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NANO SCALE POROUS SILICON MICROCAVITY OPTICAL SENSOR DEVICE FOR THE DETECTION OF METHYL PARATHION

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Methyl Parathion (MP) is one of the pesticides used in the agriculture field for the protection of cotton trees against pests. In this paper, a novel technique for the detection of MP using simple and low cost one dimensional (1D) nano scale Porous Silicon (PS) Microcavity (MC) sensor device is reported. Sensor device was fabricated by electrochemical anodization of crystalline silicon wafer and proposed as a large surface area matrix for optical sensing of MP concentrations (in ppm) present in water and Humic Acid (HA) solutions. Wavelength shift ($\Delta\lambda$) in the measured reflectance spectra were analyzed for the detection of the MP in the porous structure. Sensor device showed excellent sensing ability and good linear relation between the different concentrations of MP 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 MP liquid 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

Chemical substances used in agriculture, food and beverage industries, to kill the unwanted organisms are known as pesticides. [1-3]. It is necessary to know the concentration of pesticides during their use in any place, else it may be harmful to animals and humans, causing liver damage, birth defects and cancer. Wold wide MP is used to protect the cotton trees from the different types of pests. In India, the major non food crop of Gujarat is cotton. It plays a dominant role in its agrarian and industrial economy. Gujarat produces about 33% of India's total cotton output. Methyl Parathion (formula: $C_8H_{10}NO_5PS$ and refractive index 1.56) is the pesticide generally applied by spraying to cotton trees. The most widely used methods for detection of organophosphate pesticides are high-pressure liquid chromatography, and gas chromatography in combination with mass spectrometry [4-5]. These methods offer quantitative analysis with sensitivity and selectivity but they are slow, expensive, and laborious. Hence, it is essential to develop low cost, simple and rapid methods for the detection of MP. 1D-PSMC structures are periodic dielectric structures that control the propagation of electromagnetic wave through the photonic crystals [6]. The structural properties of 1D-PSMC exhibits the sharp photonic resonance dip in the reflectance spectra which is useful for the optical sensor applications. Due to tremendous advantages like, spongy skeleton, high surface area, strong and fast interaction with organic substances, fast resulting changes in optical properties such as reflectivity, photoluminescence, controllable morphology, easy fabrication, low cost and high sensitivity to the presence of chemical and biological species inside the pores PS is emerged as new nano material for the optical device [7-8]. Hence, in past years, a lot of researchers attention was focused on the

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characterization, devices, sensors, biosensors and other emerging and future nano scale applications using PS [9-20]

The objective of this work is to evaluate the feasibility of quantitative detection of low concentration MP solutions using 1D-PSMC sensor devices. In section 2, principle of optical sensing using 1D-PSMC is described. In section 3, experimental details for the fabrication of 1D-PSMC sensing device structure is presented with materials, fabrication procedure and sample preparations. In section 4, first structural and optical characterizations are discussed and finally, realization of MP optical sensor device with different concentrations has been studied by examining the wavelength shift in their reflectance spectra.

2. Principle of Optical Sensing

Principle of interferometric transduction is used, in which the molecular recognition events are converted into optical signals via the change of the refractive index [21]. As shown in the schematic diagram (Fig. 1), light reflected from the top interface (air-PS) and the bottom interface (PS-Si substrate) interfere with each other and form the typical Fabry-Perot fringes in the reflectance spectrum.

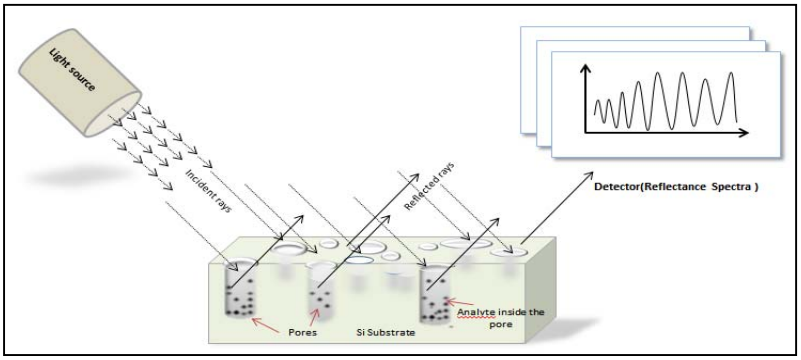

Fig. 1: Schematic Diagram of Sensor Principle

For the multilayer 1D-PSMC structures with alternating high refractive index layers and low refractive index layers [22], the fringe pattern is closely related to effective optical thickness of the structure, by the relationship shown as:

$$\frac{m\,\lambda_0}{2} = n_L d_L + n_H d_H \tag{1}$$

where, λ_0 is the photonic resonance wavelength, n_L and d_L are the refractive index and the thickness of the low index layer, respectively, while n_H and d_H *are* the refractive index and the thickness of the high index layer, respectively.

3. Experimental

A. 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 [11] containing the electrochemical etching cell [11, 15]. First, silicon wafer was cleaned using standard piranha cleaning method. PTFE bath was filled with the etching solution of 40% aqueous HF and 99% ethanol, mixed in the ratio of 1:2. 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 (d) 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 with six repetitions of a current density and etching time sequences. 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. 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). An UV-Vis-NIR Spectrophotometer (Maya Pro 2000, Ocean Optics Inc.) was used for the reflectance measurements of the prepared sensor device structures [11].

B. Oxidation of Sensor Device

Porous silicon 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 900º C in tube furnace for 5 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 [23].

C. Sample Preparation

For quantitative analysis, low concentration MP solutions (1-10 ppm) were made in (1) in pure water and (2) Humic acid (0.2 mg/ml) extracted and purified from soil. Humic solutions were chosen to represent systems similar to natural conditions where water containing pesticides have also dissolved organic matter as component. Then the solution was dropped on to the 1D-PSMC sensor devices, hence the solution reach to the pores of the sensor device. The amount of solution and the time of reaction were optimised to 10 µl and 60 seconds, respectively, for the reaction to be in the linear region. After each measurement, the device was thoroughly rinsed in the DI water for complete removal of all the MP liquid molecules from the pores.

4. Results and discussion

A. Structural and Optical Characterization of Sensor Device

After electrochemical etching, these structures were rinsed in DI water for 10 minutes and dried at room temperature. Structural morphology (plan and cross sectional view) was examined by SEM. In SEM plan view (Fig. 2 (a)), a large number of pores distributed in all direction were observed. In the SEM cross-sectional view (Fig. 2 (b)), multilayered stacks due to the periodic variation in the refractive index profile through the current density variation for different etching time were observed.

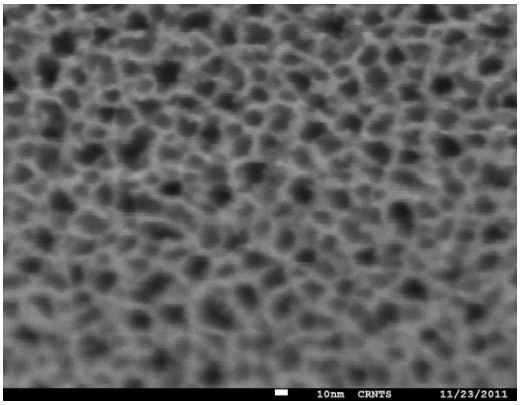

Fig. 2 (a): SEM Plan View of 1D-PSMC Sensor Device

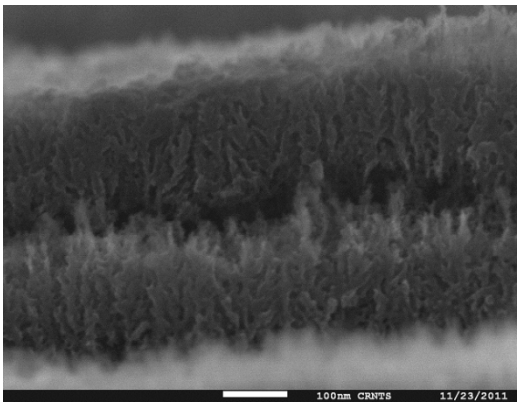

Fig. 2 (b): SEM Cross-sectional view of Multilayer 1D-PSMC Sensor Device

Optical characterization of the prepared sensor device structure has been done using optical spectrometer [11]. In Fig. 3, solid line represents the measured reflectance spectra and dotted line represents the simulated reflectance spectra of the sensor device. The resonance dip is centred at wavelength of 750 nm. Comparison of the simulation and the experimental results are done based on the simulation program was developed in the MATLAB software using Transfer matrix method and the Bruggeman's effective medium [15]. Input data for the simulation are photonic resonance wavelength and measured thicknesses from SEM.

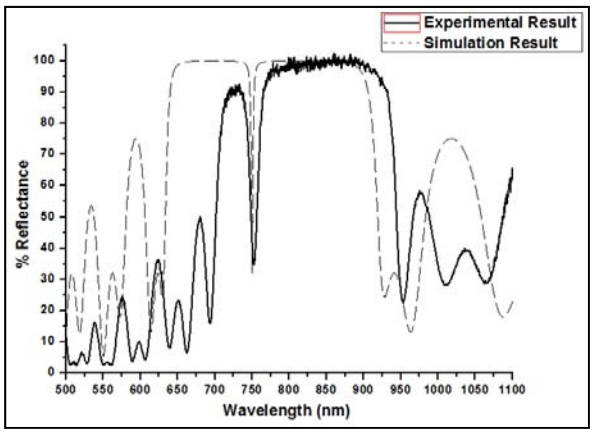

Fig. 3: Simulated and Experimental Reflectance Spectra of 1D-PSMC Structure.

In Fig. 3, some discrepancies are noticed between the simulated and the measured values in the reflectance spectra because, simulation does not take into account the fact that the top layer is in the contact with HF solution during the whole electrochemical process. The anodization

condition might drift as the sample thickness and refractive index of stacks, and the solution composition, changes with the depth because of limited exchange through the pores, which caused the difference in experimental results in comparison with the simulation results. Also, the imperfection of interfaces created by the electrochemical etching may be the cause of the deviations in the simulation and the experimental reflectance spectra.

B. MP Detection

After fabrication, characterization and oxidation of 1D-PSMC sensor device, their performance as the optical sensor device for the detection of pesticide MP was tested by analysing the wavelength shift in the reflectance spectra during their exposure to different concentrations (1-10 ppm) of MP in water and HA. Variations in the photonic resonance dip in the reflectance spectra of the sensing device during exposure to different concentrations of MP were observed. During the adsorption, wavelength in the reflectance spectra promptly shifted toward the higher wavelength (low energy) regions. This phenomenon can be attributed to the capillary adsorption of the MP liquid molecules within the pores of the porous structure. The effective wavelength shift ($\Delta\lambda$) measured from the reflectance spectra of 1D-PSMC structures for the different concentrations is listed in Table 1.

Table 1: Effective wavelength shift in reflectance spectra for different concentrations of MP

MP Concentration (ppm)	Wavelength Shift (nm)	
	MP in Water	MP in HA
1	3.14	3.64
3	6.27	8.57
5	8.52	11.71
7	11.20	13.74
10	15.23	18.88

It is clearly observed from Table 1, that the wavelength in the reflectance spectra of the 1D-PSMC sensor device were shifted towards higher wavelength, because the pores were filled with MP molecules whose refractive index, $n > 1.0$. The sensor response mainly depends on two factors: the refractive index of the MP solution and its capability of filling the pores. When solution of MP in water or HA was kept on the 1D-PSMC sensor device, air was substituted by liquid MP solution in the pores by capillary adsorption. Due to this phenomena, the effective refractive index of the PSMC structure increases, which results in the resonance wavelength shift in the reflectance spectra. The relationship between concentrations of MP and the wavelength shift is plotted in Fig. 4 from the results of Table 1.

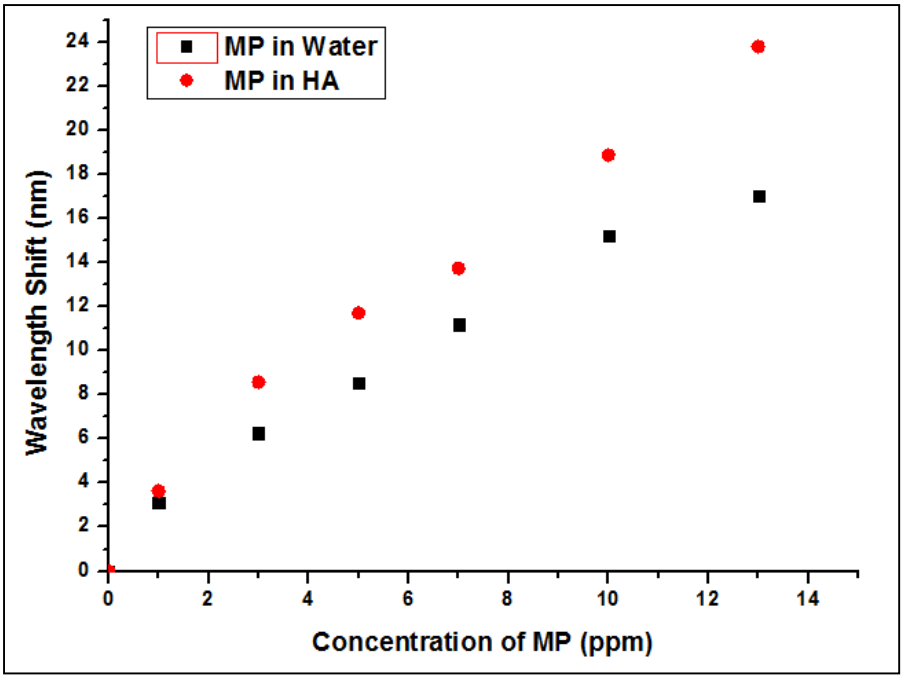

Fig. 4: MP Concentration vs Wavelength Shift

Fig. 4 shows the good linear fitting for the graph of the MP concentrations *vs.* wavelength shift. As shown in the Fig. 4, when the sensor device was exposed to MP solution of high concentrations, 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. This is due to the variations in the effective refractive index of the 1D-PSMC layers according to the different concentrations of MP solution adsorbed in pores. In the Fig. 4, it is observed that all the experimental points are on the linear fitting. Also, it was observed that the higher wavelength shift was observed in the case of MP in HA because MP with HA contains dissolved organic matter as component which have higher refractive index compare to water.

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 ($\Delta\lambda$) in the reflectance spectrum for different concentrations of MP solutions. This parameter showed to be a good indicator for sensing measurement in the 1D-PSMC sensing devices. In this sensor device, the measured sensitivity is 1.156 nm/ppm for MP in water and 1.661 nm/ppm for MP in HA.

Also it was observed that, after washing the sensor device with 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 devices.

5. Conclusions

In conclusion, successful fabrication of nano scale porous silicon microcavity as optical sensor device was done for the quantitative detection of methyl parathion pesticide. The proposed sensor device is capable for detection of 1-10 ppm concentration of the methyl parathion in water and humic acid solutions. The sensor device proposed 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 very good quality of these structures, and it is helpful in the development of reversible sensing devices.

Acknowledgments

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