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Innovative design for optical porous silicon gas sensor

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ABSTRACT

A simple system for the detection of analytes in the atmosphere employing a freestanding nanostructured porous silicon optical microcavity was designed and built. The system is based on the measurement of optical transmittance changes as a function of the incidence angle of a monochromatic laser beam. Using a matrix formalism and effective medium theories we calculate the optimal conditions for the system so as to obtain the best sensitivity of the sensor. We tested the system over a detection area of the porous silicon microcavity of 100 μm^2 with isopropyl alcohol vapor diluted in a N_2 stream. With the system proposed we were able to detect changes in the concentration of isopropyl alcohol as small as 1 ppm, which is equivalent to a change in the effective refractive index of about 3×10^{-6}. The response time is very fast, lower than 0.5 s.

1. Introduction

Porous silicon (PS) thin films can be fabricated by electrochemical anodization of doped crystalline silicon (c-Si) wafers in a hydrofluoric solution. As a result a porous net grows inside the c-Si wafer with pores sizes varying from 2 nm up to 10 m [1] depending on the resistivity of the c-Si used and on the preparation conditions. The porosity of PS may be controlled by the current density used in a self-limited process, so that a time dependent profile in the current density results in a in-depth profile of porosities. This characteristic along with the large internal surface area and the high chemical reactivity make PS a very attractive material for gas sensing applications.

By controlling the porosity through the current density and the thicknesses of the layers with the anodization times, it is possible to produce multilayer structures such as Bragg mirrors, optical microcavities and other photonic devices [2–4]. In particular, microcavities present sharp resonances in their optical transmittance and reflectance spectra as a consequence of photon confinement inside the cavities [5]. These features confer to PS devices the required sensitivity to use them as sensors.

Due to the reduced scale of its nanostructure, PS can be regarded as a nanocomposite. Therefore, its optical and electrical properties might be estimated using effective medium theories. The complex dielectric function of PS (ε_{PS}) can be obtained when the porosity parameter and the dielectric functions of the constituents media are known [3].

Many works have presented the using of single and multilayer PS structures as optical and electrical sensors. Rocchia et al. [6] and De Stefano et al. [7] developed optical microcavities and measured reflectance shifts of the cavity mode due to the interaction with external analytes (EA). Liu et al. [8] used high interferometric sensitivity of polarization interference intensity technique to measure the relative variation in the polarization interference to quantify the detected concentration of solvent vapors. Electrical devices designed by Baratto et al. [9] and Pancheri et al. [10] are based on the monitoring in conductivity changes of PS single layers due to interaction with CO and NO_2, respectively. Although the optical devices mentioned in these works are fast to recover from the contamination with EA (about 2 s in the best case [7]), their detection limit is not too good. On the other hand, electrical devices are more sensitive (12 ppb [10]) but their response time are in the order of minutes.

In this article, we propose a new method to detect changes in the optical response of a freestanding PS microcavity as a result of the penetration of isopropyl alcohol vapor inside the pores, based on the measurement of the angular shifts of the transmittance peak for a specific wavelength. When external analytes (solvents, for instance) penetrate the PS structure, ε_{PS} increases leading to a redshift in the optical response of the device [11]. This change in energy spectrum can also be detected resolving the transmittance spectrum as a function of the incidence angle using monochromatic light. In this case, there is an angle resolved resonance, and the increase of the effective dielectric function produces a shift of the resonance to higher angles.

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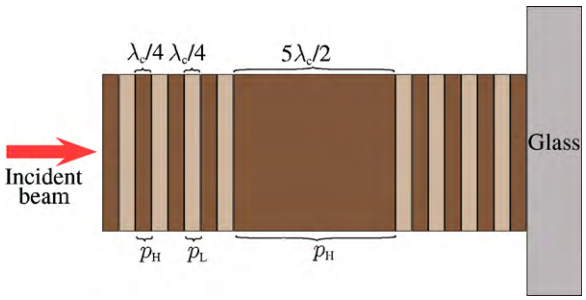

Fig. 1. Scheme of the multilayer structure of the PS microcavity designed and fabricated. Darker slabs represent layers with high porosity (p_H), while the clearer ones correspond to low porosity (p_L) layers. It is shown the laser beam incident on the left side of the multilayer and the glass substrate on the right.

The advantages of this innovative method include the use of a simple position detector and a laser as main components (avoiding white spectrum lamps with big active detection areas and energy-sensitive detectors) and there are no mobile parts. Other prominent characteristics of the device presented here, along with its high detection sensitivity, are its temporal response, which is in the order of half a second, and robustness against laser intensity variations.

2. Experimental aspects

We fabricate a PS microcavity centered at $\lambda_c = 730$ nm alternating layers of high (p_H) and low (p_L) porosities with the following sequence: 4 bilayers p_Hp_L, a central defect with a p_H layer having an optical thickness $5\lambda_c/2$, and 4 bilayers p_Hp_L. All layers have an optical thickness equal to $\lambda_c/4$, except the central defect (Fig. 1).

The microcavity was prepared by electrochemical anodization of a p-type boron doped c-Si wafer (resistivity 1–4 mΩ cm, orientation ⟨1 0 0⟩) in a HF (50%):C_2H_5OH solution with proportions 1:2 (v/v). After fabrication we applied an electropolishing current density of 320 mA/cm^2 in a HF (50%):C_2H_5OH solution with proportions 1:7 (v/v) in order to remove the PS multilayer from the c-Si substrate and transferred the freestanding multilayer onto a glass substrate. Current densities of $J_H = 128$ mA/cm^2 and $J_L = 12.4$ mA/cm^2 were used during $t_H = 3.13$ s and $t_L = 13.5$ s to obtain layers with porosities of $p_H = 86\%$ and $p_L = 54\%$, and thicknesses of $x_H = 139$ nm and $x_L = 86$ nm, respectively. The refractive index of the porous layers at 730 nm results $n_H = 1.31$ and $n_L = 2.12$.

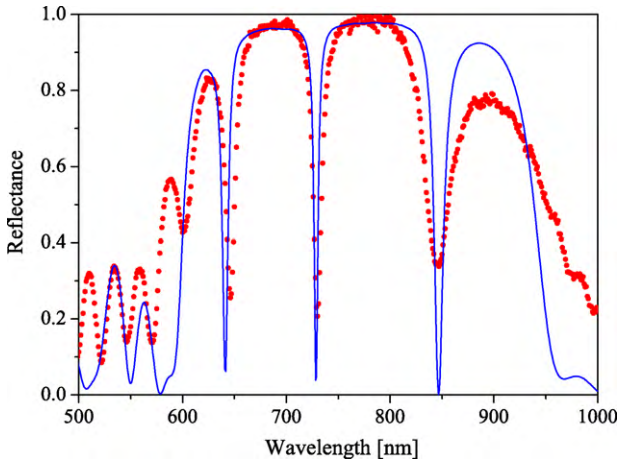

Fig. 2. Measured (dots) and calculated (line) reflectance spectra of the PS microcavity analyzed.

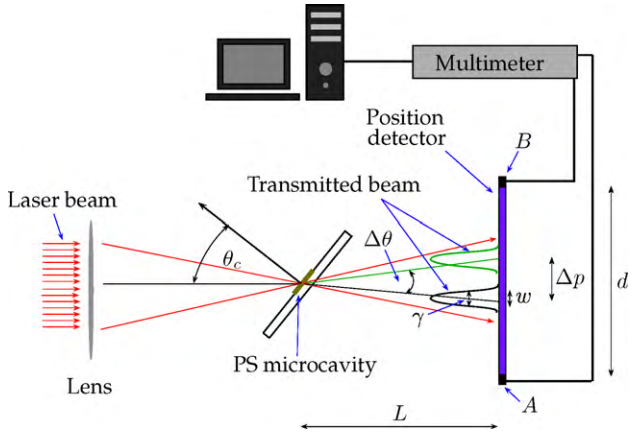

Fig. 3. System used to measure angular shifts in the optical response of the PS microcavity. A monochromatic laser beam is focused on the freestanding porous silicon microcavity probing a range of incidence angles. The PS microcavity was designed to produce a transmission sharp peak at θ_c when we use a particular wavelength. The presence of an EA shift the angular position of the peak. A simple position detector is used to measure this change.

In Fig. 2 it can be observed the measured reflectance spectrum of the constructed PS microcavity along with the calculated spectrum with the chosen parameters, at an incidence angle of 8°. The experimental spectrum was measured with an Ocean Optics HR4000 spectrometer.

Fig. 3 shows the system proposed to measure angular shifts in the optical response of the PS microcavity. A monochromatic laser beam (5 mW, 675 nm wavelength) was focused on the freestanding porous silicon microcavity probing a range of transmittance angles. The illuminated area was about 100 μm^2. The PS microcavity was designed to produce a transmission sharp peak at θ_c when $\lambda_c = 730$ nm. This can be achieved by constructing the microcavity tuned at a wavelength higher than the laser one ($\lambda_{laser} < \lambda_c$).

The contamination with an external analyte shifts the peak position to higher angles. A position detector (PIN-LSC/30D) placed at about 40 cm from the microcavity, senses the light coming from the laser beam. The transmitted light peak produce two electrical signals A and B: the difference between them depends on the position and the intensity of the incident light, while the sum of A and B is a function of the intensity only. The signal S is defined as the quotient $(A - B)/(A + B)$ which results only a function of the position of the peak, which makes measurements independent to variations in laser intensity.

3. Sensitivity analysis

According to the system schematized in Fig. 3 we performed a sensitivity analysis that allows us to maximize the sensitivity of the PS photonic device to use it as a gas sensor. We study the response of the optical microcavity as a function of the effective refractive index variations, the fraction of the optical thickness at the defect (l) and the central wavelength (λ_c).

We define the sensitivity β of the system as the change produced in the signal (ΔS) by a change Δc of the EA concentration inside the pores, i.e., the derivative of the signal respect to the concentration. In our calculations we represent Δc (a change in the concentration of the gas inside the pores) as a change in the refractive index Δn (inside the pores).

The position detector signal is proportional to the average position of the incident light weighted by their intensity. If the incident light has a symmetric peak profile, then the signal is proportional to the peak center position, provided that the peak is within the detection area (the peak width w on the detector must be smaller

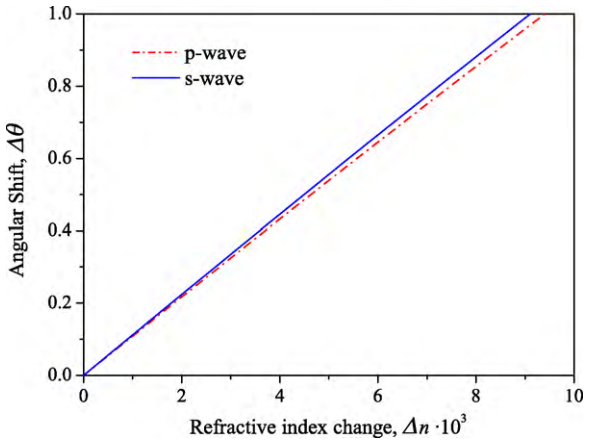

Fig. 4. Detector signal as a function of the change in the refractive index of the gas. This figure was calculated using microcavity parameters similar to that described in Fig. 1, using $\lambda_c = 730$ nm, illuminated at 675 nm (resulting $\theta_c \sim 32^\circ$) with a detector of $d = 30$ mm placed at $L = 40$ cm.

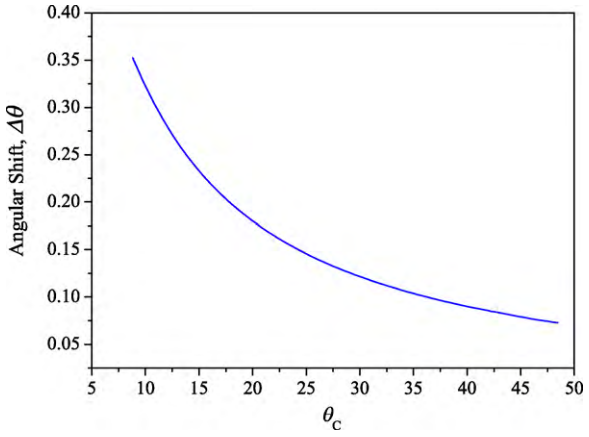

Fig. 5. Dependence of the angular shift upon the θ_c value. This calculation was performed using the same microcavity parameters of Fig. 4, but for different λ_c values in order to scan different θ_c values. This $\Delta\theta$ is produced by a change of 10^{-3} in the refractive index. The s- and p-polarized waves responses are indistinguishable.

than the detector size d, see Fig. 3). The position deviation of the peak over the detector Δp can be calculated as

$$\Delta p = L \cdot 2 \tan \frac{\Delta\theta}{2} \sim L \cdot \Delta\theta$$

where L is the microcavity-detector distance and $\Delta\theta$ is the angular shift of the peak that results by the change in the refractive index. The detector signal change ΔS is proportional to the peak position deviation Δp, hence, an increase in the distance L produces an increment in ΔS. However, higher values of L produces also an increase in the peak width w over the detector. The optimal distance is the maximum value of L that satisfy $w \leq d$. Since the peak width w can be calculated from the angular peak width γ as

$$w = L \cdot 2 \tan \frac{\gamma}{2} \sim L \cdot \gamma,$$

then $L_{\text{optimal}} \sim d/\gamma$, i.e., the peak width over the detector must be similar to the detector size.

Finally, the signal change ΔS at this optimal position results proportional to the angular shift of the peak $\Delta\theta$ and inversely proportional to the angular peak width γ. Then

$$\beta \equiv \frac{\Delta S}{\Delta n} \propto \frac{\Delta\theta}{\gamma \Delta n}. \quad (1)$$

In Fig. 4 it can be observed the expected detector signal as a function of the change in the refractive index. This figure was calculated for a similar microcavity described in Fig. 1, using $\lambda_c = 730$ nm, illuminated at 675 nm (resulting $\theta_c \sim 32^\circ$) with a detector of $d = 30$ mm placed at $L = 40$ cm. There are no significant differences between the angular shift of the transmitted peak for s- and p-polarized waves. For low changes of concentrations of EA, the device presents a linear response.

In Fig. 5 it is shown the dependence of the angular shift upon the θ_c value. In this case, we use for the calculation the same microcavity parameters of Fig. 4, but for different λ_c values in order to scan different θ_c values. This $\Delta\theta$ is produced by a change of 10^{-3} in the refractive index. The s- and p-polarized waves responses are indistinguishable.

For the same case of the Fig. 5, we calculate the angular width γ of the peak transmission as a function of the θ_c value. The results are shown in the Fig. 6. We can see that the s-polarized wave presents a narrower peak than the p-polarized wave for all values of θ_c.

From Figs. 5 and 6 it is possible to calculate the relation $\Delta\theta/(\gamma\Delta n)$, which is proportional to the sensitivity of the sensor (Eq. 1). The results are shown in Fig. 7. In this figure we can see

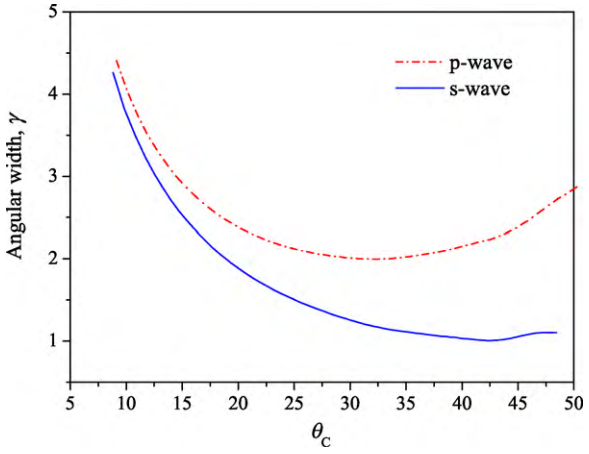

Fig. 6. Angular width γ of the transmitted peak as a function of the θ_c value. It was calculated with the same microcavity that in Fig. 4.

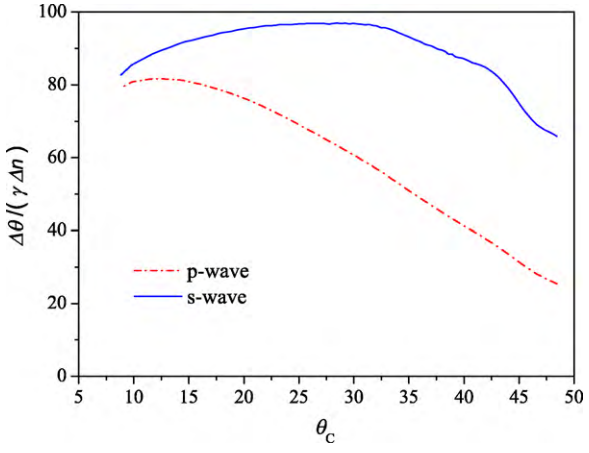

Fig. 7. Relation $\Delta\theta/\gamma\Delta n$ as a function λ_c obtained from Figs. 5 and 6.

that, for small angles θ_c, the increase of $\Delta\theta$ is compensated by the increase in the angular width γ. There exist an optimal condition at $\theta_c \sim 30^\circ$ where the s-polarized wave presents a maximum of the relation.

Figs. 8 and 9 show the variation of γ as a function of the characteristic parameters of the microcavity. In Fig. 8 it is shown the

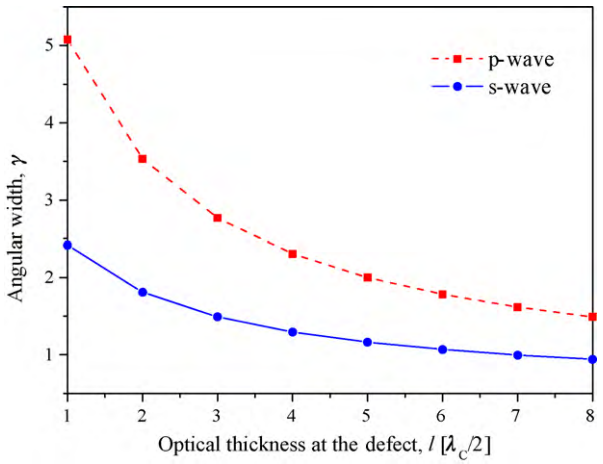

Fig. 8. Variation of γ as a function of the optical thickness at the defect (l). These calculations were performed with a change in the refractive index of 10^{-3}, $\lambda_c = 730$ nm illuminated with a $\lambda_{laser} = 675$ nm (resulting $\theta_c \sim 32^\circ$). A 4 period Bragg is used.

variation upon the optical thickness at the defect (l), and in Fig. 9 the dependence with the number of periods at the Bragg reflectors is presented. These calculations were performed with a change in the refractive index of 10^{-3}, $\lambda_c = 730$ nm illuminated with a $\lambda_{laser} = 675$ nm (resulting $\theta_c \sim 30^\circ$). In Fig. 8 a 4 period Bragg is used and in Fig. 9 a defect of $l = 5\lambda_c/2$.

According to this calculations, the greater l the lower γ. However, for $l \geq 7$ the angular peak width becomes almost independent of l. The dependence of γ with the number of periods behaves in the same way, and it appears to be almost independent of the number of Bragg periods when this parameter is bigger than 4. In both cases the s-polarized wave present a narrower peak than the p-polarized wave.

Finally, we investigate the dependence of the angular shift $\Delta\theta$ with these same characteristic parameters of the microcavity. The obtained results indicate that there is no significative variation of $\Delta\theta$ neither with l nor with the number of Bragg periods.

According to Eq. 1 and Figs. 8 and 9 it is convenient to use large values of l and number of Bragg periods. Nevertheless, the peak transmittance decreases rapidly with an increase of these parameters, affecting the detection limit of the detector. Besides, at large values of l is important to consider the mechanical requirements to prevent the collapse of the structure. We experimentally find that values of $l \geq 6$ produce fragile structures.

From this analysis we decide to fabricate the PS microcavity described in Section 2 formed by a pair of 4 Bragg period reflectors alternating high and low porosity $\lambda_c/4$ layers, with a central high porosity defect of $5\lambda_c/2$, with λ_c chosen to be 730 nm, resulting in a θ_c of about 30°. We use a s-polarized wave laser.

4. Results

Injecting a pure N_2 stream we placed the PS microcavity in the incidence angle that gives the maximum transmittance and the position detector centered at the laser beam. Fixed in this position we performed the measurements of the position detector signal (Fig. 10), varying the concentration of isopropyl alcohol (as external analyte) in the N_2 stream.

Fig. 10 shows the detector response when the mixed N_2-isopropyl alcohol penetrates into the pores of the PS microcavity, as a function of alcohol concentration. In this figure we distinguished two runs (dots and squares) for two different N_2 flow rates in the mix. We used 0.5 l/min of N_2 for measurements represented with squares, and 4 l/min for measurements shown in dots. As it can be seen this two runs match at 20 ppm showing that the optical response of the device is independent of the flow rate used to transport the EA to the microcavity. The noise level has been calculated as the standard deviation of the signal in 100 s period, and its value is also plotted in Fig. 10. According to this value of noise the detection limit [12] of the device results 1 ppm. Long term fluctuations due to temperature variations can increase the detection limit as we show below.

The slope of the logarithmic plot in Fig. 10 for low concentrations is almost 1, which means that the optical response is linear.

To obtain a relation between the EA concentration and the change of refractive index of the gas mixture we measured the position detector signal when the detector is exposed to two known different gases. We use N_2 and He as reference gases because of their large refractive index contrast (1.000282 and 1.000035 respectively at 675 nm [13]). The measured value of the signal difference was about 0.033, that is equivalent to a change of about 90 ppm of EA (see Fig. 10). Assuming a linear relation we could estimate that 1 ppm is equivalent to a change of about 3×10^{-6} in the refractive index of the gas mixture.

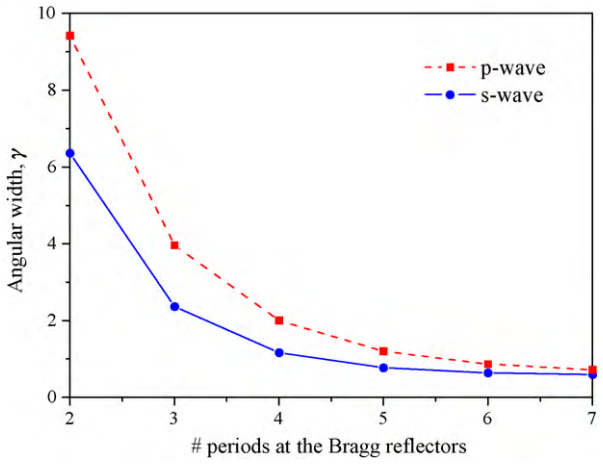

Fig. 9. Variation of γ as a function of the number of periods at the Bragg reflectors. These calculations were performed with a change in the refractive index of 10^{-3}, $\lambda_c = 730$ nm illuminated with a $\lambda_{laser} = 675$ nm (resulting $\theta_c \sim 30^\circ$). A defect of $l = 5\lambda_c/2$ is used.

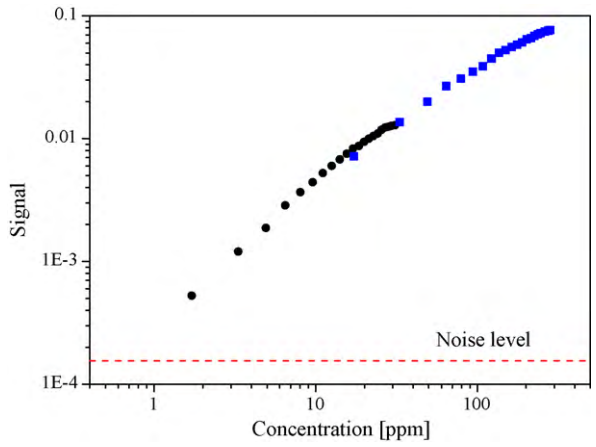

Fig. 10. Detector response when the PS microcavity is exposed to a pure nitrogen stream mixed with a controlled amount of isopropyl alcohol vapor. The background noise level is also plotted for comparison. This figure is composed by two runs with different pure nitrogen flow rates (dots and squares). Since the slope of the measurements in dots is 1, the response of the sensor in the low concentration range is nearly linear.

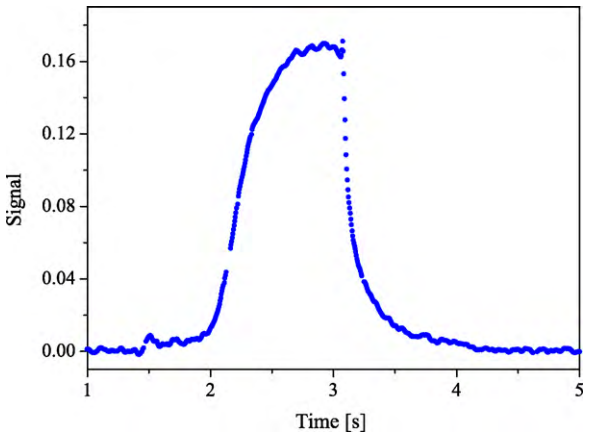

Fig. 11. Time response of the detector when a sudden change of the EA concentration is established. The rise time and fall time of the signal are lower than 0.5 s. Because this value is similar to the time expended to change the EA concentration, 0.5 s provides only an upper limit to the time response of the detector.

To estimate the time response of the detector we measure the detector signal when a sudden change of the EA concentration is established. We prepare two tubes, one conducting pure nitrogen, and the other with saturated isopropyl alcohol in nitrogen. Those tubes were placed alternately in order to face the detection area of the sensor one at time. The obtained results are shown in Fig. 11. In this figure we can see that the rise time and fall time of the signal are lower than 0.5 s. Since the time expended to interchange the tubes is of the same order, this time value provides only an upper limit to the time response of the detector.

Variations in the microcavity temperature can affect the transmission peak position. Taking into account the expansion coefficient of silicon and its refractive index dependency with temperature it is possible to estimate the peak shift expected for a change in the microcavity temperature. We calculate that a change in 1 °C is equivalent to a change in concentration of 1.5 ppm.

5. Conclusions

We developed a new method to measure changes in the optical response of a PS microcavity using the angular peak shift of the transmittance spectrum due to the presence of isopropyl alcohol as analyte. We optimize the most important optical parameters of the microcavity to obtain the maximum sensitivity.

The optical device response is almost linear for a wide range of concentrations, and the signal seems not to depend on the value of the flow rate of the stream of carrier gas. The response time is very fast, lower than 0.5 s.

The detection limit of the device is 1 ppm of isopropyl alcohol. Below this value, temperature has to be controlled in order to obtain reliable results. The detection of a change in concentration of 1 ppm is equivalent to measure a change in the refractive index of 3×10^{-6} respect to vacuum. Another remarkable feature of the system presented here is that focusing the laser beam we define an active detection area in the PS microcavity of about 100 μm^2, which makes possible to fabricate small gas sensors devices based on PS photonic.

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References

[1] G.X. Zhang, Porous silicon: morphology and formation mechanisms, in: C.G. Vayenas, R.E. White, M.E. Gamboa-Adelco (Eds.), Modern Aspects of Electrochemistry, Springer, USA, 2006, pp. 65–133.
[2] L. Pavesi, Porous silicon dielectric multilayers and microcavities, Rivista del Nuovo Cimento 20 (1997) 1.
[3] V. Kochergin, H. Föll, Porous Semiconductors—Optical Properties and Applications, Springer-Verlag, London, 2009.
[4] O. Bisi, E. Ossicini, L. Pavesi, Porous silicon: a quantum sponge structure for silicon based optoelectronics, Surface Science Reports 38 (2000) 1–126.
[5] A.V. Kakovin, J.J. Baumberg, G. Malpuech, F.P. Laussy, Microcavities, Oxford University Press, 2007.
[6] M. Rocchia, A.M. Rossi, G. Zeppa, Determination of ethanol content in wine through a porous silicon oxide microcavity, Sensors and Actuators B 123 (2006) 89–93.
[7] L. De Stefano, L. Moretti, I. Rendina, A.M. Rossi, Time-resolved sensing of chemical species in porous silicon optical microcavity, Sensors and Actuators B 100 (2004) 168–172.
[8] R. Liu, T.A. Schmedake, Y.Y. Li, M.J. Sailor, Y. Fainman, Novel porous silicon vapor sensor based on polarization interferometry, Sensors and Actuators B 87 (2002) 58–62.
[9] C. Baratto, E. Comini, G. Faglia, G. Sberveglieri, G. Di Francia, F. De Filippo, V. La Ferrara, L. Quercia, L. Lancellotti, Gas detection with a porous silicon based sensor, Sensors and Actuators B 65 (1999) 257–259.
[10] L. Pancheri, C.J. Oton, Z. Gaburro, G. Soncini, L. Pavesi, Very sensitive porous silicon NO_2 sensor, Sensors and Actuators B 89 (2003) 237–239.
[11] H. Ouyang, M. Archer, P M Fauchet, Porous silicon electrical and optical biosensors, in: D.L. Andrews, Z. Gaburro (Eds.), Frontiers in Surface Nanophotonics: Principles and Applications, Springer Series in Optical Science, Springer, 2007, pp. 49–72.
[12] I.M. White, X. Fan, On the performance quantification of resonant refractive index sensors, Optics Express 16 (2008) 1020–1028.
[13] M.J. Weber, Handbook of Optical Materials, CRC Press, 2003.

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