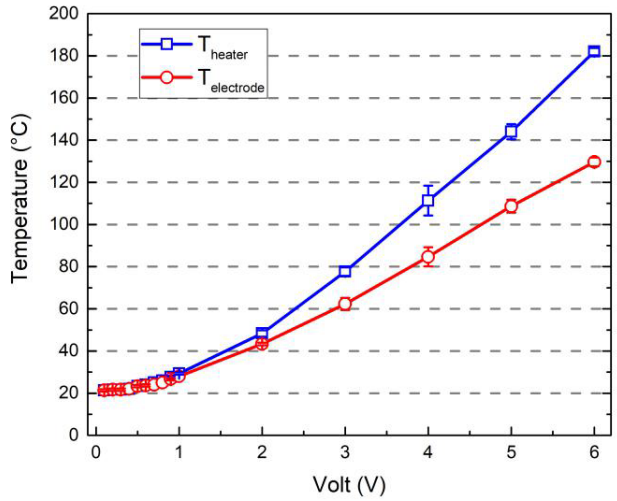

Figure 3 Heater calibration curve.

Gas sensing material

Fabrication

Tin oxide (SnO_2), a widely used wide band gap *n*-type semiconductor, is utilized as the active sensor material. SnO_2 nanostructures have attracted immense interest in various applications, e.g., gas sensors, optical devices, catalysis, energy storage, biosensors due to its biocompatibility, chemical stability, and environment-friendly nature. Nano particles (NPs) of SnO_2 are prepared chemically to make it operational at a low temperature compared to the bulk SnO_2.[11] It is worth to note that the manipulation of electronic band structures with different defects such as cationic (Sn) and anionic (O) vacancies are pivotal for sensor activities. The detailed synthesis of the SnO_2 NPs is given elsewhere.[12] In brief, 0.05M NH_4OH (MERCK) is added drop wise to stannic chloride ($SnCl_4$, Alfa Aesar), which results in the formation of a gel. Then, this gel is washed several times with Millipore water. Subsequently it is dried at a temperature of 100°C for overnight to obtain SnO_2 NPs. For fabrication of sensor electrodes, an ultrasonicated dispersion of SnO_2 NPs (2 mg/ml) in iso-propylalcohol is made. A drop cast technique is then employed to dispense a certain amount (20 µl) on the Au- IDE electrode. After drying under an IR light, the fabricated IDE electrodes are used for sensor study.

Functionality

The metal oxide deposited on the inter-digitated electrodes of the sensing probe induces a potential when the sensor is heated through the heating element on the other side of the electrode substrate. This further induces a change in resistance across the electrodes. In this condition, when the sensing probe is exposed to toxic gases, it lowers/increases the resistance measurable across the sensing electrodes depending upon nature of semiconducting oxide and whether the gas is reducing or oxidizing in nature. The change in resistance offered by the sensing probe placed in the timing circuit of the LGO reflects in the pulse frequency output. Hence the pulse frequency output of LGO is a measure of the sensed parameter, i.e., variable concentration of the toxic gases.

Experimental setup

Initially experiments are carried out in a closed chamber (1L) (Figure 4a). The sensing electrode and the heater element are soldered to conducting tracks provided in the chamber (Figure 4c) using a suitable four-lead connector through thin copper wires. From the chamber outlet connections, the sensing probe connectivity is routed to the LGO placed near the chamber (Figure 4b). The LGO is powered by the interfacing instrumentation hardware and the pulse frequency output from the LGO is further enrouted to the hardware. The frequency response of the sensor probe is communicated to PC via the application software for online plotting of the data and in parallel store the data for offline analysis (Figure 4d).

Calibration of the gas sensor

Studies were carried out to standardize the LGO configuration desirable for this application. Based on the resistance offered by the sensing probe at required working conditions (at high temperatures), LGO configuration was standardized with 3.3kΩ value series resistor (Rs) and two 33pF capacitors in parallel combination (C). Later the LGO was calibrated for variable fixed value resistors in place of the sensing probe, to obtain an offline relationship between the pulse frequencies generated in response to the resistance offered by the fixed resistors. Calibration curve of the LGO is depicted in Figure 5a.

Results and Discussion

Further experiments were carried out using sample probes generated from a single batch of fabrication. Assuming fabrication of samples in a single batch is same in all aspects; three samples were taken for experiments.

Experiments were carried out to optimize the operational temperature and to obtain maximum sensitivity of the gas sensor probe. In this connection, gas sensing probe was subjected to varying heater voltages at a constant chamber pressure of

50 mbar and exposed to 500ppm concentration of methane gas. The experiment was repeated for three cycles and the response of the sensing probe with respect to heater voltage from 2 to 6V in steps of 0.5V is represented in Figure 5c.

The sensor response of the sensing probe calculated with respect to varying heater voltage is represented in Figure 5d. Maximum sensitivity of the sensor ~10 Hz/ppm was obtained at 4V and 4.5V of heater voltage. Hence, further experiments were carried out with higher heater voltage.

Observing the performance of the sample with respect to heater voltage as discussed above, it was decided to repeat experiments for 4V, 4.5V, 5V heater voltage (corresponding temperatures ~80, 95, 110°C) and by varying methane gas concentration from 100ppm to 500ppm. The results are plotted and represented as shown in Figure 5b. The response of the gas sensor for varying concentration of methane gas was analyzed and the precision in measurement was found to be <100ppm. It was also observed that response of the sensor is maximum at 5V heater voltage where as in previous experiments it was observed that for 4.5V heater voltage the response was maximum for 500ppm gas concentration. Based on the performance of the sensor with methane gas, it is found that 4.5-5V heater voltage shall be optimum for this gas sensor. This corresponds to a temperature of 100°C on the electrode surface. With this technique, a concentration of 100 ppm can be detected unambiguously. Further experiments shall be carried out to study the performance of sensor for other toxic gases.

Using pulsating-sensor method we could avoid using complex analog circuits like filters, amplifiers and signal conditioning circuits. This reduced the design complexity of instrumentation hardware.[13] As seen from the sensitivity distributions, pulsating-sensor based transduction could achieve 12-bit resolutions (4096 Hz) with minimum 1-bit noise levels. As the output signals are generated as TTL compatible digital pulse train, it is easy to transmit and measure using simple digital counter circuits built within in microcontrollers. The methodology eliminates the use of additional analog to digital

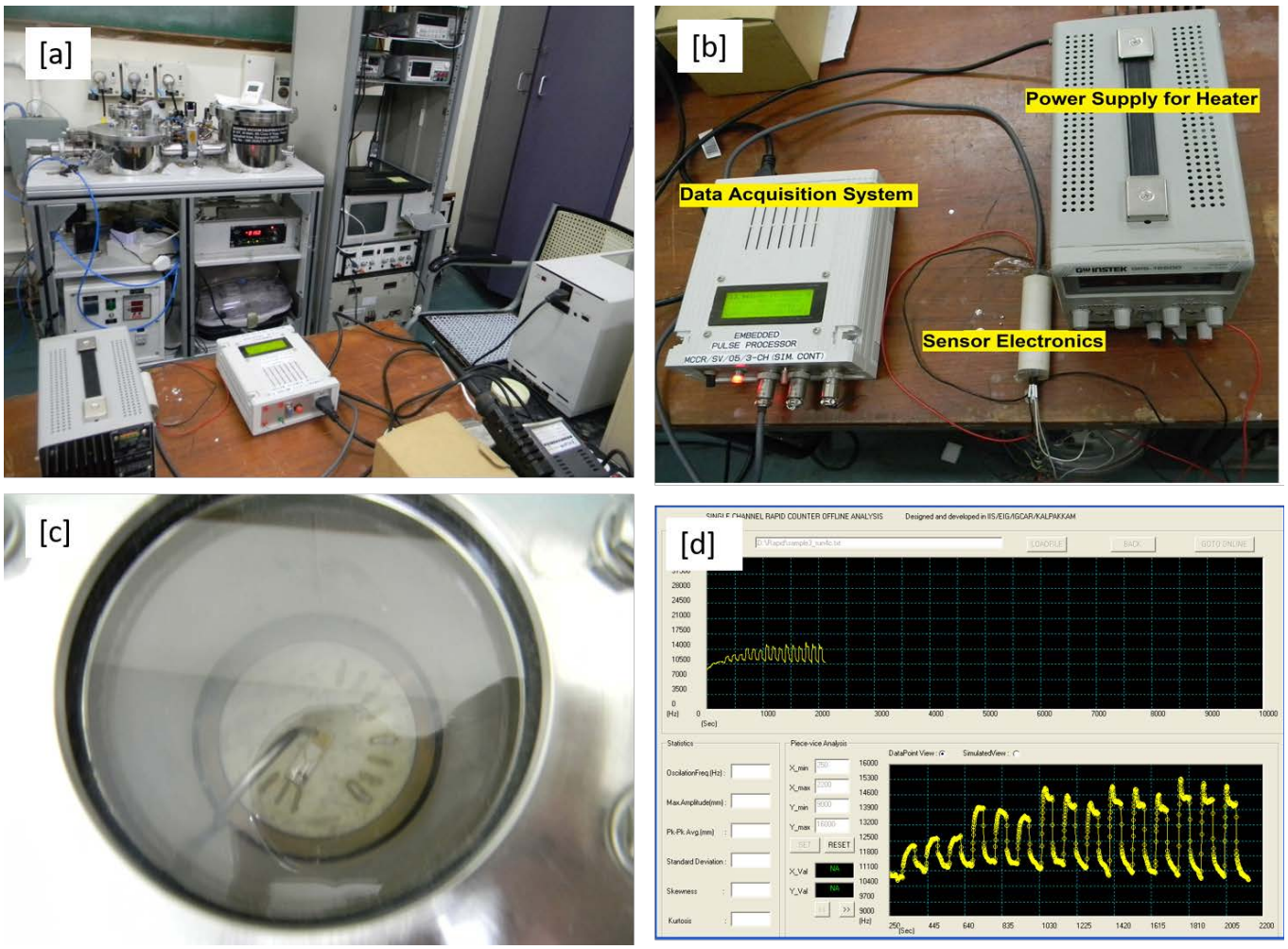

Figure 4 a) Experimental setup; b) Data acquisition instrument, sensor electronics and heater power supply; c) Gas sensing probe inside the chamber; d) Graphical user interface of data acquisition system.

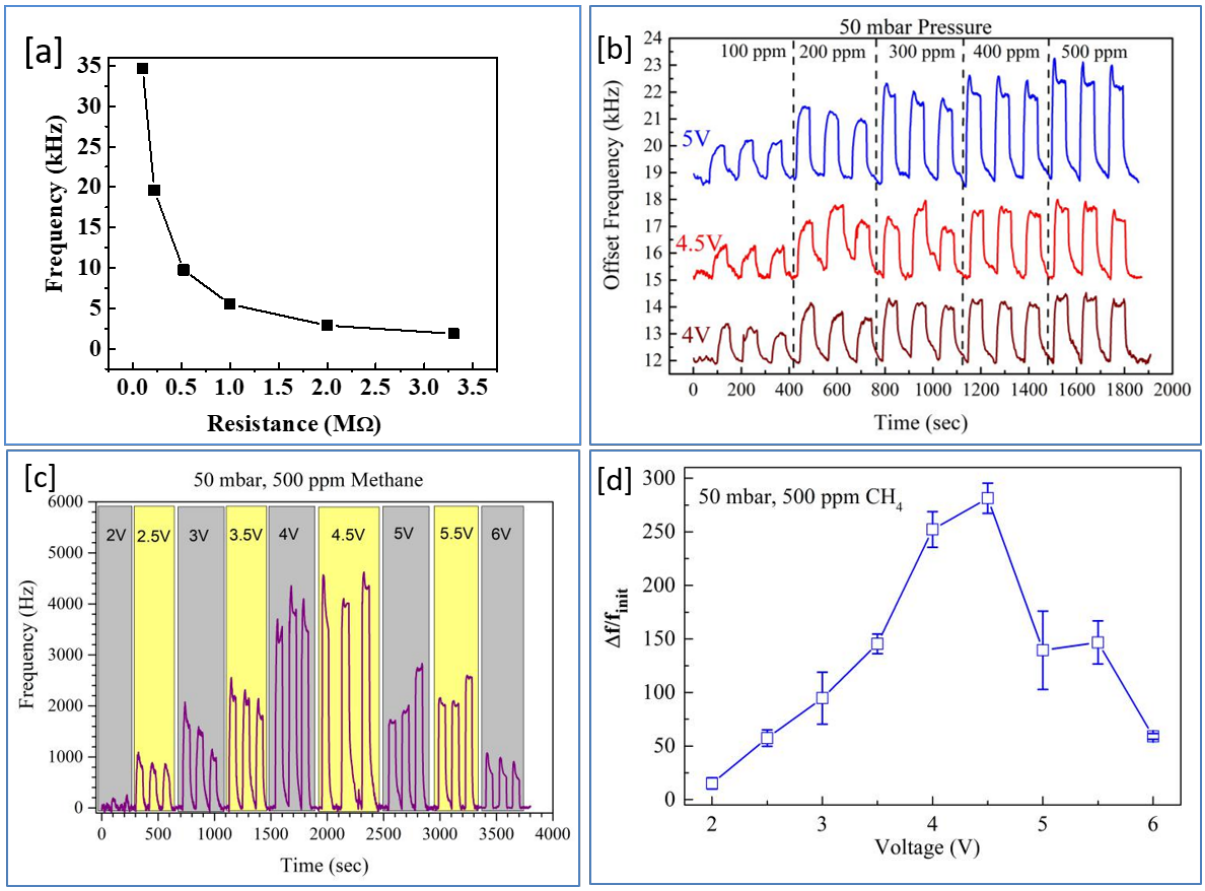

Figure 5 a) Calibration curve of sensor electronics; b) Transient response of sensor for different concentration of methane gas; c) Transient response of sensor for different heater voltage; d) Sensor response of probe at various heater voltages.

Table 1. Comparison between different transduction techniques used in gas sensors

Transduction method	Conversion	Electric signal Output	Signal processing	Read out	Signal conditioning hardware	Signal Transmission
Pulsating[4,5,7,8]	Resistance to frequency	Digital pulse	Digital	Counter	Single CMOS inverter IC based Logic gate oscillator	Long distances, Single ended OR differential
Time period conversion[14]	Resistance to time period	Digital pulse	Mixed (Analog & Digital)	Timer	ASIC based op-amp, cascade current mirror, Schmitt trigger	Short distance, Single ended
Trans impedance[15]	Current to voltage	Analog voltage	Analog	ADC	Pre amplifier, Peak-detect and hold circuit, saturation detector, ADC	Short distance, Common mode
Thermal filtering[16]	Thermal conductivity to phase angle	Bit stream	Mixed (Analog & Digital)	Phase-domain ADC	Phase shifter, Multiplier and Integrator	Short distance, Single ended mode

converters for measurements. Table 1 depicts comparison between different transduction techniques used in gas sensors with the pulsating sensor based method. The minimum hardware overhead, simple signal conditioning circuits, direct digital conversion and easy transmission are the highlights of pulsating sensor based transduction method. This simple design technique offers design flexibility in optimizing desired sensor parameters such as resolution, sensitivity and interfacing modes. Hence

pulsating sensor technique shall be adapted for minimizing the gas sensor signal transduction, transmission and instrumentation. This enables to adapt this method in gas sensing modules for wearable devices.

CONCLUSION

Pulsating-sensor based instrumentation approach is extended to develop gas sensors for application in laboratories and industries. Presently the functionality of the gas sensor is studied for methane gas at different conditions to optimize the operating methodology for field application. Through this work we have demonstrated the function of the gas sensor for methane, using a PC based data acquisition system. The work shall be further extended to design a stand-alone measurement system for plant applications and to sense other toxic gases.

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CONFLICT OF INTEREST

Authors declared no conflict of interest.

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