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## Time Evolution of Photoluminescence Response from Porous Silicon in Hydrocarbon Gas Sensing

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A photoluminescence (PL) response (S-band) of porous silicon to specific amounts of organic vapors of n-hexane, toluene and methanol in gas phase reveals the presence of two reversible processes: one relatively fast responsible for PL quenching and one relatively slow which is responsible for a remarkable PL enhancement. The fast PL quenching (with time constant of several seconds) can be utilized for sensing the studied organic vapors within a concentration range of about 1–500 ppm.

**Introduction** Porous silicon (PS) attracts much interest during the last decade due to its efficient photoluminescence (PL) in the visible region. Considerable effort has been devoted to optimization of PL efficiency and PL wavelength tunability. Most of the studies were performed bearing in mind potential applications for electroluminescence (EL) devices. The main drawback of EL from PS is its instability due to its reactive surface [1]. This drawback of PS large reactive surface can be, on the other hand, utilized for sensing applications. Various sensor properties of PS have been studied in gas phase, e.g. conductivity [2], refractive index [3], PL quenching [4, 5, 6]. Despite an enormous amount of performed studies understanding of the PL mechanism and surface chemistry of PS still remains a great challenge.

We report on time evolution of PL response from PS in presence of various vapors of organic compounds. We evidence, for the first time, that two processes are responsible for the PL response: a fast PL quenching and a relatively slow PL enhancement. At present, we cannot specify the mechanism of the PL enhancement process. We demonstrate the application of the fast PL quenching process for gas sensing purposes.

**Experimental Procedure** PS samples were prepared by anodic oxidation ( $10 \text{ mA cm}^{-2}$ , 15 min, in dark) of p-type Si wafer ( $\approx 10 \text{ } \Omega \text{ cm}$ ) in 40% HF:ethanol (1:2) solution. The porosity of samples was 80% as determined by gravimetric method.

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PL was measured at room temperature in an experimental set-up with closed gas circulation operating with air as a carrier gas (in order to simulate operation conditions of a real sensor). The total volume of the system was 1258 ml. The set-up consists of a measurement cell connected to a reservoir bottle (where precise amounts of high purity solvents were injected) and a membrane pump. PL was excited through a quartz window either by a Xe-lamp with an excitation monochromator (360 nm, spectral width of the slit was 8 nm, excitation power  $\leq 1 \text{ mW cm}^{-1}$ ) or the He–Cd laser line 325 nm ( $P \approx 15 \text{ mW cm}^{-2}$ ). The signal was collected in perpendicular direction by means of a glass optical fiber connected to an emission monochromator, detected by a photomultiplier and processed by means of a lock-in amplifier.

**Results and Discussion** A time evolution of PL signal at 680 nm (near PL spectral maximum) of freshly prepared PS samples after injection of 50  $\mu\text{l}$  (40 ppm) of n-hexane, toluene and methanol into the measurement system is presented in Fig. 1. After initial decrease of PL intensity with time constant of  $\approx 1\text{--}2 \text{ s}$  a slow increase of the PL is observed, resulting in net PL enhancement. The PL quenching after injection of organic solvents into the system amounts for this hydrocarbon concentration up to 10% of initial PL intensity, the subsequent rise in PL intensity is relatively slow and at this vapor concentration saturates approximately within 1 h. The time constant of the PL enhancement process depends on vapor concentration and varies from minutes to tens of minutes.

The magnitude of the fast initial PL decrease of PS by vapors of organic compounds depends on the amount of organic solvent injected into the system. Therefore, we performed a systematic study of PL changes as a function of vapor concentration. Various doses of n-hexane, toluene and methanol were injected into the system and the initial response of PL intensity was recorded. After some time the vapor was blown off the system and after stabilization of the PL signal a new dose was applied. The time evolution of PL signal at 680 nm from PS in presence of methanol vapors with various concentration is depicted in Fig. 2. The relative change of the PL intensity during initial decrease as a function of concentration is shown in the inset of Fig. 2. This dependence is linear for low concentrations only, for higher values deviations from linear behavior for all studied vapors were observed. Simultaneously, a baseline degradation (Fig. 2) due to partial oxidation of PS surface in air-methanol mixture is observed [7, 8].

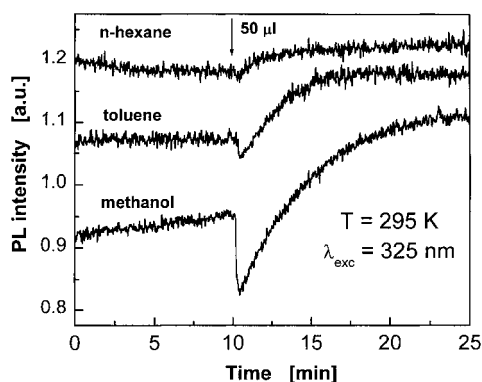


Fig. 1. PL time response of PS to n-hexane, toluene and methanol vapors under He–Cd laser excitation ( $\lambda_{\text{exc}} = 325 \text{ nm}$ ,  $P = 15 \text{ mW cm}^{-2}$ ), detection wavelength 680 nm

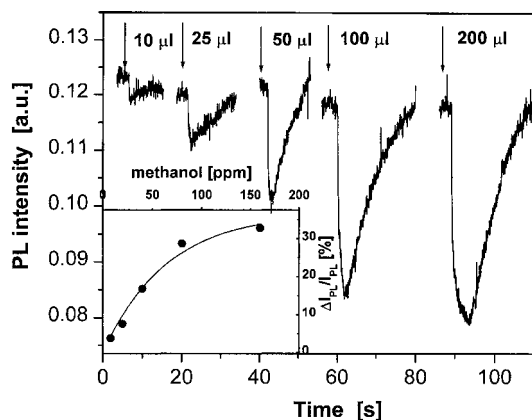


Fig. 2. PL time response of PS sample to various amounts of methanol injected into the system. Excitation with a Xe lamp ( $\lambda_{\text{exc}} = 360 \text{ nm}$ ,  $P \leq 1 \text{ mW cm}^{-2}$ ), detection wavelength 680 nm. The time of injection is marked by arrows. Inset: relative change in PL intensity during the initial decrease as a function of the methanol concentration (the full line is a guide for the eye)

It is worth mentioning that the time evolution curves for various vapor concentrations differ mainly close to the minima of the curves (Fig. 2). They have sharp (V-like) shapes for low concentrations while the minimum rounds off for higher concentrations. This observation strongly suggests that the overall PL temporal evolution is due to the simultaneous effect of both quenching and enhancement processes, each of which occurs with a considerably different rate in dependence on vapor concentration. At higher vapor concentrations the rate of PL enhancement process may be comparable with the PL quenching rate from the very beginning of the PS-hydrocarbon interaction.

For this reason we studied the time evolution of the slow PL response (enhancement) in more detail for higher hydrocarbon concentration. Figure 3 presents PL intensity at 680 nm as a function of time for a 500  $\mu\text{l}$  toluene dose. When toluene was injected into the system, after the fast initial PL signal decrease an intermediate regime with minimum of PL signal (where the quenching and the enhancement compensate each other) was observed, followed by a relatively slow PL increase. When the PL intensity stabilized, the toluene was blown off. A short and very fast rise of PL intensity was then observed followed by a slower decrease down to the value slightly ( $\approx 10\%$ ) below the initial PL intensity. Also in this case a partial oxidation of the PS sample studied in the toluene vapor took place as confirmed by FTIR spectra (not shown).

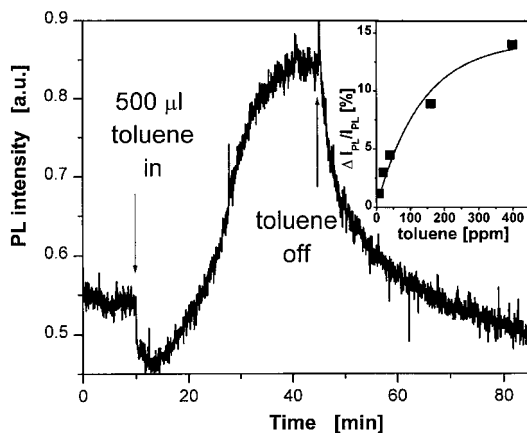


Fig. 3. PL time response of PS to injection of 500  $\mu\text{l}$  of toluene into the system and after blowing the toluene off. Excitation with a Xe lamp ( $\lambda_{\text{exc}} = 360 \text{ nm}$ ,  $P \leq 1 \text{ mW cm}^{-2}$ ). Inset: relative change in PL intensity during the initial quenching as a function of the toluene concentration (the full line is a guide for the eye)

Relative PL quenching as a function of toluene concentration is shown in the inset of Fig. 3.

The mechanism of PL quenching in PS is usually explained by the formation of non-radiative centers usually supposed and the quenching kinetics can be described by the Stern-Volmer equation. An interpretation by Lauerhaas et al. [9] suggests that PL quenching is caused by attraction and subsequent trapping of electron or holes at the surface by polar molecules. Another interpretation due to exciton dielectric quenching was reported by Fellah et al. [10]. At present, we can only speculate about the origin of the PL enhancement mechanism. The most probable origin is a kind of a reversible photoinduced reaction (kinetics of which is not known) leading to a passivation of some type of nonradiating centers.

**Conclusions** Measurements of PL response from PS in presence of hydrocarbon vapors as a function of time revealed the presence of two reversible processes controlling the PL intensity, a fast PL quenching with time constant of few seconds and a relatively slow PL enhancement with time constant ranging from minutes to tens of minutes. In the extended time scale the PL degradation processes due to partial oxidation of the PS surface were observed. The fast PL quenching can be utilized for gas sensing purposes.

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## References

- [1] L. T. CANHAM, M. R. HOULTON, W. Y. LEONG, C. PICKERING, and J. M. KEEN, *J. Appl. Phys.* **70**, 422 (1991).
- [2] I. SCHECHTER, M. BEN CHORIN, and A. KUX, *Anal. Chem.* **67**, 3727 (1995).
- [3] S. ZANGOIE, R. BJORKLUND, and H. ARWIN, *Sensors and Actuators B* **43**, 168 (1997).
- [4] R. R. CHANDLER-HENDERSON, B. SWERYDA-KRAWIEC, and J. L. COFFER, *J. Phys. Chem.* **99**, 8851 (1995).
- [5] G. DI FRANCIA, V. LA FERRARA, L. QUERCIA, and G. FAGLIA, *J. Porous Mater.* **7**, 287 (2000).
- [6] M. T. KELLY and A. B. BOCARSLY, *Chem. Mater.* **9**, 1659 (1997).
- [7] J.-N. CHAZALVIEL, *J. Electroanal. Chem.* **233**, 37 (1987).
- [8] J. HARPER and M. J. SAILOR, *Langmuir* **13**, 4652 (1997).
- [9] J. M. LAUERHAAS, G. M. CREDO, J. L. HEINRICH, and M. J. SAILOR, *J. Amer. Chem. Soc.* **114**, 1911 (1992).
- [10] S. FELLAH, R. B. WEHRSPHON, N. GABOUZE, F. OZANAM, and J.-N. CHAZALVIEL, *J. Lum.* **80**, 105 (1999).