

# OPTICAL SENSING AND ANALYSIS SYSTEM BASED ON POROUS LAYERS

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## ABSTRACT

Analysis concept of gaseous or liquid media using porous silicon multilayers with optical sensing is presented. The sensor consists of optical filter with  $\lambda/4$  layers, fabricated by electrochemical etching in HF/ethanol. The optical system is tested with ampicillin and shows a linear dependence with increasing ampicillin concentration. For general sensing applications the influences of porosity and pore size on the optical output are investigated. Additionally, transport processes of gases and fluids in the nanostructured porous layer are investigated to optimize the sensor response time and to evaluate further specific material properties of the investigated media which are needed for analytical information.

**KEYWORDS:** optical sensing, porous multilayers, analysis system

## INTRODUCTION

Si-based microporous or mesoporous layers with pore size in the range 2-40 nm – tunable to the specific application – provide large inner surface ( $100\text{m}^2/\text{cm}^3$  -  $800\text{m}^2/\text{cm}^3$ ) [1]. Such materials are quite sensitive for analytical measurements, i.e. material properties changes considerably by filling media into the pores or by attachment of molecules to the pore walls of the large inner surface. The optical output is based on a characteristic spectral shift of multilayers formed by periodically modified porous layers with slightly different porosity and thus effective refractive index. However, the sensor's optical output provides in this case only integral information on effective refractive index of filled media and on the pore filling state. Further sensor characteristics have to be used to obtain material specific data (e.g. permeance  $\rightarrow$  viscosity, time response  $\rightarrow$  vapor pressure).

## THEORY

The porous layers are generated by anodization of silicon in a wet electro-chemical process which is a one-step and low-cost method to build porous optical multilayers e.g. as  $\lambda/4$  layers with well-defined thicknesses and refractive indices (depending on porosity) as shown in Figure 1. The periodic structures of alternating  $\lambda/4$  layers are defined by the refractive indices and physical thicknesses of the corresponding high ( $n_H$ ) and low ( $n_L$ ) refractive layers fulfilling the condition  $\lambda_c/4 = n_H \cdot d_H = n_L \cdot d_L$  and thus forming a so-called Distributed Bragg Reflector (DBR) with a central peak wavelength of the reflectance spectrum at  $\lambda_c$ .

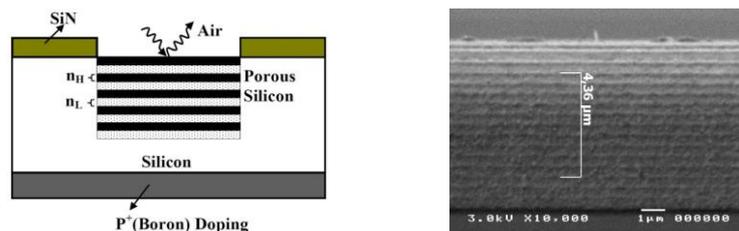


Figure 1: Schematic and SEM cross-section of a porous DBR-multilayer optical filter

The multilayer's optical output can be tuned in respect to the needed sensor performance (measurement range, sensitivity, time response). Additionally, the multilayers provide mechanical filter characteristics which can be used to get additional information about the analyzed media. A tight control of pore size and a narrow pore size distribution is essential to provide analytical information when using porous multilayers. Low temperature anodization allows an accurate control of the critical process parameters and thus material properties. The use of tunable optical multilayers have been reported already for different sensor applications [2, 3, 4, 5]. The basic sensor signal is based on a change of the effective refractive index by filling the porous multilayers with the media under investigation (Figure 2) and is therefore in general not material specific.

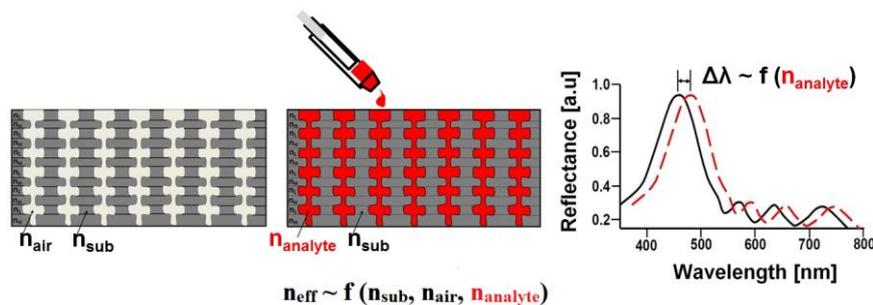


Figure 2: Empty stacks (left) and analyte filled stacks for tunable nanostructured optical multilayers with schematic pore structure and redshift of optical spectrum induced by pore filling with analyte

## EXPERIMENTAL

Porous Si is generated by anodization of low doped (10-15 $\Omega$ cm) and high doped (0.01-0.02 $\Omega$ cm) (100)-oriented p-Si substrates in a solution of typically 30wt% aqueous HF (48%) with ethanol using a double-cell configuration using a current density of about 20-70mA/cm<sup>2</sup>. Micro- and mesoporous layers are obtained with typical mean pore radius from 1,5nm to 40nm. Porosity values in the range of 60-80% are realized to achieve fast transport processes through the nanostructured sensor or filter layer. Surface stabilization is realized by a two step oxidation process [5]. The specific inner surfaces and the wetting behavior are characterized by desorption and adsorption measurement using nitrogen adsorption/desorption isotherms measured in Belsorp-mini of Co. Rubotherm/Bel at 77K. Pore size, pore size distribution and specific surface area (SSA) are evaluated from the measurements using the BET and BJH theory, thus providing an independent measurement of critical layer properties for the optical system.

## RESULTS AND DISCUSSION

The optical sensing system was tested with different organic and non-organic solutions using in gaseous or liquid state. As example, the sensitivity in case of ampicillin (peak shift as function of concentration in water) is shown in Figure 3a and in case of different organic solutions in Figure 3b. The peak shift (redshift) shows a linear dependence in the investigated range with increasing ampicillin concentration in water and with increasing refractive index of organic analytes. The resulting spectral shift of some nm can be extracted from the full spectrum by using light with specific wavelengths (e.g. two spectral points). However, for large sensitivity (detection of small concentrations), the layers have to be optimized. A key parameter is the pore size as shown in Fig. 4.

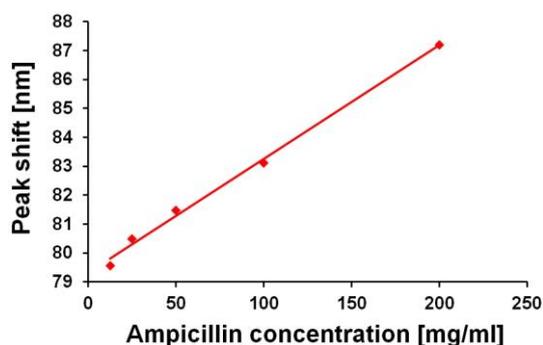


Figure 3a: Sensitivity (peak shift) as function of ampicillin concentration

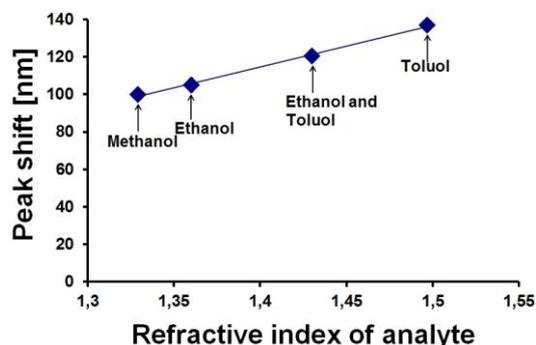


Figure 3b: Sensitivity (peak shift) for native PSMLs as function of the refractive index of the used organic analytes

The pore size and pore filling properties have a strong impact on the sensitivity (Figure 4). Simulation of the peak shift was performed with commercial software Essential McLeod for optical simulation of the corresponding peak shift (redshift) caused by the effective refractive index change induced by the investigated medium. The effective medium approximation and partial pore filling model in different pore diameters of the low and high refractive index layers with  $t$  as coating thickness on the pore wall were used in the simulation. Figure 4 shows that at very small pore size (around 5nm/7nm for the mean value of the pore size distribution for the high and low refractive index layers used to form multilayers, the two axes correspond to the according layers) with increasing coating thickness ( $t=1.2nm$ ) the sensitivity is quite high ( $\Delta\lambda=48nm$ ). Even at very low covering thickness ( $t \ll 1nm$ , monolayer) of the investigated media an evaluable optical peak shift ( $\Delta\lambda=4nm$ ) is detectable. Saturation of the peak shift is achieved if the thickness of the coating layer is equal to the pore radius. On the other side the reduction of pore size is limited by the molecular weight (size) of the molecules within the media as these molecules have to penetrate throughout the porous multilayer structure in order to provide a shift of reflectance spectrum [6]. However, by an appropriate choice of pore size both, sensitivity and filtering conditions for analytical information, can be provided by the multilayer system. The porous layer properties (porosity, pore size) need to be adjusted to the sensor application to achieve a high and good measurable optical output signal.

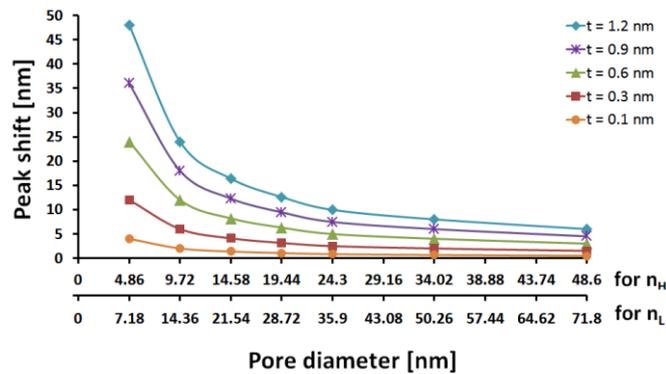


Figure 4: Simulated peak shift (sensitivity) as function of pore diameter. The peak shift is depending on the assumed thickness of the layers formed within the very tiny pores (partial pore filling)

For gas molecules, the permeance of such micro- or mesoporous layers depends strongly on the molecular weight as shown in Figure 5 and allows a certain separation of the molecules by an according porous layer. The sensing response time depends strongly on transport properties of gases or aqueous solutions from outside into the nanostructured layers. Transport processes in nanostructured layers are depending on the layer morphology (pore size, porosity, tortuosity), surface treatment, surface interactions between adsorbate and adsorbent, adsorbate properties (molecular weight) and vapor pressure of the investigated adsorbates.

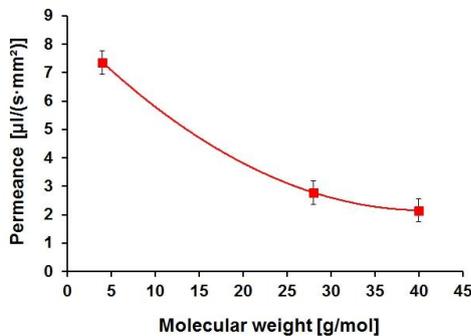


Figure 5: Permeances of different gases in dead-end configuration of porous filters

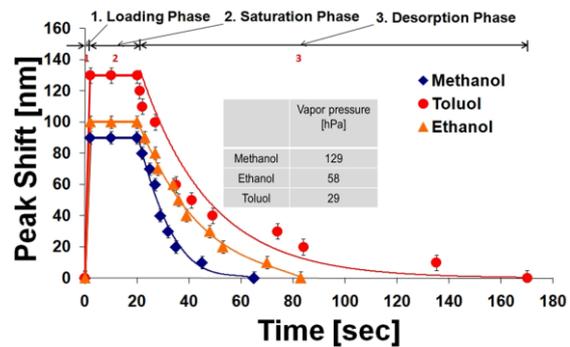


Figure 6: Time response of spectral peak shift due to desorption out of the porous multilayers for different liquid analytes; in the table vapor pressure of the analytes are listed

Therefore, the response time is another material specific sensor output signal is shown in Figure 6. Due to differences in vapor pressure the time dependence of natural desorption out of the porous layers and the corresponding time dependence of peak shift allows to distinguish the materials.

## CONCLUSION

Porous optical multilayers are fabricated and tested for detection and analysis of gaseous or liquid media. The output signal of the optical multilayer is the peak shift, which is directly related to integral information about the analyzed material (refractive index and filling state). The porous optical filter was tested with ampicillin. The peak shift shows a linear dependence with increasing ampicillin concentration. By combination of several output data of the sensor system and adjustment of the porous optical multilayer properties it is possible to obtain additional material specific information which can be used to extend the sensor function to an analysis system.

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