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Nanocrystalline silicon based chemosensors – principles of operation and applications

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Abstract

Changes of photoluminescence intensity and photoluminescence decay time from silicon nanocrystals of macroporous silicon in the presence of chemical species were used for sensing purposes. Magnitude of sensor response for specific measurands at given concentration of chemical compound corresponds to principal mechanisms of photoluminescence quenching in porous silicon sensors - exciton dielectric quenching and capillary condensation effect. Improvement of sensor response selectivity was performed by simultaneous measurements of photoluminescence intensity and photoluminescence decay time.

Introduction

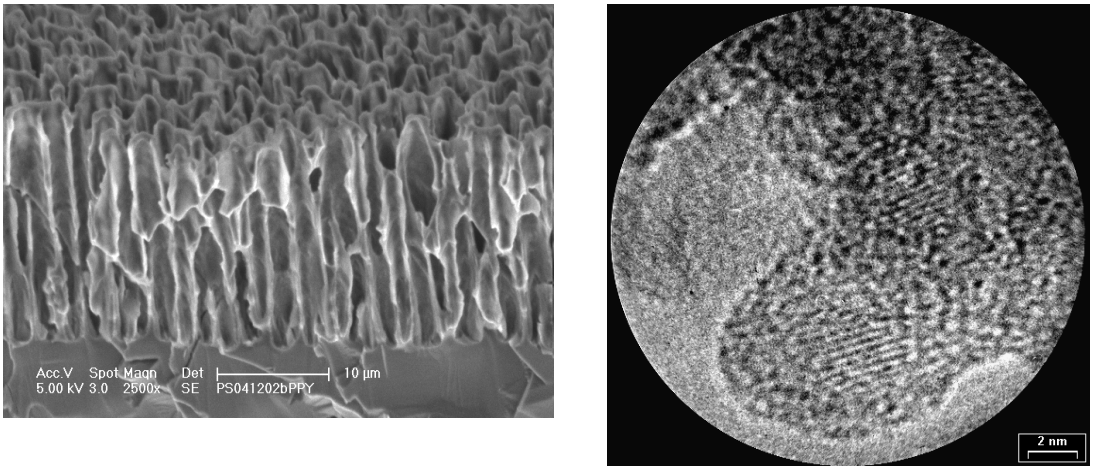
Porous silicon (PS) is of great interest in sensing of chemical species due to its material compatibility with silicon microelectronics [1]. Photoluminescence (PL) based detection is based on measurements of changes of PL intensity [2] or PL decay time [3] in the presence of chemical species. Principal mechanism behind reversible PL quenching of PS in presence of chemical species in liquid phase are energy and electron transfer to adsorbed molecules [4], and exciton dielectric quenching [5]. In this paper we demonstrate the simultaneous detection of multiple measurands (PL intensity and PL decay time) and evaluate sensor sensitivity for both measurands. Improvement of selectivity of sensor response toward specific groups of organic analytes is presented. The application potential of surface functionalization of porous silicon sensor elements for molecular recognition is briefly discussed.

Experimental :

Porous silicon samples were prepared by anodic etching of crystalline silicon (boron doped, (100) orientation, ρ~10 Ωcm) in a HF(50%):ethanol(96%)=1:2.5 mixture for 30 min at current density of 10 mA cm^{-2}. Measurements were performed in a photoluminescence setup adapted for gas and liquid phase measurements. For excitation we used square wave modulated light from UV LED ((λ=375 nm, P~1mW cm^{-2}). PS sample was placed in a bulk optode where controlled amounts of various analytes in nitrogen stream were introduced. PL from the PS sample was analyzed in a 20 cm monochromator (Jobin Yvon HRT20), detected by a photomultiplier (Hamamatsu R3896). After amplification in a current preamplifier (Stanford SR570) signal was simultaneously processed by a Lock-in Amplifier (SR830) and by a 500 MHz digital oscilloscope (Tektronix TDS 3052B).

Results and discussion :

For measurements of PL quenching response we used various types of PS samples. Morphology of a typical as prepared sample is shown in Fig.1a where we can see macropores of about 2-3 μm in diameter. In Fig. 1b a detailed structure of PS surface with silicon nanocrystal is presented.



a **b**

Figure 1 : (a) Porous silicon sample morphology as revealed by SEM, (b) silicon nanocrystals in macroporous silcon sample observed in HR TEM.

PL intensity from as prepared porous silicon sample is quenched in the presence of chemical species. In Fig. 2a there are typical responses of PL intensity when various amounts of ethanol were introduced into the optode, in Fig. 2b there are PL decay curves taken during simultaneous acquisition of the PL intensity in Fig. 2a.

The magnitude of PL quenching depends on alcohol concentration inside porous silicon matrix. In order to quantify the strength of PL quenching, the sensor response is defined as a relative decrease of PL intensity, i.e. change of PL intensity related to the baseline intensity.

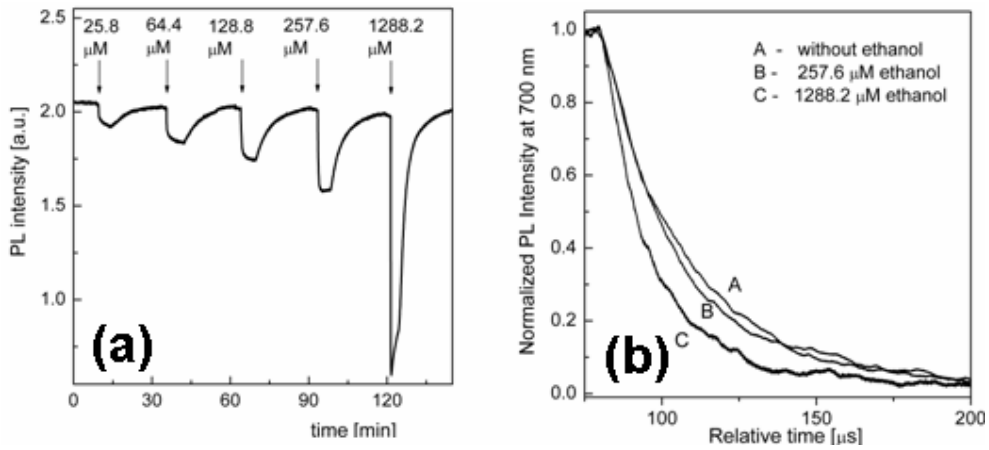


Figure (2) : (a) Time evolution of PL intensity of porous silicon sensor for various concentrations of ethanol. (b) Photoluminescence decay time curves (normalized intensity) for various amounts of ethanol.

Concentration dependences of the sensor responses of these two measurands for ethanol are in Fig. 3a. Similar curves were observed for other analytes. We observed small changes of PL parameters for nonpolar hydrocarbons and alkyl halides, medium responses for water and aromatic compounds and strong response for linear alcohols (rising with the length of alcohol chain). This observation corresponds to the dielectric quenching mechanism extended for capillary condensation effect in gas phase measurements [6].

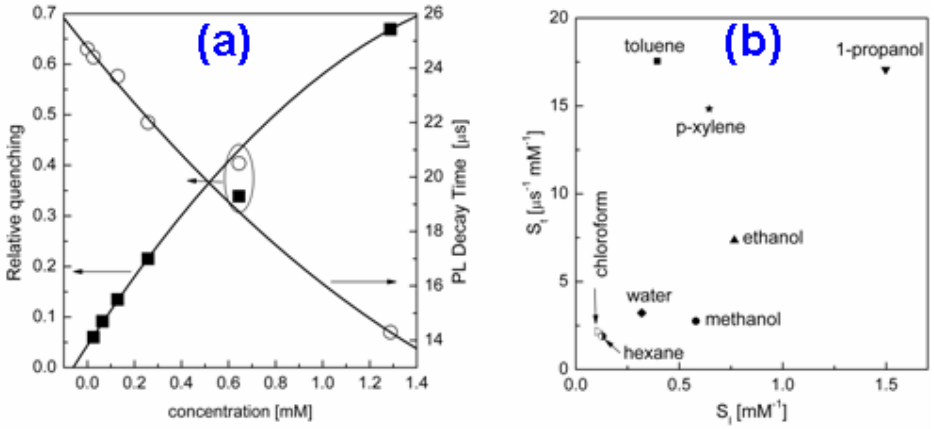


Figure (3) : (a) Concentration dependence of relative PL quenching and PL decay time for a standard porous silicon sample, (b) Correlation between sensitivity of PL quenching S_I and PL decay time shortening S_τ for selected analytes.

Simultaneous measurements of PL intensity and PL decay time enable simple indication of experimental errors. In Fig.3a at gas phase concentration of about 0.6 mM values of both measurands are shifted from the calibration curve and we can ascribe this discrepancy to error in analyte concentration in the detection system. Extended information on selectivity of sensor response can be obtained when we depicted sensitivities (positive values of the slope of the linear part of the concentration dependence) of both PL parameters in one figure. From Fig. 3b it follows that studied aromatic compounds are more sensitive when detecting PL decay shortening as compared to aliphatic hydrocarbon derivatives. This behavior represents a new

possibility for enhancement of the sensor response selectivity to various groups of organic molecules. Another interesting feature is nearly linear correlation between the sensitivities of PL sensor responses in a homological set of linear alcohols. Further improvement in selectivity of photoluminescence quenching response was recently observed for porous silicon sensors with various surface functionalization [7,8,9].

Conclusion :

Porous silicon sensors provide fast and sensitive detection of chemical species according to their concentration inside porous matrix and quenching strength determined by dielectric constant. Simultaneous detection of two sensor measurands (PL intensity and PL decay time) enables to improve detection reliability and reveals new possibility for enhancement of the sensor response selectivity to various groups of organic molecules.

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