# A Nanoporous Silicon 1-D Photonic Band Gap Microcavity as a Selective Optical Sensor

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## ABSTRACT

A nanoporous silicon (pSi) one dimensional photonic band gap (1-D PBG) with a microcavity was prepared for selective sensing in the optical regime. The cavity resonance of the localized mode was tuned by the thickness of the defect layer, and this localization led to a selective reflectance. The band gap was demonstrated in the optical regime (450-600 nm) and the microcavity was centered at 588 nm when illuminated with incident light to the normal. Crystal Violet dye (absorption at 593 nm) was adsorbed into the structure due to its absorption match with the microcavity (593 nm). Uv-vis spectroscopy was used to characterize the sensitivity of the dye. Since there was a decrease in the reflectance intensity at the microcavity center, the intensity could be used to detect the analyte type and its concentration. In addition, there is a high selectivity for the wavelength of interest. The new feature of this sensor is that an absorbing dye was adsorbed into the structure to match the cavity in the PBG structure in the optical regime.

***Keywords***: photonic band gap (PBG), microcavity, porous silicon, optical sensor, dielectric bragg reflector (DBR)

## 1 INTRODUCTION

Over the past two decades photonic band gap (PBG) in photonic crystals (PBG structures) have been proposed and demonstrated [1-2]. PBGs are a range of wavelengths of electromagnetic waves that are not allowed to penetrate within a PBG structure due to Bragg like diffraction thus can easily be used as a Fabry-Perot filter. PBG structures are macroscopic crystal structures that have certain ordering (e.g., hexagonally closed packed) due to the assembly of two or more materials with large variations in their indices of refraction [3]. A 1-D PBG structure (also called a Dielectric Bragg Reflector (DBR) can easily be constructed by etching alternating layers of highly porous and less porous silicon (pSi) layers of particular thicknesses, essentially producing a mirror. The desired wavelengths of the PBG are related to the layer thickness by Eq (1)

$$m\lambda = 2nL \qquad (1)$$

where m is the spectral ordering, $\lambda$ is the wavelength, of light, L is the thickness of the film and n is the index of refraction. When a defect (e.g., larger thickness) is placed in the center of the1-D PBG light is allowed to penetrate within the PBG but only at a localized wavelength. This PBG resultant structure is a porous silicon microcavity (PSM) or a microcavity between two mirrors.

Over the last decade, various research groups have demonstrated the use of the 1-D PBG pSi microcavity for applications in biological and chemical optical sensors [4-11]. In one case the nanoporous feature of the DBR pSi structure was investigated to enhance the sensitivity of the pSi as a biosensor by determining the concentration of adsorbed enzymes within the high surface area of the pores [10-11]. In another chemical sensor the 1-D PBG pSi microcavity was used to detect organic molecules due to a shift in the photoluminescence spectra of a silicon due to a change of the refractive index in the pores of the structure caused by binding of organic molecules [4]. Similarly, a DNA biosensor was established by the same principle caused by binding a DNA strand to a complementary strand of DNA in the pores of the structure [6]. Here we report on the establishment of a different principle of this structure as a sensor, mainly highlighting the feature that the 1-D PBG microcavity can be used as a filter, so that an absorbing dye can be easily detected within the structure. In this structure we consider not only the contrasting indices of refraction between two materials, but also the absorbing dye that makes contributions mainly to the imaginary component or lossy part of the index of refraction. This concept can be further developed for applications in chemical and biosensing in particular DNA based biosensing.

## 2 EXPERIMENTAL PROCEDURE

The 1-D PBG pSi with a microcavity was prepared by anodizing boron-doped silicon (0.008-0.01 Ω cm, PCA Corp) in an HF solution with ethanol (66 v% ethanol, 14 v% HF, and 20 v% water). The electrochemical cell was designed with a Teflon spacer of a 2 mm distance between the Si anode and the Pt foil cathode. The current density and etching time were controlled by a computer controlled power supply (LKB 2197).

A PBG structure was prepared with 24 bilayers of low and high porosity (i.e., high and low index of refraction) by alternating the current density between 10 mA/cm$^2$ for 3 sec and 70 mA/cm$^2$ for 8 sec, resulting in approximately 56% and 81% porous layers, respectively. Another pSi PBG structure with a microcavity and 14 bilayers was accomplished by alternating the current density between 10 mA/cm$^2$ for 3 sec and 70 mA/cm$^2$ for 8 sec, but this time by placing a defect (81%) designed to be a half wave at the center of the structure while holding the current density at 70 mA/cm$^2$ for 7 sec. The samples were thermally oxidized in air at 900ºC for 20 min

A gravimetric method was used to determine the resulting porosity for a high and a low porosity layer. Two structures were prepared for this measurement 1) low porosity layer and 2) a high porosity layer. The entire structure was weighed and then the porous layers were etched from the silicon with KOH (3 v% in water) and reweighed. The weight difference was used to calculate the percent porosity. The index of refraction for the high and low porosity layers were calculated by the Bruggman equation [4].

Scanning electron microscopy (SEM, Hitachi 2800N) was used to characterize the thickness of the layers of each resultant structure. The structures were characterized by uv-vis spectroscopy (HR2000, Ocean Optics) in reflectance mode.

Crystal Violet dye ($10^{-6}$ M in water, absorption at 593 nm, J.T. Baker) was adsorbed into the structure by immersing the structure in the dye for 24 hr. Crystal violet dye was chosen because of its match to the PBG microcavity.

## 3 RESULTS AND DISCUSSION

An SEM image of the PBG pSi structure with 24 alternating high and low indices of refraction is shown in Figure 1. The white and dark color in the SEM represents the low (high index n=1.96) and high (low index n=1.53) porosities of the layers, respectively. The thicknesses of the layers were 95.3$\pm$14 nm for the high porous layer and 56.7±12.3 nm for the low porous layer. It is also noteworthy that there was a decrease in the layer thickness ($\Delta$thickness≈ 22nm) as the anodization is at an advanced stage (towards the bottom layers). This may be due to a reduction in etching rate due to a diffusion limited electrochemical reaction. The relatively fast switching between the two currents also may have transient effects (e.g. polarization) on the anodization [7]. In addition the index of refractions and thicknesses of the DBR structure that were experimentally inferred and measured were modeled by a transfer matrix method (TMM) computational approach, however, the experimental results did not match the simulated results. The computations indicated a greater index of refraction change ($\Delta$n~0.8) then expected from the calculated value from the Bruggman equation ($\Delta$n~0.4). Further experiments will use angle resolved reflection spectroscopy to attain the actual indices of refraction for each porous layer.

Figure 2 shows the uv-vis spectra obtained for % reflectance verses wavelength for the pSi PBG structure with and without the absorption of Crystal Violet dye. The apparent PBG is between ~440 and 620 nm. The % reflectance intensity decreases with the application of the dye is hypothesized to be due to the absorbance of the dye at 593 nm and also can be used to explain the asymmetric decrease of the PBG with dye insertion.. However, there was no spectral shift in the observed spectra on insertion of the dye, even though the shift is usually expected for even small changes in the index of refraction which result from the addition of an absorbent dye (imaginary index of refraction). Since these observations did not completely, agree with the expected results, future work is still warranted on studying the photoluminescence and its effect on white light reflection of the dye insertion.

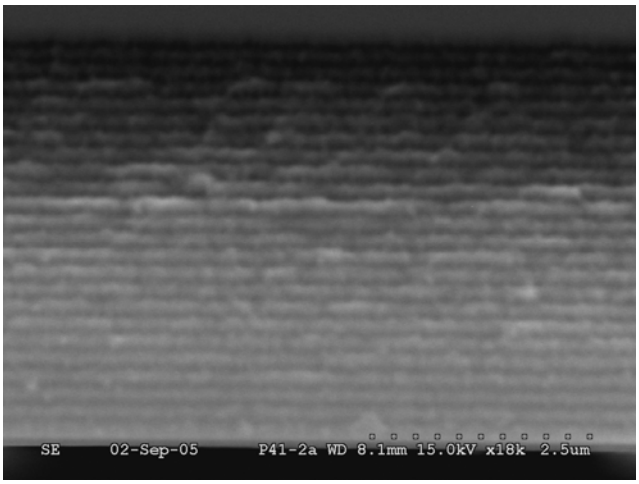


Figure 1: SEM image of a 1-D PBG pSi structure.

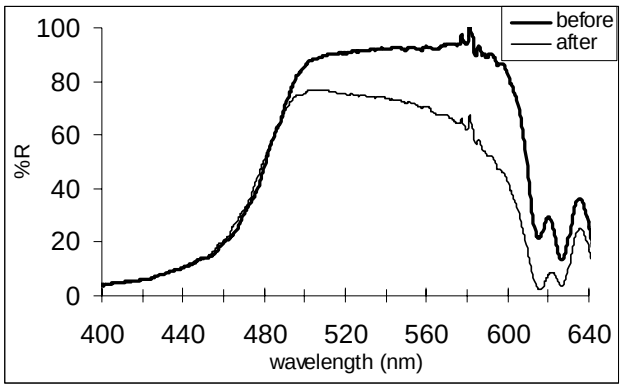


Figure 2. Uv-vis spectra before and after dye insertion into a 1-D PBG pSi structure

An SEM image of the PBG pSi structure with 14 alternating high and low indices of refraction and a defect

layer is shown in Figure 3. The thicknesses of the layers were 95.7±11.2 nm for the high porous (white), 69.5±12.9 nm for the low porous (dark) and 127±14.6 nm for the defect layer.

Figure 4 shows the uv-vis spectra of the 1-D PBG pSi with microcavity before and after the dye was absorbed into the structure. The PBG was between ~465 and 680 nm with a microcavity at 588 nm. After dipping the film in the dye solution, the transmission peak of the defect was wider and the reflection intensity decreased. The widening was probably due to the absorption increase. The reflection intensity was lower due to the change in the imaginary component of the index of refraction of the layers when they were covered with dye molecules.

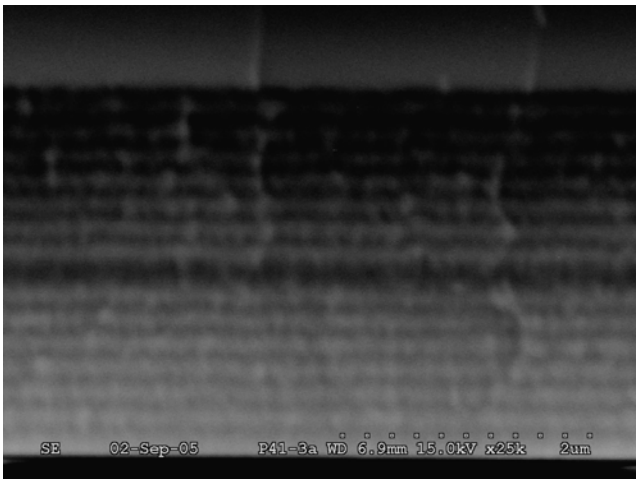


Figure 3: SEM image of the 1-D PBG pSi microcavity structure.

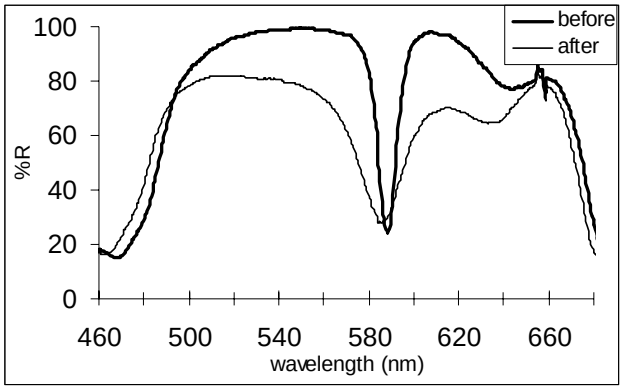


Figure 4. Uv-vis spectra before and after dye insertion into the 1-D PBG microcavity structure

Insertion of water inside the structure without the dye did not affect the PBG to any significant extent.

Figure 5 shows the uv-vis spectra for a PBG structure that had a PBG between 390 nm and 510 nm before and after the insertion of the dye. There was no significant change in the uv-vis spectra after dye insertion in this case (See figure 5). This is because the stop band in this case is blue shifted and hence the absorption of the dye lies outside the stop-band. The small observed shift in figures 5 is attributed to the sample being slightly repositioned during the measurement.

This filter device may be used as an inexpensive biosensor. For example, high extinction coefficient molecules (e.g., quantum dots or gold nanoparticles) may be attached to ssDNA and absorbed within the nanoporous surface of the Si PBG structure. If complimentary DNA hybridization takes place, then the particles will agglomerate changing the absorption wavelength at the microcavity wavelength resulting in loss of the signal.

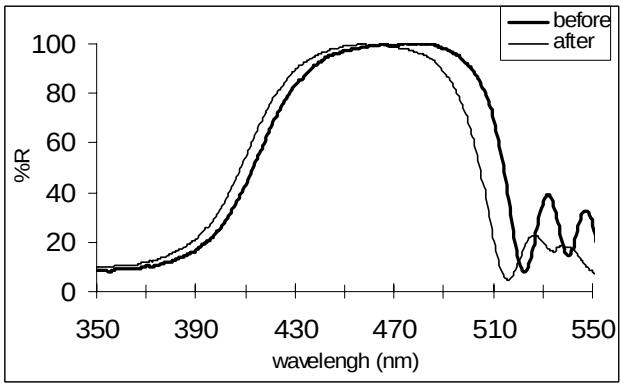


Figure 5. Uv-vis spectra for a pSi PBG structure before and after dye insertion.

## 4 CONCLUSIONS

We have demonstrated the use of a 1-D photonic band gap porous silicon microcavity as a filter for selective detection of dye absorption. Ultimately this type of device could be used as an inexpensive optical chemical and biological sensor.

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## REFERENCES


[1] S. John, Phys Rev. Lett. 58, 2486 1987.
[2] A. Z. Genack and N. Garcia, Phys. Rev. Lett., 66, 2064 (1991).
[3] B. Gersten and J. Synowczynski, , Mat. Res. Soc. Symp. Proc., 692, K5.6-6, 2002.
[4] V. S.-Y. Lin, K. Motesharei, K.-P. S. Dancil, M. J. Sailor, M. R. Ghadiri, Science, 278, 840-844, 1997.
[5] V. Mulloni, Z. Gaburro and L. Pavesi, Phys Stat Sol A, 182, 479, 2000.
[6] S. Chan, Y. Li, L. J. Rothberg, B. L. Miller, P. M. Fauchet, Mat. Sci. and Eng.C, 15, 277, 2001.
[7] Claudio Vinegoni, Massimo Cazzanelli, and L. Pavesi, 2, "Properties and Devices", Ed. by H.S. Nalwa, 123-192, 2001.
[8] L.A. DeLouise and B.L. Miller, Mat. Res. Soc. Symp. Proc., 782, A5.3.1, 2004.
[9] L.A. DeLouise and B.L. Miller**,** Proceedings of SPIE Vol. 5357, pg. 111, 2004.
[10] L.A. DeLouise and B.L. Miller, Analytical Chemistry, 76, 6915, 2004.
[11] L.A. DeLouise and B.L. Miller, Analytical Chemistry, 77, 3222-3230, 2005.