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# Batron P–Si microsensor for methane and its derivatives

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ABSTRACT

Baytron P–Si chip was made by depositing Baytron P onto a gap of two parallel gold plates on a silicon wafer separated by 150 μm such that the gold plates contact the polymer only in the gap region. The resistance of the polymer was examined at ambient room temperature before and after the exposure of the chip to different concentrations of methane or its derivatives such as chloroform, carbon tetrachloride and methylene chloride. The chip response to methane gas opens up the prospects of its usage at ambient temperature for the industrial and environmental detections in the range of 200–1300 ppm. Among the derivatives of methane, methylene chloride showed the highest response for detection. The mechanism of sensing is discussed.



## 1. Introduction

During the last two decades, a large number of gas sensors have been developed [1–18] based on physical or chemical properties of the polymers that would change upon exposure to the analytes. The common physical properties used for developing sensors are color, light absorption, dielectric, electrical resistance, magnetic, and thermal conductivity. Several gas sensors are based on electrical conductivity changes; such sensors use oxides kept at elevated temperatures. Methane gas detector is developed using near IR-LED where the IR radiation is absorbed by methane at 1660 nm [1]. This detector is capable of detecting methane in harsh environment with a temperature variation between 20 and 50 °C.

In another method methane was dissociated with high power femtosecond laser and the CH radical fluorescence was detected [2]. A nanosized tin oxide powder doped with antimony oxide and Pd mixture showed a conductivity change upon exposure to methane that was used as the detector [3]. A photo acoustic sensor was developed using an IR semiconductor laser emitting at 1.65 μm [4] and is suitable for methane detection in a small range of concentrations. Spinel type oxides have also been used for methane detection; a mixture of oxides, $ZnCr_2O_4 + Cr_2O_3$ (1:1 mole ratio), showed a most promising response [5]. In another interesting method a metal wire is kept at 500–1000 °C in the presence of methane for emitting positive ions. When methane burns it leaves carbon on the metal which in turn is burnt off to leave a clean wire. The current decays to zero during this process. A selective gas sensor is proposed based on clean metal and carbon contaminated metal response [6]. Optical fibers that can sense methane has been based on optical absorption of the He–Ne laser output wavelength of 3.392 μm. A single fiber of 1.8 μm diameter and 10 mm length of $SiO_2$ fiber is used for methane gas [7].

A review of the literature suggests that there are no sensors developed using organic conducting polymers that would operate at room temperature. An earlier attempt at making methane sensor using poly(3-methyl thiophene) composite [18] has not been successful. The need for developing a methane sensor arises due to its importance as fuel and its utilization in the fuel cells [19]. In addition, it is an important green house effect gas that would require its concentration to be monitored in the atmosphere. The present paper discusses the electrical conductivity response of Baytron P–Si chip for methane and its derivatives at room temperature. This is probably the first report of the development of a room temperature portable conductive polymer sensor for the detection of methane gas in the range of 200–1300 ppm. This sensor also responds to substituted methanes with a response comparable with that of methane. This study is a continuation of our efforts to develop a suitable methane gas sensor at room temperature due to the absence of its response with a carbon nanotube composite [18]. In relevance to using Baytron P–Si chip for the determination of green house gases such as carbon dioxide, nitrous oxide, ozone and choroflurocarbons further studies are required. We hope to report these results in future.

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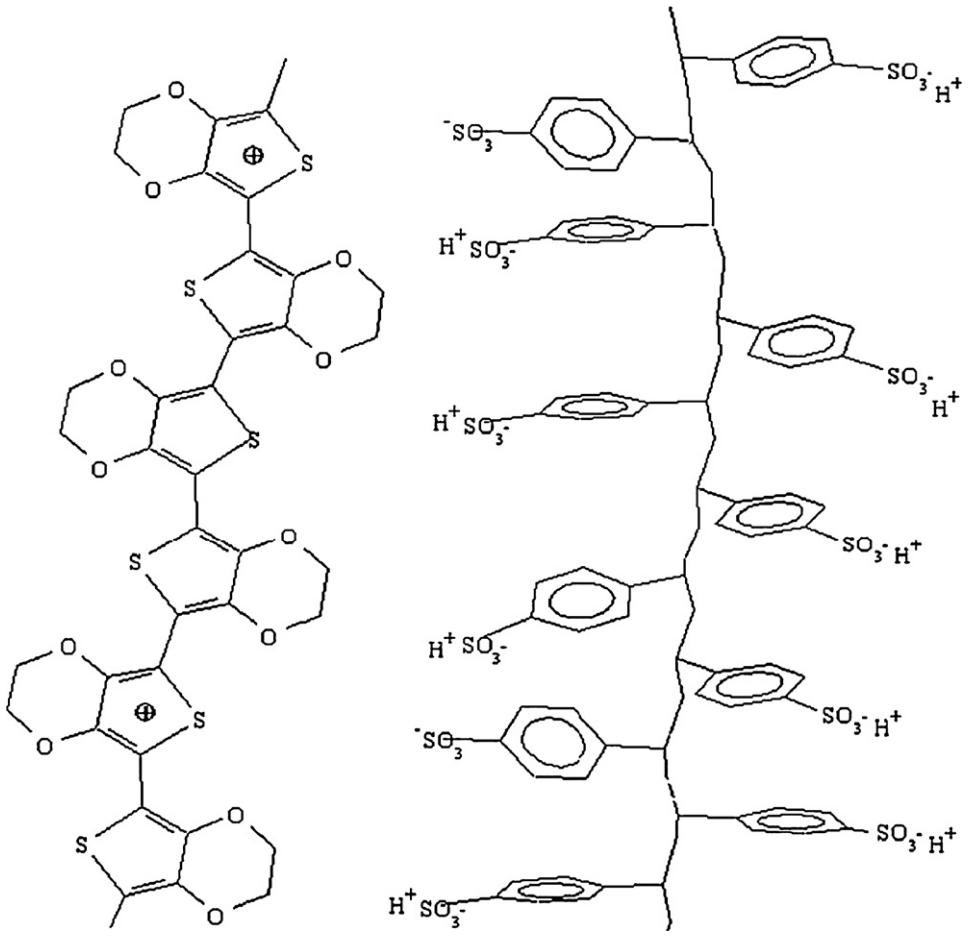

**Fig. 1.** Structure of Baytron P.

## 2. Experimental

### 2.1. Chemicals

Baytron P is 3,4-polyethylenedioxy-thiophene/polystyrene-sulfonate (CAS# 155090-83-8) was gifted by H.C. Starck, Newton, MA. It is water based polymer. The structure of Baytron P is shown in Fig. 1. Methane gas cylinder research grade was obtained from Air gas, Radnor, Pa. Chloroform (Aldrich, 99.99%), carbon tetrachloride (Aldrich, 99.95%) and methylene chloride (J.T. Baker, 98%) were used as received.

### 2.2. Sensor fabrication

Silicon wafer (0.5 cm × 0.5 cm) was used in the fabrication of the sensor. The chip design was a crystalline silicon base with Zn/chrome overlay patterned to provide a gap of 150 μm. Using an appropriate mask, thin gold layer was overlayed onto Zn/chrome by either evaporation or sputtering techniques. The two gold electrodes were contacted with thin copper wire for electrical measurements. The sensing area is about 0.03 $cm^2$. Fig. 2 shows the arrangement of the sensor. The conductivity of the films is in the range of 0.5–1 S/cm.

### 2.3. Procedure

#### 2.3.1. Sensor A

The sensor chip was cleaned and dried before use. Baytron P was deposited on the electrodes gap by dip coating at room temperature for periods ranging from 2 min to 1 h. The chip was annealed at 60 °C. The thickness of the deposit is estimated at 1 μm.

#### 2.3.2. Sensor B

The cleaned sensor chip was deposited with Baytron P on the electrode gap by dip coating at room temperature for not more than 1 min. The chip was annealed at 60 °C. The thickness is estimated at 0.2 μm.

The sensor was placed in a glass jar with a Teflon® stopper with its leads connected to the measuring circuit. The analyte ($CH_4$, $CH_2Cl_2$, $CHCl_3$ or $CCl_4$) was injected into the jar. As the chemical vapors come into contact with the sensing area of Baytron P, its resistance changes and reaches a stable value. The glass jar was flushed with helium between successive runs for 10 min. The response time was measured on the computer using an internal

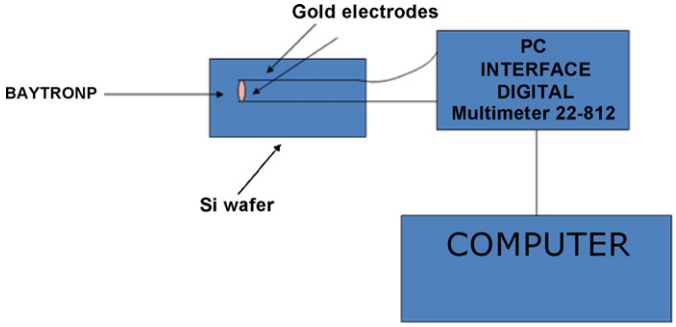


**Fig. 2.** Experimental setup.