Armenian Journal of Physics, 2013, vol. 6, issue 2, pp. 103-110

NANOSCALE POROUS SILICON PHOTONIC MICROCAVITY STRUCTURES FOR OPTICAL SENSING OF ETHANOL

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Received 12 November, 2012

Abstract–Porous silicon (PS) is emerged as a unique and promising nanomaterial for the optoelectronic devices and the sensing applications. In this study, nanoscale PS photonic microcavity (MC) sensor device structures, prepared by anodization of crystalline silicon wafer, are proposed as a large surface area matrix for sensing the different concentrations of ethanol solution. Fabry–Perot reflectance fringes were observed from the PSMC structures prepared under the anodization conditions with different current densities and etching time profiles. The optical characterization of the PSMC structures, before thermal oxidation, showed a sharp photonic resonance and blue shifted and narrowed after thermal oxidation process. The photonic resonance wavelength of PSMC sensor device showed significant red shift after capillary adsorption of ethanol because the structure refractive index changes after infiltration of the pores of the PSMC sensor device structures. The resonance wavelength shift showed a linear relationship with the different concentrations of ethanol for the natural oxidized PSMC structures and thermal oxidized PSMC structures. The thermal oxidized structures showed better sensibility feature and this result was attributed to passivation of the surface devices. Also, we observe the ability of reversible sensing by PSMC sensor device structures.

Keywords: porous silicon, microcavity, thermal annealing, electrochemical etching, ethanol sensor

1. Introduction

Selective and accurate sensing of different analytes such as chemical, biochemical and biological analyte is today's prime need. Ethanol is volatile, flammable and colorless liquid and can be employed as a solvent to dissolve other substances for consumption or use. Ethanol is used in many applications of house hold, bio-fuel, medical, pharmacology etc. Hence it is necessary to measure the concentrations of ethanol for the industries. Porous silicon (PS) is emerged as a unique and promising material for the optoelectronic devices and the sensing applications because of sponge-like structure, high surface to volume ratio, low-cost, capable of room-temperature operation, and compatible with standard silicon fabrication technology [1]. Its spongy skeleton makes it ideal material as a host for the sensing of gas, chemicals and the bioanalytes inside the pores. The optical properties [2] of PS are highly sensitive to the presence of species inside the pores. Porous silicon microcavity (PSMC) is the periodic dielectric structures that control the propagation of electromagnetic wave through the photonic crystals [3]. Several groups have reported the applications of PS structures in the optical devices and sensing applications. Many research groups are working related to characterization and applications using PS structures [4-10].

The objective of this work is to evaluate the feasibility for fabrication of PSMC structures as optical sensor device for the sensing of ethanol concentrations using fiber optic spectrometer. First, experimental detail for the fabrication and oxidation process of PSMC structures is presented. After

that, principle of optical sensing, structural and optical characterizations of PSMC structures are discussed. Finally, the testing of these structures as an optical sensor device have been done by sensing of different concentrations of ethanol by examining the resonance wavelength shift in their reflectance spectra before, during and after exposure to the ethanol.

2. Experimental

PSMC structures were fabricated by electrochemical etching of p-type Si wafer (with orientation <100>, resistivity 0.01–0.02 Ω cm, and thickness 275 μm, respectively). Fabrication was done in the electrochemical etching cell. The base of the electrochemical etching cell was made with stainless still. Silicon wafer was placed inside the base, sealed with an O-ring and exposed to the electrolyte. The electrolyte mixture was kept in the highly HF resistant polymer polytetrafluoroethylene (PTFE/Teflon), which was in contact with the platinum grid, used as a cathode. 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. The cathode was immersed in the electrolyte solution. Periodic constant current square wave was applied by programmable DC power supply (PWS 4305, Tektronix). A constant current mode was used for anodization process as it is beneficial in terms of regulation [11]. 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. The fabrication schematic diagram of the PSMC structure is shown in Fig.1, where n_s is the refractive index of the silicon substrate and N is the number of period. The microcavity was realized by inserting a cavity layer of high current density between two identical DBR1 and DBR2 with six repetitions of current density and etching time sequences as shown in Fig.1.

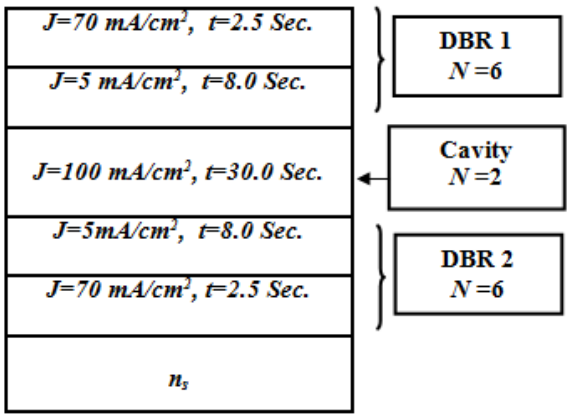

Fig.1. Fabrication Schematic of PSMC structures.

After electrochemical etching, PSMC structures were rinsed in deionized water for 10 minutes and dried at room temperature which makes natural oxidation of the structures. The structural

morphology of the PSMC sensor device was characterized by scanning electron microscopy (SEM). Few PSMC structures were passed through the thermal oxidation process at 900° C temperature for 5 minutes in the ambient conditions in the tube furnace. An UV-VIS-NIR Spectrophotometer (Maya Pro 2000, Ocean Optics Inc.) was used for the reflectance measurements of the prepared sensor device structures (Fig.2). As shown in the Fig.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 with a wavelength range of 200–1000 nm with resolution of 0.5 nm. Finally, the reflectance spectrum is displayed on computer screen. All measurements were done in the air. Polished silicon wafer was used as reference in the reflectance measurements.

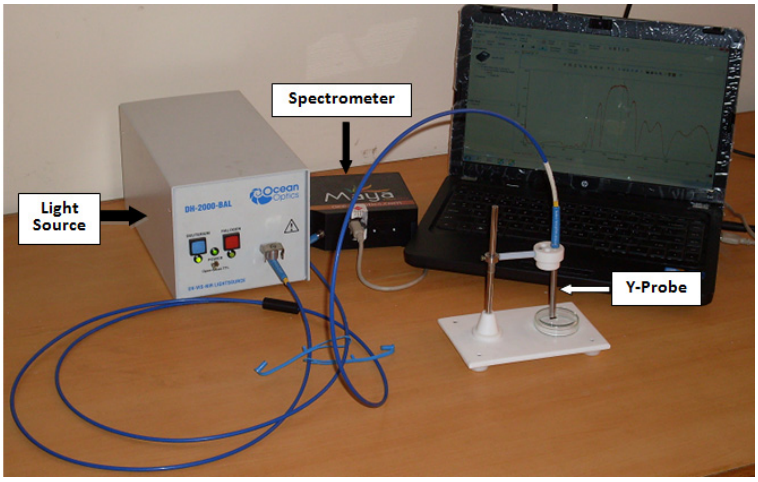

Fig.2. Optical spectrometer with light source and accessories.

3. Results and Discussion

According to the optics theory, the reflectance spectrum of PS structure is governed by the Fabry-Perot relationship [8, 10]. 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. The fringe pattern is closely related to effective optical thickness, which is product of physical thickness and refractive index of the structure, by the relationship shown in as:

$$m\lambda = 2nd, \tag{1}$$

where m is an integer (the spectral peak order) and λ is the peak wavelength. For bare PSMC structures (without any analyte), the refractive index of the structure is n. When the pores are filled with an analyte (e.g., chemicals or biochemicals), the effective refractive index of the structure increases from n to $n+\Delta n$ with shift in wavelength from λ to $\lambda+\Delta\lambda$ in the reflectance spectra due to increased optical thickness of the structure.

The prepared structures showed green colour uniformly distribution over the entire surface. Porous structure in the bulk silicon is strongly responsible for the change in the surface colour due

to the shifting in the band gap energy of silicon [12]. Fig.3a and b shows the structural morphology of the natural oxidized PSMC structure in SEM plan and cross sectional view, respectively.

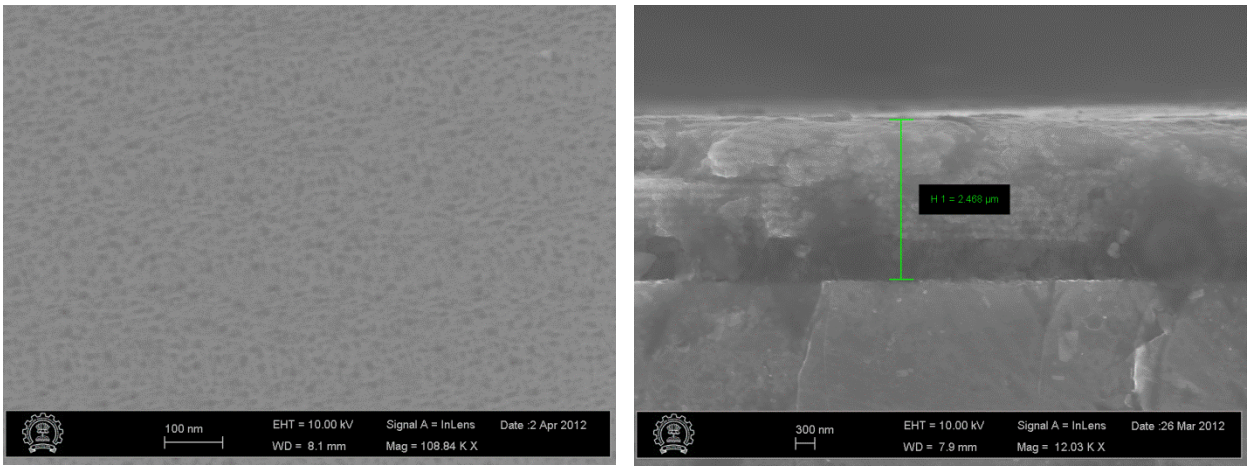

Fig.3. a) SEM plan image and b) cross-section view of natural oxidized PSMC structure.

The array of void spaces (dark) in silicon matrix (bright) can be seen clearly in the plan view SEM image (Fig.3a). Surface morphology of the structures shows that the electrochemical etching is done uniformly on the surface and created the granular structure in a spherical shape. Large number of pores with mean pore size of 24 nm distributed in all direction can be observed in Fig.3a. Multilayered stacks of periodic variation in the refractive index profile through the current density variation for different current density and the etching time are clearly visible in the SEM cross sectional view of Fig.3b.

Reflectance spectrum of the simulated and the measured natural oxidize PSMC structure with the sharp photonic resonance dip centered at 594.56 nm is shown in Fig.4.

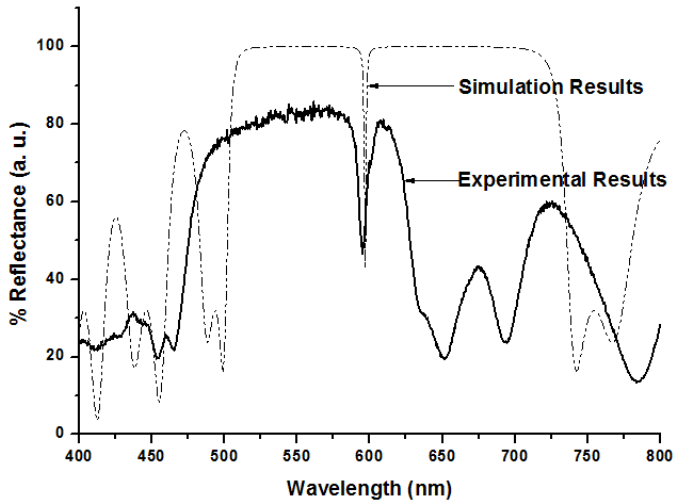

Fig.4. Simulated and measured reflectance spectra of natural oxidized PSMC structures.

Some discrepancies are noticed between the simulated and the measured values in the reflectance spectra of Fig.4 because, the 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.

After the anodization process, the few PSMC structures were thermally oxidized in tube furnace at 900°C for 5 minutes in the ambient conditions. This process is necessary because PS is a material characterized by a high chemical reactivity. In ambient air, the PS texture becomes naturally oxidized, which leads to a decrease of the refractive index due to the fact that silicon oxide has a much lower refractive index than silicon. To stabilize the PS and to eliminate the problem of aging, thermal oxidation of the structure is necessary [1]. Thermal oxidation makes highly stable structure which is important condition for any type of sensor device [13].The measured reflectance spectra of naturally and thermal oxidized PSMC structures are shown in the Fig.5. As shown in Fig.5, after thermal oxidation process the resonance wavelength of the PSMC sensor device shifted to 527.19 nm (high energy region). Significant blue shift of 67.37 nm is observed in the reflectance spectra. These results could be explained as follow: because of the thermal treatment, the structure becomes more compact due to the re-crystallization of the PSMC layers. Also, due to thermal oxidation process, the oxide face in the PS layers increase and the composite PS structure is now formed by three face materials; Si–SiO_2–air, since the silicon oxide has low refractive index the composite structure must has low refractive index after annealing process [1]. It is also observable in Fig.5, that, the cavity resonance band in the thermal oxidize PSMC sensor device showed dipper feature than of the natural oxidized PSMC sensor device. These results could be due to the extinction coefficient decrease in the annealed PSMC sensor device improving the cavity effect. However, the reflectance of the annealed PSMC sensor device decrease that could be attributed to the increase on the interface roughness during oxidation [1,13].

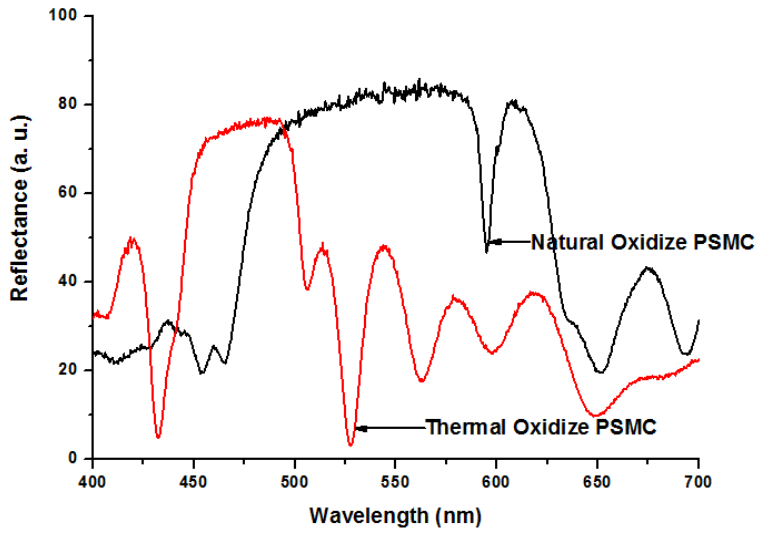

Fig.5. Reflectance spectra of natural and thermal oxidized PSMC structures.

Testing of the both the PSMC structures as optical sensor device for the sensing of the different ethanol concentration was done by examining the photonic resonance wavelength shift in their reflectance spectra before, during and after exposure to the ethanol concentrations. Variation in the reflectance spectra of the natural and thermal oxidized PSMC sensor device structures during their exposure to different ethanol concentration are shown in the Fig.6a and b, respectively.

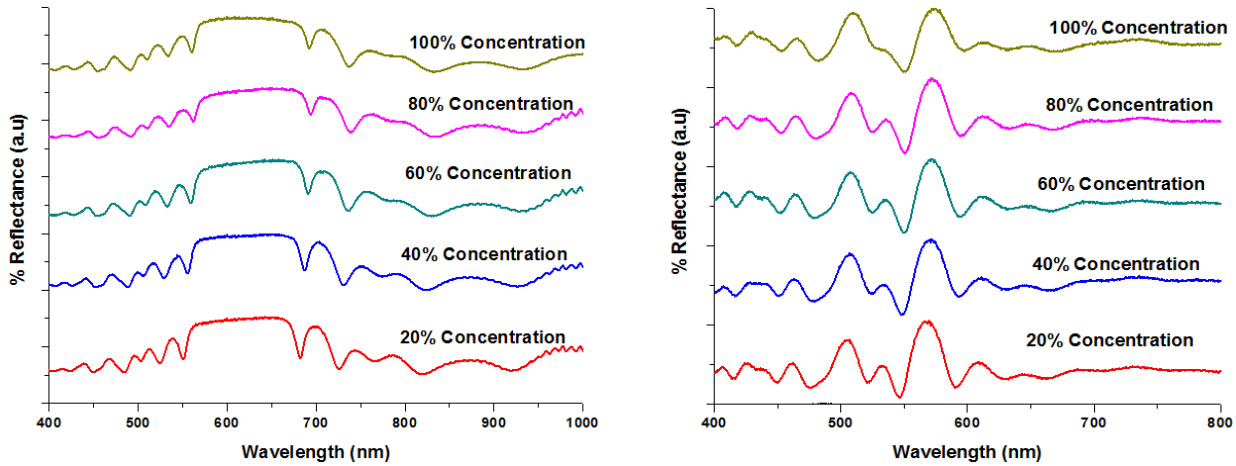

Fig.6. a) wavelength shift (Δλ) in the reflectance spectra of natural oxidized PSMC sensor device, b) wavelength shift (Δλ) in the reflectance spectra of thermal oxidized PSMC sensor device.

As can be seen from Fig.6a and b, during the ethanol adsorption, resonance wavelength in the reflectance spectra promptly shifted toward the higher wavelength (low energy) regions. This phenomenon can be attributed to the capillary adsorption of ethanol within the pores of both the porous PSMC sensor devices. The filled pores with ethanol $(n > 1.0)$ increase the overall effective refractive index of the structure and consequently increasing their optical thickness. This effect promotes the wavelength shift in the reflectance spectrum. The strength of the wavelength shift depends on the ethanol concentrations. Higher the concentration of ethanol, higher the refractive index of the solution and hence, higher the wavelength shift is observed in both the PSMC sensor devices. The wavelength shift measured from the reflectance spectra of both the PSMC sensor device for the different ethanol concentrations is listed in Table 1.

Table 1. Wavelength shift in reflectance spectra of PSMC sensor devices.

Ethanol Concentration (%)	Wavelength Shift (nm)	
	Natural Oxidized PSMC Sensor Device	Thermal Oxidized PSMC Sensor Device
20	86.47	18.20
40	92.70	20.93
60	97.15	21.84
80	103.42	22.74
100	104.35	24.57

As shown in the Table 1, the standard variation in the wavelength shift of the natural oxidized PSMC sensor device structure is consistently higher than thermal oxidized PSMC sensor device.

These could be understood as: in the case of the thermal oxidized PSMC sensor device structure, the overall effective refractive index of the structure is less due to the formation of SiO_2 (refractive index is approximately 1.50) by thermal oxidation treatment, hence the overall refractive index of the structure decreases, which decreases the wavelength shift compare to naturally oxidized PSMC sensor device.

The relationship between ethanol concentrations and the wavelength shift is plotted in Fig.7 from the results of Table 1. Fig.7 shows the good linear fitting for the graph of the ethanol concentrations values vs wavelength shift for both the PSMC sensor devices.

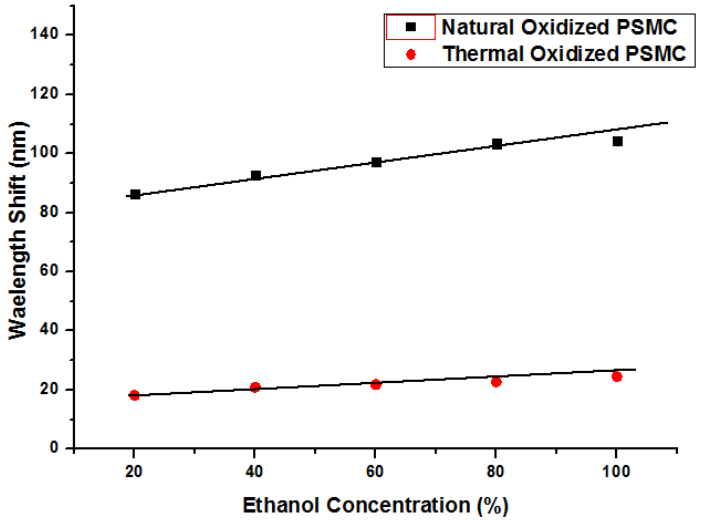

Fig.7. Ethanol concentrations vs wavelength shift.

Sensitivity is one of the most important issues to evaluate the performance of the sensors. In this case, the response of the sensor device structure was evaluated throughout the change of the wavelength shift $(\Delta\lambda)$ in the reflectance spectrum for change in the ethanol concentrations (Δx). Sensitivity S is defined as:

$$S = \Delta\lambda/\Delta x. \qquad (2)$$

Calculated sensitivity is 4.47 nm/ethanol concentration (%) for the natural oxidized and 12.55 nm/ethanol concentration (%) for the thermal oxidized PSMC sensor device structures respectively. Sensitivity is higher in the case of thermal annealed PSMC and also it gives the better stability compare to other sensor device structure.

It is also observed that, after complete evaporation of ethanol from the porous structure, the reflectance spectra of the structures promptly returns to their original waveform position for both the sensor devices. This implies that the change in reflectance spectra is indicative of the presence or absence of the ethanol in the pores and that the change in the spectra of the sensor device structure is temporary. These results are very much useful for the development of effective reversible sensors using PSMC.

4. Conclusions

In conclusion, successful fabrication of porous silicon photonic microcavity optical sensor device structures was done. It is shown that porous silicon microcavity can be used as a chemical sensor for detecting concentrations of ethanol solution. Fabry–Perot fringes measured from the PSMC sensor device structure in ethanol solution were changed due to the change in the effective optical thickness of the structure by variations in the concentration of the ethanol solution. Both the sensor devices with different ethanol concentrations showed to have a good linear relationship with wavelength shift. However, the thermal oxidized PSMC sensor device showed to have a good sensitivity and stability features due to passivation of surface of the device. Also, it was observed that, after complete evaporation of the ethanol solution from the pores, the reflectance spectra of the structures promptly returns to their original waveform position in both the sensor devices. This is a very good quality of PSMC sensor device these structures in the development of a reversible sensing device.

Acknowledgments

This work was supported by the grant from Defence Research and Development Organization (DRDO), Govt. of India. Authors are also thankful to CRNTS, SAIF, IIT Bombay for the structural characterization of the samples.

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