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2007 J. Phys.: Condens. Matter 19 395008

(http://iopscience.iop.org/0953-8984/19/39/395008)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **19** (2007) 395008 (7pp) doi:10.1088/0953-8984/19/39/395008

Optical microsystems based on a nanomaterial technology

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Received 13 February 2007
Published 30 August 2007
Online at stacks.iop.org/JPhysCM/19/395008

Abstract

In this work, we present an optical sensor for quantitative determination of the alcohol content in hydro-alcohol mixtures, realized by using porous silicon (PSi) nanotechnology. The device is an oxidized PSi micro-cavity (PSMC) constituted by a Fabry–Perot layer between two distributed Bragg reflectors. Due to the capillary condensation, a red shift of the PSMC reflectivity spectrum is observed on exposure to vapour mixtures. The phenomenon is completely reversible. Moreover, to reduce the analysis time, we have designed the integration of the sensor in a thermally controlled lab-on-chip, by merging PSi and anodic bonding technologies. Numerical calculations have been performed to study the thermal behaviour of the integrated device.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The fast and intensive development of the lab-on-chip (LOC) for sensing applications is due to several factors that are essential for routine analytical determinations, such as very limited sample consumption and short analysis time, which can be obtained by measuring a transient signal in a flow-through detector. Due to their intrinsic features, in particular contactless monitoring capability, optical sensors are very attractive for many application fields.

In recent years, many devices based on porous silicon (PSi) technology have been realized for several sensing applications [1, 2]. PSi, fabricated by electrochemical etching of a silicon (Si) wafer in HF-based solution, is an ideal material for an optical transducer, due to its sponge-like nanostructure (specific surfaces up to 500 m^2 cm^{-3}) [3], that assures an effective interaction with several chemicals and biological molecules. On exposure to chemical substances, several physical parameters, such as refractive index, photoluminescence, and electrical conductivity,

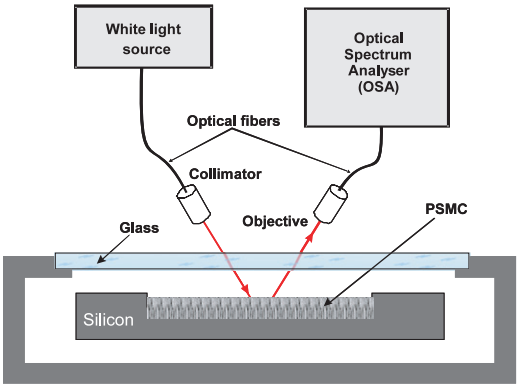

Figure 1. Experimental optical set-up used for the sensing experiments.

change drastically. It is also possible to realize in a single process multilayered structures that exhibit a high selective optical response, which is very attractive for sensing [4].

Silicon–glass anodic bonding (AB) is one of the most promising techniques in the micromachining field; it easily allows the encapsulation and sealing on silicon chips of three-dimensional microfluidic structures, such as channels, chambers, cavities and other complex gas and liquid routes. Additionally, glass transparency at optical wavelengths enables simple, but highly accurate, alignment of pre-patterned or structured glass and silicon wafers.

We have recently demonstrated the compatibility of PSi and AB technologies for the realization of sensing microcomponents for LOC applications [5, 6]. The integration was not easy or straightforward: the microfabrication techniques are typically optimized for the microelectronic industry and are not well appropriated or compatible with the non-standard materials such as the ones used in biological or chemical sensing.

We present here a simple optical sensor for the analysis of hydro-alcohol mixtures, based on PSi nanotechnology. Faster time analysis can be obtained by integrating the silicon–glass sensor for LOC applications by merging the PSi and AB technologies.

2. Materials and methods

For this study, we fabricated a $\lambda/2$ Fabry–Perot optical microcavity sandwiched between two Bragg reflectors of seven periods each, realized by alternating layers with high and low refractive indices. The porous silicon microcavity (PSMC) was obtained by electrochemical etch in a HF-based solution (50 wt% HF:ethanol = 1:1) in dark light and at room temperature. A current density of 400 mA cm^{-2} for 0.8 s was applied to a highly doped p^{+}-type standard silicon wafer, $\langle 100 \rangle$ oriented, with 10 mΩ cm resistivity, 400 μm thick, producing the high-refractive index layer (with a porosity of 75%), while a current density of 80 mA cm^{-2} was applied for 1.9 s in the case of the low-index layer (with a porosity of 67%). The $\lambda/2$ layer is a low-refractive-index one. This structure has a characteristic resonance peak at 1110 nm in the middle of a 280 nm wide stop band. To ensure the infiltration of aqueous solution, the device, which (as etched) is hydrophobic due to the presence of SiH bonds on its surface, was made hydrophilic by thermal oxidation at 1000 °C for 30 min. The optical set-up required for our sensing experiments was very simple (see figure 1). The PSMC was placed in a test chamber equipped with a glass window. A white light source interrogated the sensor through an optical fibre and a collimator. The reflected beam was collected by an objective, coupled into

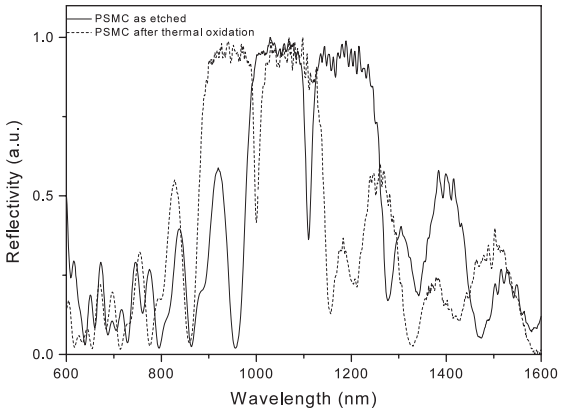

Figure 2. Optical spectra of the PSMC as etched and after thermal oxidation.

a multimode fibre, and then directed in an optical spectrum analyser (Ando model AQ6315A). The reflectivity spectra were measured over the range 600–1600 nm with a resolution of 0.2 nm. We studied the resonance peak shift on exposure to an ethanol/deionized water (DI) binary mixture at different concentrations, placing a drop of solution in the test chamber. Due to the capillary condensation of the solution vapours into the pores of the PSMC, a change in its reflectivity spectrum was observed: the partial substitution of air by liquid in each layer determines an increase of the average refractive index of the microcavity and, consequentially, a red shift of the spectrum. Measurements are stored when equilibrium conditions are reached, i.e. when the signal does not change any more in time. The phenomenon is completely reversible and reproducible.

3. Experimental results and discussion

In figure 2, the reflectivity spectra of the PSMC as etched and after thermal oxidation are reported. The oxidation process causes a blue shift in the spectrum of 110 nm due to the lower value of the SiO_2 refractive index ($n_{SiO_2} \approx 1.45$) with respect to the Si refractive index ($n_{Si} \approx 3.6$). We have not observed degradation in cavity quality ($Q = \lambda/\Delta\lambda \approx 70$ in both cases).

A very simple method, commonly used in analytical chemistry, in quantitative determinations of binary mixtures is the external standard method: calibration curves can be obtained by measuring the parameter under monitoring, such as an optical intensity, while the content of one component varies between 0 and 100%. In our case, the curve has been obtained by plotting the peak shift measured as a function of the volume percentage of ethanol in the binary mixture, as shown in figure 3. The errors on the experimental points are the standard deviations on five measurements, using the same chip and the same hydro-alcohol solution. After the calibration, unknown concentrations of the same mixture can be quantitative determined with a single measurement of the peak shift: the volume concentrations of both components can be picked out from the curve obtained by interpolating the experimental calibration data. In order to limit the wide error bars and the time necessary for the PSMC to reach equilibrium with the mixture (by limiting the volume), integration in a single chip of the device is proposed.

The compatibility of the porous silicon technology with the standard integrated circuit fabrication processes allows the design of complex microsystems in which the porous silicon

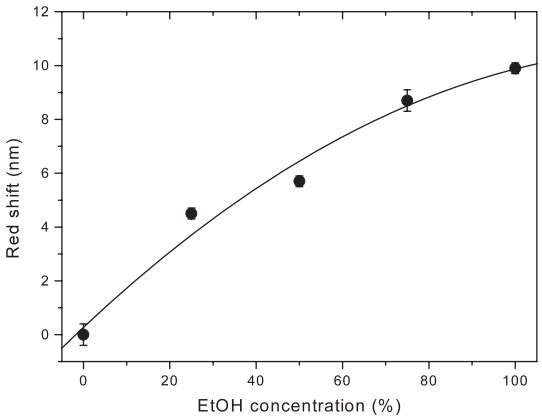

Figure 3. The calibration curve in case of an ethanol/DI binary mixture.

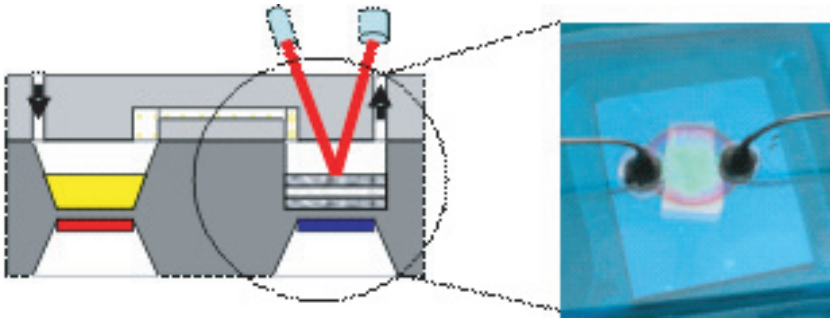

Figure 4. Sketch of the alcohol microsensor.

optical device is the transduction element. In figure 4, we report a rough and somehow intuitive sketch of the alcohol microsensor. The PSMC can be integrated in an LOC consisting of two μ-chambers thermally controlled by integrated heaters, and sealed by a cover glass after the anodic bonding process. The mixture is injected in the left μ-chamber by means of an appropriate microsyringe and here the integrated heater induces the hydro-alcohol mixture evaporation. The vapours produced diffuse and reach the second μ-chamber, cooled by another integrated element, where the PSMC is and the capillary condensation happens.

4. Numerical calculations

Before proceeding towards the real fabrication steps of the whole device depicted in figure 4, it is mandatory to simulate its thermal behaviour since this is one of the key features in the measurement process. The precision and the accuracy in the quantitative determination of the mixture concentration strongly depend on the thermodynamic parameters such as the equilibrium time, i.e. the time required to have the same evaporation and condensation into the PSMC, and the temperature distribution in each layer used to realize the LOC. In order to simulate the thermal response of the device, a finite element model has been implemented with the commercial FEM code ANSYS Multiphysics 9.0 [7]. We have restricted the analysis to a two-dimensional (2D) model corresponding to the device middle cross section sketched (not to scale) in figure 4. Ignoring the minimal border effects at the device ends, a temperature

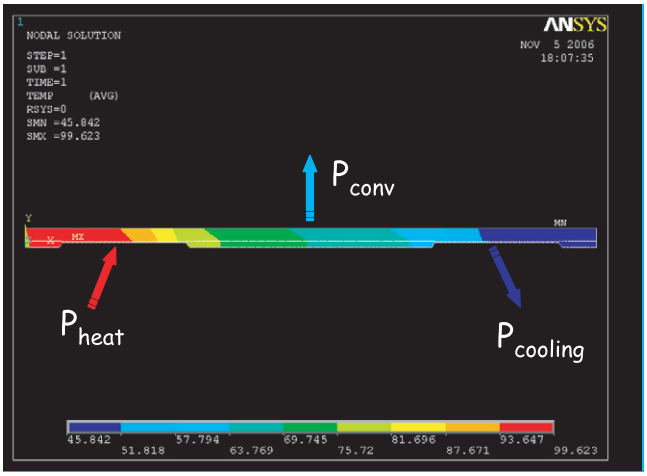

Figure 5. Temperature distribution in the device when the tank μ-chamber is heated with a power density of 1.0 W cm^{-2}.

Table 1. Physical parameters for lab-on-chip materials used in thermal simulations.

Material	Thermal conductivity (W m^{-1} K^{-1})	Density (kg m^{-3})	Specific heat (J kg^{-1} K^{-1})
Silicon	156	2640	917
Glass	1.05	2500	840
Water	0.58	1000	4186
Air	0.025	1.225	1005

gradient in fact exists only in this plane. This hypothesis can be justified by the observation that, for the proposed geometry, the aspect ratio between its width (46 mm) and thickness (1.5 mm) is about 1/30. Of course, a full 3D model could be more accurate, though it is very time consuming during the FEM analysis. The structure has been meshed with 2242 *isoparametric* linear elements of the type *plane 55*, with a mesh refinement in the active regions of the device. In table 1 we have reported the main physical parameters of the materials used for ANSYS thermal simulations.

The results of the numerical simulations depend on the boundary conditions fixed: we have supposed a natural convective heat exchange on the upper face of the glass slide which is in contact with air at 20 °C. We have assumed an exchange coefficient of 27 W m^{-2} K^{-1} [8]. Lateral and lower surfaces have been considered adiabatic; this model could be a good approximation of a device mounted on a plastic case. The lower surface of the left μ-chamber, which is our tank for the liquid substance, is kept hot at constant temperature by a heater element. The right μ-chamber is cooled by a Peltier μ-cell with a maximum heat flux equal to 0.4 W cm^{-2} (i.e. micro modules from TE Technology Inc., USA). In figure 5 we report the 2D steady-state thermal distribution, when the tank chamber is heated with a power density of 1.0 W cm^{-2}, corresponding to a maximum temperature on the hot side of about 100 °C. From this calculation it is clear that the PSMC region reaches a temperature of about 50 °C, which is a little bit higher of the evaporation temperature of ethanol; in this case the alcohol cannot condense inside the pores of the PSMC.

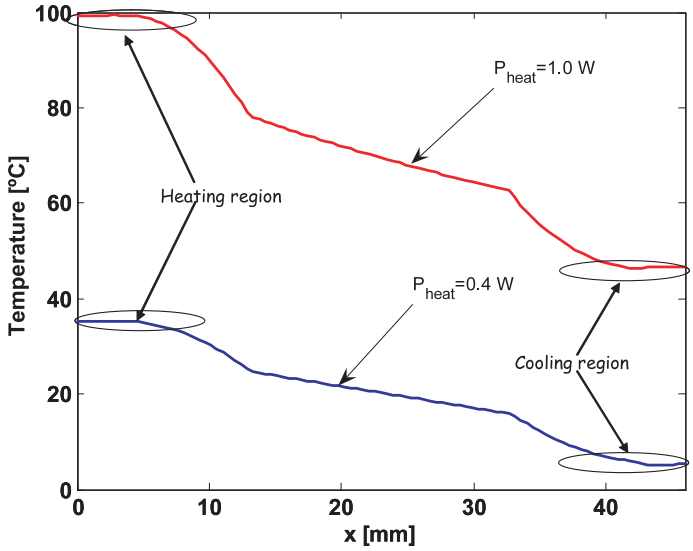

Figure 6. Temperature distribution versus the lateral dimension of the device for two different heating power densities.

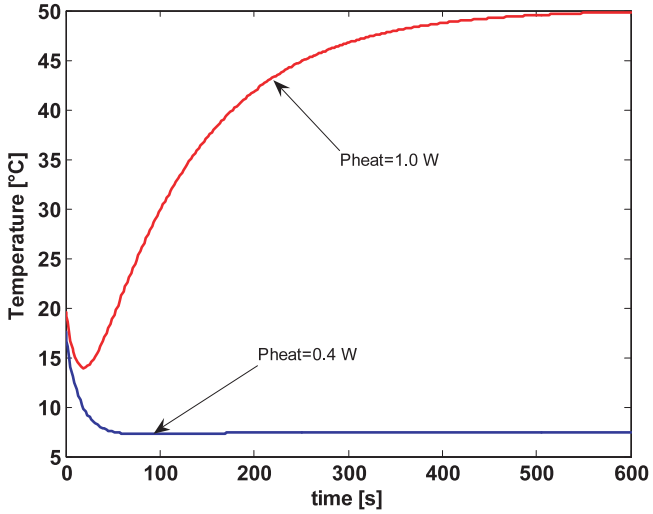

Figure 7. Temperature dynamic in the condensation chamber for two different heating power densities.

We have repeated the simulation considering a lower heating power density, 0.4 W cm^{-2}, corresponding to heating the tank μ-chamber to 35 °C. In this case, the PSMC is cooled, thanks to the Peltier module, at about 5 °C: the analysis chamber temperature decreases quite linearly with the heat source temperature, as expected. These results are shown schematically in figure 6, where the 1D lateral temperature distribution, calculated at the silicon–glass interface, is reported versus the lateral dimension of the device for the two different heating power densities. We have also calculated the PSMC average temperature as a function of time for the two different heating power densities. The transient solver *Antype4* was used to perform

the analysis, using the *multi load-step method* provided in the code. From the plot in figure 7, it is well evident that, in the case of a heating power of 0.4 W cm^{-2}, the porous silicon–vapour system is at thermal equilibrium after about 50 s. In contrast, if we apply a heating power of 1.0 W cm^{-2}, a much longer time is necessary.

5. Conclusions

We have presented a simple and well performing optical sensor for ethanol/DI binary mixture analysis, based on PSMC. Due to capillary condensation, the reflectivity spectrum of the device shifts towards higher wavelengths on exposure to vapours. The shift is characteristic of the concentration of each component of the mixture. The sensing process is completely reversible. In order to limit the time needed for the PSMC to reach equilibrium with the mixture, we have proposed the integration of the device in a single chip that is thermally controlled. The thermal behaviour of the designed LOC has been studied by proper FEM numerical calculations.

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