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REALIZATION OF POROUS SILICON NANO STRUCTURES FOR OPTICAL DETECTION OF PETROL ADULTERATION

V. MISHRA*, P. N. PATEL, T. VOHRA
Electronics Engineering Department, S. V. National Institute of Technology, Surat-395007, Gujarat, India

In India, adulteration of petrol with kerosene is a common malpractice. As the domestic fuel for a larger section of the society, kerosene has been made available at prices cheaper than petrol by the Government. Petrol is used mainly in the automobile industry and its adulteration leads to an increase in environmental pollution, decrease in the efficiency of the engine or failure of machine components and lower returns for the buyers' money. This paper reports experimental study for detection of kerosene in petrol using one dimensional (1D) nano scale Porous Silicon (PS) Micro cavity (MC) sensor device, refractive index sensing property of nano-porous silicon has been exploited here, the fabrication, oxidation, sample preparation. Sensor device was fabricated by electrochemical anodization of crystalline silicon wafer and proposed as a large surface area matrix for optical sensing of kerosene concentration (in ml) present in petrol. Wavelength shifts ($\Delta\lambda$) in the measured reflectance spectra were analyzed for the detection of kerosene in the porous structure. Sensor device showed excellent sensing ability and relation between the different concentrations of kerosene and the wavelength shift. Also, it was observed that, the resonant wavelength in the reflectance spectra of the 1D-PSMC sensor device promptly returned to its original states after removal of kerosene from the porous structure. This is a very good quality of these structures, as it is helpful in the development of reversible sensing devices.

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1. Introduction

The air pollution has been on the rise due to fast increasing use of petroleum products. In particular, the automobile sector has emerged as a major consumer of fuel oil and a major contributor to air pollution. In developing countries like China, India, Brazil the automobile industry is expected to grow at a faster rate in coming years accompanied by proportional increase in the air pollution [1]. The issue is essentially international in nature as the emissions from the tail pipe of automobiles result in the enhancement of the greenhouse gases in the atmosphere leading to global warming. Fuel adulteration is a main problem of these days due to its contribution to increase in environment pollution and a decrease in the engine performance of the vehicle. Addition of kerosene in petrol is one such practice which reduces the fuel cost thereby encouraging this malpractice [2]. Such adulteration methods are rampant due to unavailability of on the spot standard checking techniques which do not consume much time and detect adulterant concentrations below 20% [3]. Adulteration of automobile and diesel fuels leads to increased tailpipe emission and the consequent ill effects on public health. Mixing kerosene with diesel or petrol does not lead to an increase in tailpipe emissions rather add on to air pollution indirectly [4]. For the prevention of adulteration, check on the fuel quality at the distribution point, therefore, is highly crucial. In India, the gasoline is adulterated by mixing diesel and petrol adulterated by mixing of kerosene [5]. This is because these types of adulterations when limited to small volume percent are difficult to detect by the automobile user, while more than 30% adulteration is likely to be easily detected by the user from the degradation of the engine performance caused by the adulterated fuel [6].

* Corresponding author: vive@eced.svnit.ac.in

To check the adulteration efficiently, it is essential to supervise the fuel quality at the distribution point itself. For this purpose, the equipment should be portable and the measurement method should be quick, competent of providing test result within a very short span of time. The measuring equipment should also be preferably inexpensive and easy to use. Recently, Porous Silicon (PS) is emerged as the nano material with unique promising properties such as easy fabrication, light weight; nano size pores and controllable morphologies. Also, it is more convenient for the refractive index based optical sensing [7] using PS. 1D-PSMC structures are periodic dielectric structures that control the propagation of electromagnetic wave through the photonic crystals. The structural properties of 1D-PSMC exhibits the sharp resonance dip in the reflectance spectra. The refractive index sensing property of nano-porous silicon has been exploited for the optical detection of the adulteration in petrol studied by examining the wavelength shift in the reflectance spectra.

The objective of this work is to evaluate the feasibility for fabrication of 1D-PSMC structures as optical sensor device for the sensing of quantitative detection of fuel adulteration Kerosene in Petrol using fiber optic spectrometer. First, experimental detail for the fabrication and oxidation process of 1D-PSMC structures is presented. After that, principle of optical sensing, structural and optical characterizations of 1D-PSMC structures are discussed. Finally, the testing of these structures as an optical sensor device have been done by sensing of different concentrations of petrol by examining the resonance wavelength shift in their reflectance spectra..

2. Experimental setup

2.1 Fabrication of Sensor Device

P-type Si wafer (<100>, 0.01- 0.02 ohm-cm, 275 μm, 20 cm^2) was used for the fabrication of 1D-PSMC sensor devices. Fabrication was performed in the portable fume hood chamber [8] containing the electrochemical etching cell [8, 9]. First, silicon wafer was cleaned using standard piranha cleaning method. The solution for the piranha cleaning was composed of H_2SO_4 (98%, Finar Chemicals Ltd.) and H_2O_2 (30%, Fisher Scientific Ltd.) mixed in the ratio of 3:1. Polytetrafluoroethylene bath was filled with the etching solution of 40% aqueous HF and 99% ethanol, mixed in the ratio of 1:2 [10]. The wafer was then placed inside an electrochemical cell and periodic constant current square wave was applied by programmable DC power supply (PWS 4305, Tektronix). Applied current density (J) and the etching time (t) profile are responsible for the change in refractive index (n) and the physical thickness (h) profile of the layer, respectively. Fabrication of the 1D-PSMC structure was realized by inserting a cavity layer of high current density between two identical DBR1 and DBR2 [11] with six repetitions of a current density and etching time sequences. Similarly, two symmetric DBRs were realized by applying alternate current densities of 70 $mA/cm^2$for 2.5 seconds and 5 $mA/cm^2$for 16.0 seconds while cavity layer was realized by applying current density of 140 $mA/cm^2$for 3.2 seconds. In Figure.1, n_s is the refractive index of the substrate and N is the number of periods. The 1D-PSMC structure was realized by inserting a cavity layer of high current density between two identical DBR1 and DBR2 with ten repetitions of a current density and etching time sequences [12].

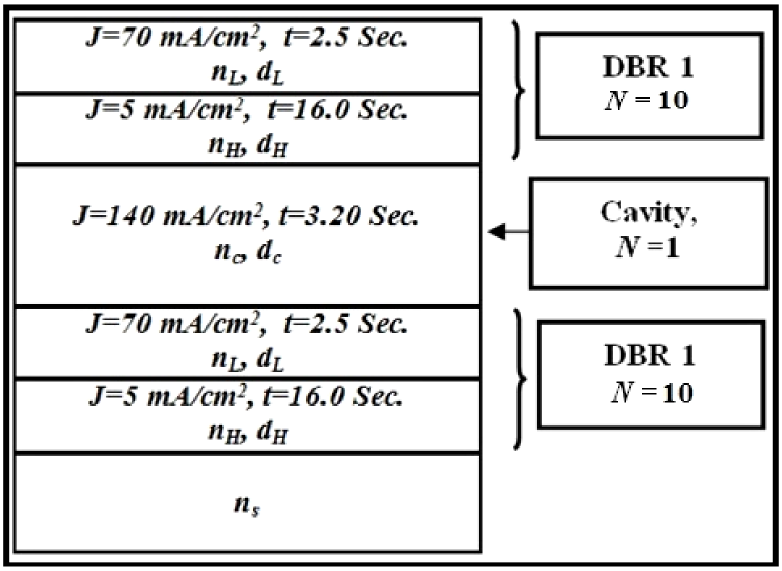

Fig. 1. Fabrication Schematic of 1D-PSMC structures.

After electrochemical etching, these structures were rinsed in DI water for 10 minutes and dried at room temperature. The structural morphology of the 1D-PSMC sensor devices was characterized by scanning electron microscopy (FEG SEM, JSM-7600, JEOL). A UV-Vis-NIR Spectrophotometer (Maya Pro 2000, Ocean Optics Inc.) was used for the reflectance measurements of the prepared sensor device structures.

2.2 Oxidation of Sensor Device

PS is a material characterized by a high chemical reactivity; if it is stored in ambient air, the texture becomes partially oxidized and leads to decrease of the refractive index of the structure which may change its optical properties. To stabilize the PS structure from chemical reactions and to eliminate the problem of aging, the thermal oxidation of the structure is necessary. Besides, the hydride covered surface is hydrophobic and thus makes it hard to fully interact with biomolecules in aqueous solution. Considering this, fabricated sensor device structure was thermal oxidized at 650º C in muffle furnace for 15 minutes after structural and optical characterizations. Thermal oxidation reduces or completely removes the Si from the skeleton and substituting it with SiO_2. Thermal oxidation makes highly stable structure, which is important condition for any type of sensor device.

2.3. Sample Preparation

Different concentrations of petrol with varying percentage of kerosene 0% to 50% were prepared to get a homogenous mixture. The solution was then dropped on to the 1D-PSMC biosensor devices, hence the solution reaches to the pores of the sensor device. The amount of solution was optimized to 20 µl for the reaction to be in the linear region. After each measurement, the device was thoroughly rinsed in the isopropyl alcohol for 5 minutes followed by DI water for 2 minutes and proper drying for the complete removal of all the kerosene liquid molecules from the pores.

2.4 Experimental Set-Up

As shown in the Figure 2, sensor device is illuminated with halogen lamp through a Y-shaped bifurcated fiber probe which has the central fiber providing incidence light and a bundle of six fibers around the central fiber to collect the reflected light. The reflected light is analyzed by spectrophotometer. Finally, the reflectance spectrum is displayed on computer screen.

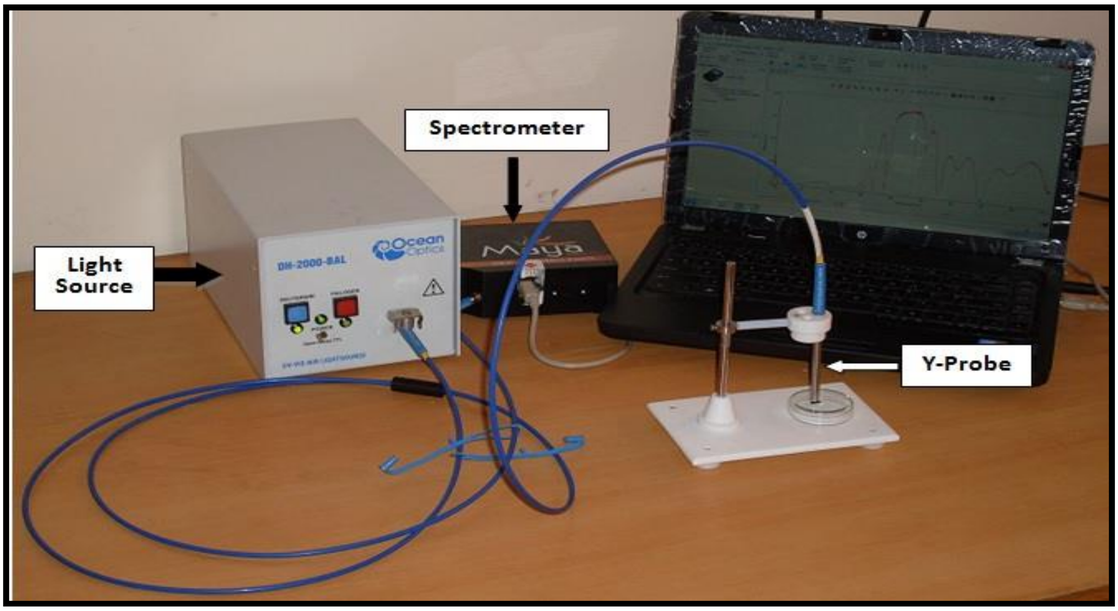

Fig. 2. Optical Spectrometer with Light Source and Accessories

3. Results and discussions

3.1. Structural and Optical Characterizations of Sensor Device

Structural morphology (plan and cross sectional view) was examined by SEM. In SEM plan view Figure. 3 (a), a large number of pores distributed in all direction were observed. In the SEM cross-sectional view Figure. 3 (b), multilayered stacks due to the periodic variation in the refractive index profile through the current density variation for different etching time were observed.

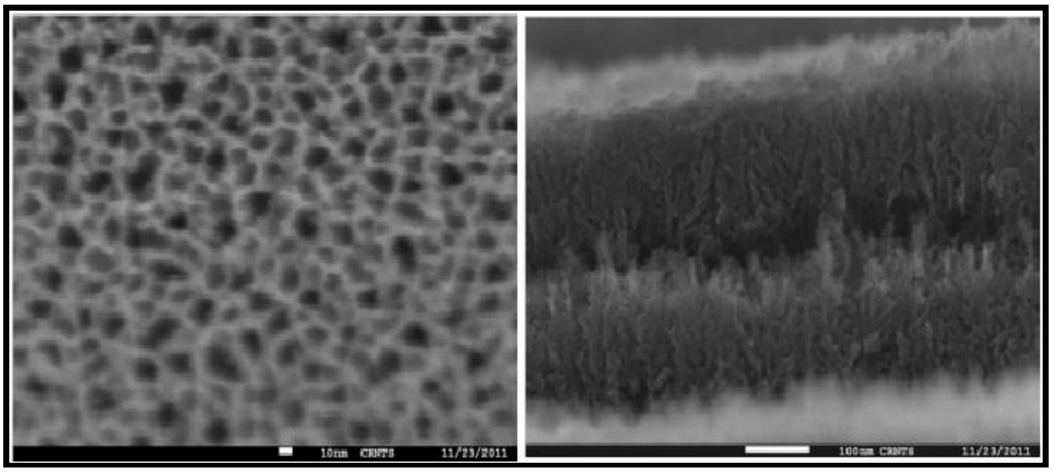

Fig. 3. (a) SEM Plan View of 1D-PSMC Sensor Device (b) SEM Cross-sectional view of Multilayer 1D-PSMC Sensor Device

Optical characterization of the prepared sensor device structure was done using optical spectrometer. Reflectance measurements were done in the air and the polished silicon wafer was used as a reference. The reflectance spectra of 1D-PSMC is shown in Figure. 4 the photonic resonance dip of the 1D-PSMC is observed near 800nm.

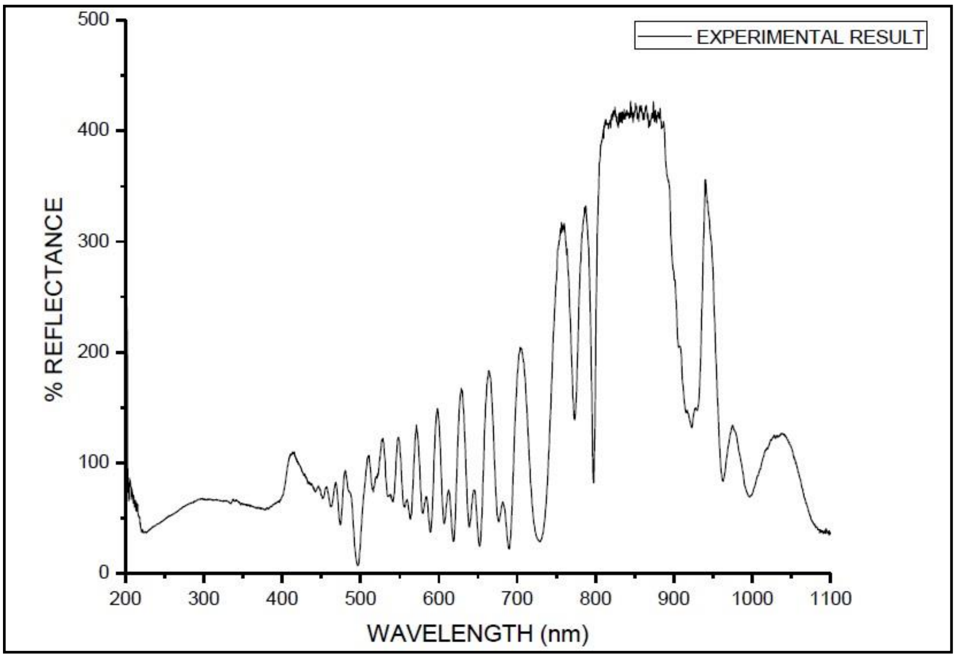

Fig. 4. Experimental Reflectance Spectra of 1D-PSMC Structure

3.2. Kerosene Detection

After fabrication, characterization and oxidation of 1D-PSMC sensor device, their performance as the optical sensor device for the detection of kerosene in petrol was tested by analyzing the wavelength shift in the reflectance spectra during their exposure to different concentrations of kerosene in petrol (0%, 10%, 20%, 30%, 40%, 50%) Variations in the photonic resonance dip in the reflectance spectra of the sensing device during exposure to different concentrations of kerosene in petrol were observed. During the adsorption, wavelength in the reflectance spectra promptly shifted toward the higher wavelength (low energy) regions as shown in Figure 5. This phenomenon can be attributed to the capillary adsorption of the liquid molecules within the pores of the porous structure [10]. The pores filled with kerosene molecules increase the overall effective refractive index and consequently optical thickness of the porous structure [13]. The strength of the wavelength shift depends on the kerosene concentration. Higher the concentration of kerosene, higher is the refractive index of the solution and hence, higher the wavelength shift. The mixture was then allowed to dry and a final stable shift in the wavelength was noted.

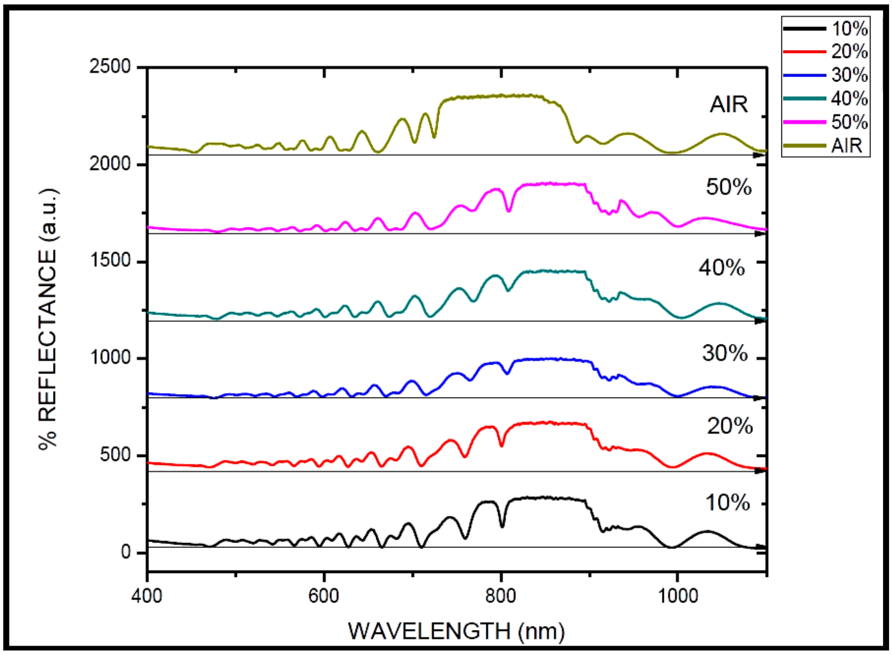

Fig. 5. Reflectance spectra of various concentration of petrol adulterated with kerosene.

As shown in the Figure.5, when the sensor device was exposed to high concentrations of kerosene, large variations in the reflectance spectra were observed; correspondingly, when the sensor device was exposed to low concentrations solutions, small variations in the reflectance spectra were observed. The effective wavelength shift ($\Delta\lambda$) measured from the reflectance spectra of 1D-PSMC structures for the different concentrations is listed in Table 1 and the result are plotted in Figure. 6.

Table 1: Concentration of Kerosene in Petrol and their wave length shift.

Sr. No.	Concentration of Kerosene in Petrol (%)	Wavelength Shift (nm)
1.	0	0
2.	10	77.63
3.	20	80.82
4.	30	82.03
5.	40	83.73
6.	50	85.48

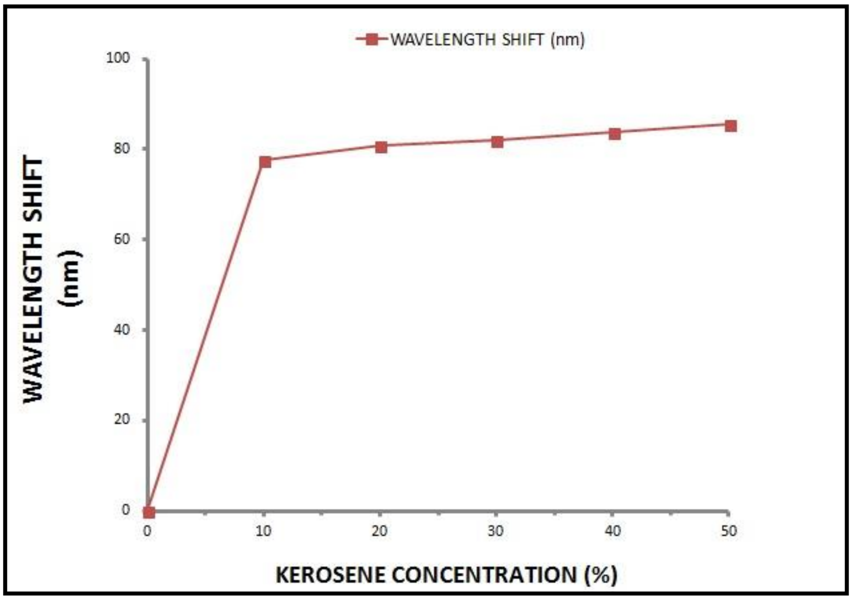

Fig. 6: Wavelength Shift vs Concentration of kerosene.

Fig.6 shows the good linear fitting for the graph of the kerosene concentrations *vs.* wavelength shift. Sensitivity is one of the most important issues to evaluate the performance of the sensors. In this case, the response of the sensor structure was evaluated throughout the change of the wavelength shift in the reflectance spectrum for different concentrations of kerosene solutions. This parameter showed to be a good indicator for sensing measurement in the 1D-PSMC sensing devices.

Also it was observed that, after washing the sensor device with isopropyl alcohol followed by DI water, the resonance peak of the sensor device promptly came to its original position. Hence the sensor operation is total reversible, which is good characteristic of this sensor device to develop the reversible sensor.

4. Conclusions

In conclusion, successful fabrication of Nano scale porous silicon micro cavity as optical sensor device was done for the quantitative detection of fuel adulteration Kerosene in Petrol. The proposed sensor device is capable for detection of 0% - 50% concentration of kerosene in petrol. It is simple and well performing optical Nano scale sensor with low cost compared to other existing technologies. Experiments showed that, after complete removal of the liquid molecules from the porous structure, reflectance spectra of the structures promptly returns to their original waveform position. This is a remarkable quality of these structures, and it is helpful in the development of reversible sensing devices. The only challenge was to find an appropriate washing agent which along with cleaning the liquid molecules from the porous structures should not hamper the fabricated wafer in any manner. Therefore it was found that isopropyl alcohol served as a good cleaning agent by unclogging the porous structures.

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