

Novel porous silicon vapor sensor based on polarization interferometry

Rong Liu^{a,*}, Thomas A. Schmedake^b, Yang Yang Li^b,
Michael J. Sailor^b, Yeshaiahu Fainman^a

^aDepartment of Electrical and Computer Engineering, University of California, La Jolla, San Diego, CA 92093, USA

^bDepartment of Chemistry and Biochemistry, University of California, La Jolla, San Diego, CA 92093, USA

Accepted 20 May 2002

Abstract

Optical form birefringence property of porous silicon is used in a compact polarization interferometer to demonstrate a novel optical transduction mechanism for vapor or gas sensing applications. This technique uses high interferometric sensitivity of polarization interference intensity when the porous silicon sample is exposed to solvent vapors. We experimentally demonstrate that the relative variation in the polarization interference intensity at a fixed incidence angle provides means to quantify the detected concentration of solvent vapors. Examples of detecting heptane and ethanol vapors indicate good potential of the novel transduction mechanism for other chemical and biological sensing applications.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Porous silicon; Sensor; Optical form birefringence; Polarization interference

1. Introduction

In recent years, porous silicon has attracted much attention in the field of sensor technology due to its diverse applications for detection of different analytes. Unique properties that make porous silicon attractive for these applications include significantly increased surface interaction area, simplicity and repeatability of fabrication, and compatibility with well established silicon microfabrication technology. The sensing mechanism is based on a change in the physical properties of porous silicon when it is exposed to analytes. The early attempts to use porous silicon in sensing applications were based on variations of its electrical properties such as capacitance [1] and conductivity [2]. Recently, optical properties of porous silicon have been exploited for chemical and biological sensing due to their fast response time and relative safety for operation in hazardous environments such as flammable vapors or gases. The most popular optical techniques are based on the change in optical reflectivity [3–7], photoluminescence [8–11], birefringence [12,13], and the properties of optical waveguides [14].

It is well known that silicon is an isotropic optical material due to its cubic structural symmetry. Isotropic optical materials can be made anisotropic by simply introducing a geometric nanostructure producing a form birefringence effect [15–17].

Porous silicon is an example of such an artificial birefringent material [18–26]. This is largely due to its morphological anisotropy (the preferential aligned nano-scale pores in the direction perpendicular to the wafer surface) that leads to a difference in average dielectric properties depending on the direction of propagation and the polarization of the optical field. In this paper, we exploit the polarization interference caused by the optical anisotropy in porous silicon to detect heptane and ethanol vapors, providing characteristics in selectivity and quantitative measurement of the technique.

2. Experimental details

2.1. Principle of operation

We assume that a porous silicon sample obtained from etching p type $\langle 100 \rangle$ silicon wafer consists of uniformly distributed pores in the direction of the surface normal. We further consider that due to the in-plane rotational symmetry, our form-birefringent porous silicon sample acts as a positive uniaxial anisotropic material (see Fig. 1) with its optic axis normal to the wafer surface [21]. The sample is rotated in the x - z plane such that its surface normal is oriented at angle α with respect to the z -axis. Consider an optical wave polarized in the x - y plane at 45° with an incident angle α propagating in the anisotropic porous silicon sample. It will

* Corresponding author.

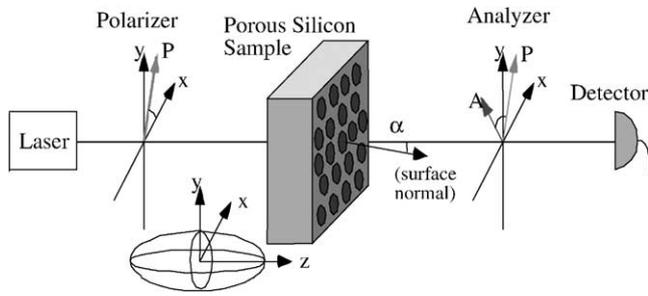


Fig. 1. Schematic diagram for characterization of optical anisotropy in porous silicon samples.

produce two linearly polarized components oscillating in the x - z plane and perpendicular to the x - z plane, corresponding to extraordinary and ordinary polarized light components, respectively. At the output of the porous silicon sample the ordinary and the extraordinary polarized light components will acquire a relative phase shift depending on sample's birefringence:

$$\Delta\phi(\alpha) = \frac{2\pi}{\lambda} [n_e(\alpha)l_e(\alpha) - n_o(\alpha)l_o(\alpha)], \quad (1)$$

where λ is the wavelength of the optical field, $n_e(\alpha)$ and n_o are the effective refractive index for extraordinary and ordinary polarized light components, respectively, $l_e(\alpha)$ and $l_o(\alpha)$ represent the geometric path lengths inside the sample for extraordinary and ordinary polarized light components, respectively.

An output analyzer A (see Fig. 1), oriented at 90° with respect to the direction of the polarizer P, produces interference between projections of the ordinary and extraordinary polarized light components, yielding the output intensity:

$$I(\alpha) = [a^2 + b^2 + 2ab \cos(\Delta\phi(\alpha))] \frac{I_{in}}{2}, \quad (2)$$

where a and b are the amplitude transmittances of the porous silicon sample for the extraordinary and ordinary polarized light components, respectively, and I_{in} is the input intensity on the porous silicon sample. Eq. (2) shows that the output interference intensity depends on the relative phase shift between the ordinary and extraordinary polarized light components at the output, which in turn depends on the angle of incidence α .

Next we consider exposing the porous silicon sample to gases or vapors. The absorption of gases or vapors to the sample surface changes the effective refractive indices for both extraordinary and ordinary polarized light components. With the same incidence angle, the induced phase shift leads to a change in the polarization interference intensity. Over a certain range of incidence angles, these variations in the ordinary and extraordinary refractive indices result in a simple shift of polarization interference pattern, thereby, polarization interferometry offers a new transduction mechanism for optical sensing of vapors and gases.

2.2. Experimental apparatus

For experimental characterization of the porous silicon optical sensor based on polarization interferometry, we prepared a porous silicon sample by anodic etching of a p type $\langle 100 \rangle$ silicon wafer with resistivity of about $0.001 \Omega \text{ cm}$ in a solution of aqueous HF (49%) with ethanol in the ratio of 3:1 at room temperature. After etching for 90 min at a current density of 75 mA/cm^2 , we performed an electropolishing process in order to lift-off the porous silicon membrane by applying a current density of 50 mA/cm^2 for 30 s in 3.3 wt.% HF solution. While kept in the etching cell, the sample was carefully rinsed with ethanol to remove the etchant. Then the sample was transferred to an aluminum tray and immersed in pentane. The aluminum tray was tapped gently to release the freestanding porous silicon membrane from silicon substrate. The silicon substrate was moved away and the freestanding porous silicon membrane was left to dry in the air. The porous silicon sample was inspected by atomic-force microscope, showing an average pore size of less than 20 nm in diameter. The porosity was determined to be 82% using gravimetric method applied to test samples prepared with the same etching condition.

The optical anisotropy of porous silicon sample was evaluated experimentally using a set-up shown schematically in Fig. 1. To operate the silicon-based sensor in transmission configuration with minimal loss (i.e. photon energy below silicon bandgap), we use an external-cavity tunable diode laser (New Focus Inc., Model 6427) operating at $1.52 \mu\text{m}$. A pair of crossed Glan-Thompson-type polarizers was orientated at $\pm 45^\circ$ in the transverse plane x - y (see Fig. 1). The freestanding porous silicon sample was attached to a plastic sample holder with a $4 \text{ mm} \times 8 \text{ mm}$ transmission window in the center. Normally the size of our porous silicon samples was about 10–13 mm in diameter to match the dimension of the transmission window. The sample was placed between the pair of polarizers and was mounted on a motorized rotation stage (Polytec PI, Model M-037.PD). The resolution of the rotation stage is $8.75 \mu\text{rad}$, which enables us to accurately control and record the incidence angle of the input light on the sample. A Ge photodetector (Newport Inc., Model 818-IR) was used to measure the output transmitted light intensity.

For testing the sensor characteristics, the porous silicon sample was placed in a custom-made glass flow cell for exposure to solvent vapors and the flow cell was connected to a gas-mixer/mass-flow controller (Cole-Parmer). A nitrogen carrier gas was saturated with solvent vapor by passing through a bubbler containing the solvent under study. The saturated vapor was then diluted with a second nitrogen stream in the mixer. At a constant total flow rate, it is possible to obtain different concentration of the solvent vapor by adjusting the flow of carrying nitrogen and saturated vapor.

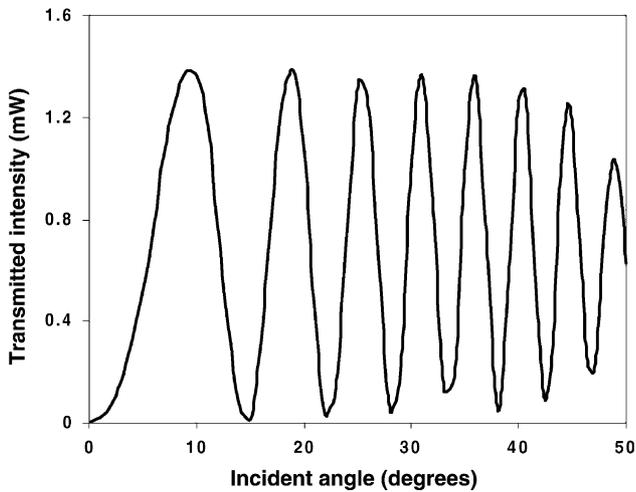


Fig. 2. Transmitted intensity at the output of the polarization interferometer as a function of the incidence angle on the porous silicon sample.

3. Experimental results and discussion

The measured polarization interference intensity versus the incidence angle for the fabricated porous silicon sample is illustrated in Fig. 2. The uneven oscillation in polarization interference intensity indicates a nonlinear dependence between the incidence angle and the phase shift between the extraordinary and ordinary polarized light components. It is evident that the oscillation frequency of polarization interference intensity increases with the increase of incidence angle, which in turn increases the relative phase shift for extraordinary and ordinary polarized light components (see Eq. (1)).

For characterization of the new sensing transduction mechanism, we used heptane and ethanol vapors. Fig. 3(a) shows the detected polarization interference intensity in air (solid line) and after exposed to heptane with concentration of 2.0% (dashed line) at the incidence angle varied from 40° to 50°. Fig. 3(b) shows the shift in polarization interference pattern when the porous silicon sample is exposed to ethanol with concentration of 2.0%. We use large incidence angles to access high sensitive region of the polarization interference intensity. It is noticeable from comparing Fig. 3(a) and (b) that there is a larger shift in polarization interference pattern when porous silicon sample is exposed to heptane than to ethanol. This occurs because the freshly prepared porous silicon sample is hydrophobic and it adsorbs heptane more efficiently as compared to ethanol, resulting in a larger change in refractive indices and consequently in the polarization interference intensity. It should be noted that we used the same sample to test the shift of polarization interference pattern in Fig. 3(a) and (b). After we finished the first experiment with heptane, we evacuated and flushed the flow cell with pure nitrogen until the polarization interference intensity back to the initial conditions, i.e. when the sample was exposed to air. Then we performed the second test with

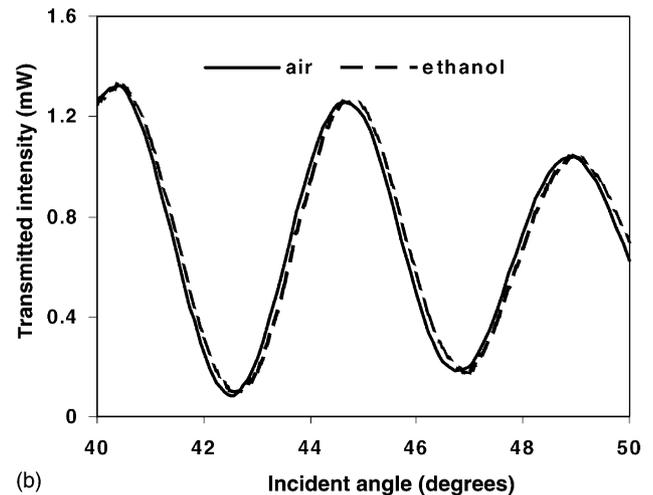
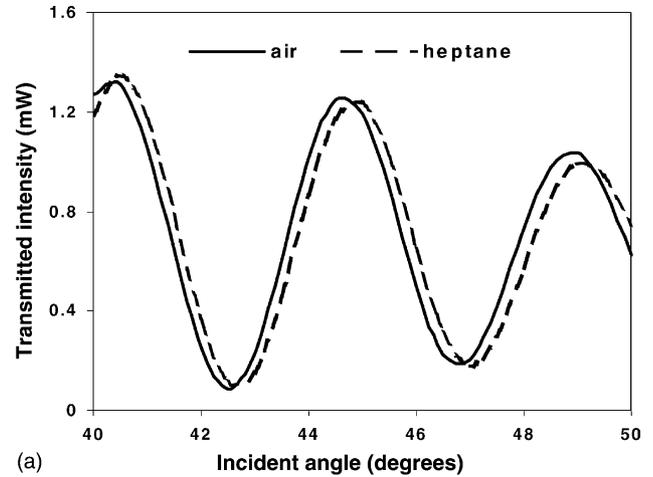


Fig. 3. Transmitted intensity at the output of the polarization interferometer when the porous silicon sample is exposed to air and vapors of heptane and ethanol. (a) Solid line: air; dashed line: heptane with concentration of 2.0%. (b) Solid line: air; dashed line: ethanol with concentration of 2.0%.

ethanol. The data shown in Fig. 3 was reproduced within 3% accuracy (when we used the same sample). However, although the shift of polarization interference pattern is comparable from sample to sample, the sensor needs to be recalibrated to compensate for changes due to sample variations, sample alignment, etc.

It can be easily seen from Fig. 3 that at a fixed incidence angle the relatively large change in polarization interference intensity can be used to provide quantitative detection of vapor concentration. Fig. 4 shows the polarization interference intensity versus heptane concentration at fixed angles. As heptane concentration varies from 342 ppm to 2.0%, the polarization interference intensity increases and decreases monotonically at the incidence angles of 46.1° and 48.1°, respectively. It should be noted that this study does not contain any optimization of the sample (pore size, pore distribution and porosity) that may further improve the sensitivity of this novel detection transduction mechanism.

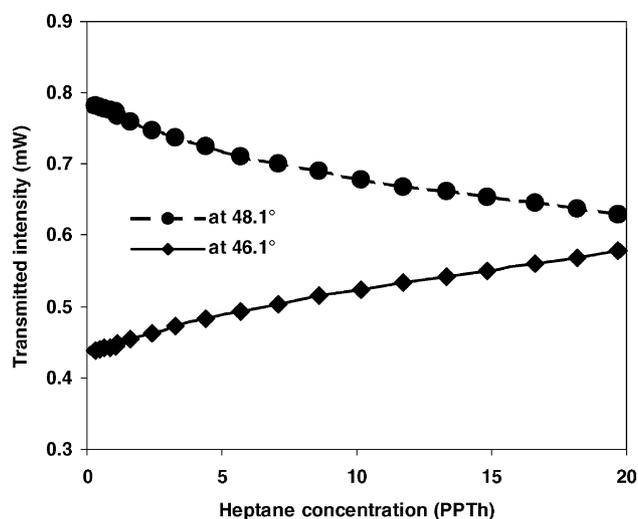


Fig. 4. Transmitted intensity at the output of the polarization interferometer as a function of heptane concentration in unit of part per thousand at fixed angles of 46.1 and 48.1°.

We also investigate the performance of our proposed optical sensor when exposed to a mixed solution of ethanol and heptane. Fig. 5 shows the different responses of polarization interference intensities at a fixed incident angle of 41.8° to the vapors of pure heptane, pure ethanol, and a mixture of these two solvents in a ratio of 1:1. It clearly indicates that the transduction mechanism in our sensor is capable of distinguishing between two different solvents, as well as their mixtures. According to Eqs. (1) and (2), the polarization interference intensity at a fixed angle depends on the refractive indices of extraordinary and ordinary polarized light components as well as the resulting different geometric path lengths. While the porous silicon sample is exposed to a solvent vapor, the absorption of vapor to the sample surface changes the effective refractive indices for

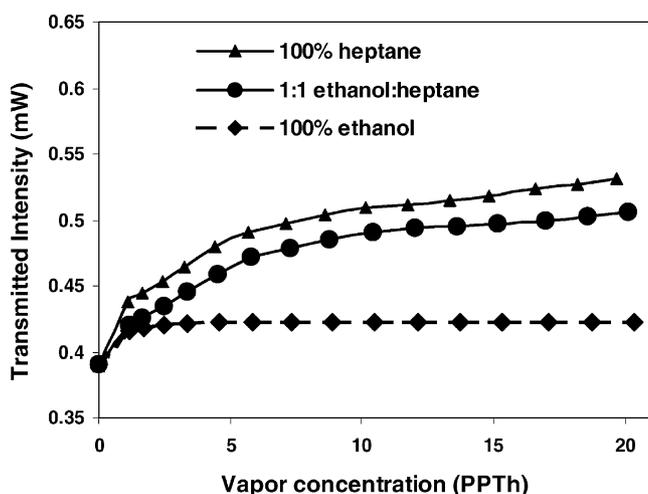


Fig. 5. Transmitted intensity at the output of the polarization interferometer when the porous silicon sample was exposed to pure heptane, the mixture of heptane and ethanol, and pure ethanol, respectively.

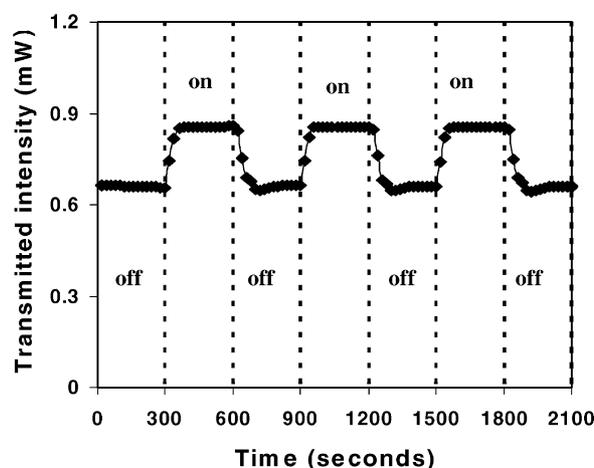


Fig. 6. Reversibility of the porous sensor vapor sensor upon switching heptane off and on.

both extraordinary and ordinary polarized light components. These changes are subject to the refractive index of solvent and the efficiency of the absorption. It is evident that the refractive index for the mixture is between the individual refractive index of ethanol (1.3611) and heptane (1.3878) [27] and the absorption efficiency of the mixture is also a trade-off between that of ethanol and heptane. We believe this is the reason for the distinguished behavior of the mixture from that of ethanol and heptane. As for other solvent vapors and gases with different refractive indices and unique absorption properties, the proposed scheme could be a good candidate for these sensing applications.

Reversibility of the detection process has also been tested by switching the concentration of heptane between zero and 2.0%, shown in Fig. 6. The polarization interference intensity of each stage could be repeated, indicating that our sensing process is reversible, as it does not involve any chemical reactions.

4. Conclusions

We demonstrate a novel optical transduction mechanism for vapor or gas sensing by using the optical form birefringence property of porous silicon in a compact polarization interferometer. This technique utilizes high interferometric sensitivity of polarization interference intensity. The validity and selectivity of the optical sensor are proven by exposing our fabricated freestanding porous silicon sample to heptane and ethanol vapors. We also experimentally demonstrate a method of quantitative detection of vapor concentration by monitoring the relative change in the polarization interference intensity at a fixed incidence angle using pure heptane, pure ethanol, and the mixture of these two solvents. The experimental results of detecting heptane and ethanol vapors indicate great potential of this novel transduction mechanism for other applications of chemical and biological sensing.

Acknowledgements

This work is supported by the National Science Foundation, ONR, and DARPA/SPAWAR.

References

- [1] R.C. Anderson, R.S. Muller, C.W. Tobias, Investigation of porous silicon for vapor sensing, *Sens. Actuators A21/A23* (1990) 835–839.
- [2] M. Ben-Chorin, A. Kux, I. Schechter, Adsorbate effects on photoluminescence and electrical conductivity of porous silicon, *Appl. Phys. Lett.* 64 (1993) 481–483.
- [3] V.S.Y. Lin, K. Motesharei, K.P.S. Dancil, M.J. Sailor, M.R. Ghadiri, A porous silicon based optical interferometric biosensor, *Science* 278 (1997) 840–843.
- [4] P.A. Snow, E.K. Squire, P.St.J. Russell, Vapor sensing using the optical properties of porous silicon Bragg mirrors, *J. Appl. Phys.* 86 (1999) 1781–1784.
- [5] S.E. Letant, M.J. Sailor, Detection of HF gas with a porous silicon interferometer, *Adv. Mater.* 12 (2000) 355–359.
- [6] J. Gao, T. Gao, M.J. Sailor, Porous silicon vapor sensor based on laser interferometry, *Appl. Phys. Lett.* 77 (2000) 901–903.
- [7] H.K. Min, H.S. Yang, S.M. Cho, Extremely sensitive optical sensing of ethanol using porous silicon, *Sens. Actuators B* 67 (2000) 199–202.
- [8] J.M. Lauerhaas, M.J. Sailor, Chemical modification of the photoluminescence quenching of porous silicon, *Science* 261 (1993) 1567–1568.
- [9] J.L. Coffey, S.C. Lilley, R.A. Martin, L.A. Files-Sesler, Surface reactivity of luminescent porous silicon, *J. Appl. Phys.* 74 (1993) 2094–2096.
- [10] S. Fellah, R.B. Wehrspohn, N. Gabouze, F. Ozanam, J.N. Chazaviel, Photoluminescence quenching of porous silicon in organic solvents: evidence for dielectric effects, *J. Lumin.* 80 (1998) 109–113.
- [11] V. Mulloni, L. Pavesi, Porous silicon microcavities as optical chemical sensors, *Appl. Phys. Lett.* 76 (2000) 2523–2525.
- [12] S. Zangoie, R. Bjorklund, H. Arwin, Vapor sensitivity of thin porous silicon layers, *Sens. Actuators B* 43 (1997) 168–174.
- [13] E. Gross, D. Kovalev, N. Kunzner, V.Yu. Timoshenko, J. Diener, F. Koch, Highly sensitive recognition element based on birefringent porous silicon layers, *J. Appl. Phys.* 90 (2001) 3529–3532.
- [14] H.F. Arrand, T.M. Benson, A. Loni, R. Arens-Fischer, M. Kruger, M. Thonissen, H. Juth, S. Kershaw, Novel liquid sensor based on porous silicon optical waveguides, *IEEE Photon. Technol. Lett.* 10 (1998) 1467–1469.
- [15] I. Richter, P.-C. Sun, F. Xu, Y. Fainman, Design considerations of from birefringent microstructures, *Appl. Opt.* 34 (1995) 2421–2429.
- [16] F. Xu, R.-C. Tyan, P.-C. Sun, Y. Fainman, C.-C. Cheng, A. Scherer, Fabrication, modeling, and characterization of from-birefringent nanostructures, *Opt. Lett.* 20 (1995) 2457–2459.
- [17] F. Xu, R.-C. Tyan, P.-C. Sun, Y. Fainman, C.-C. Cheng, A. Scherer, Form-birefringent computer-generated holograms, *Opt. Lett.* 21 (1996) 1513–1515.
- [18] F. Ferrieu, A. Halimaoui, D. Bensahel, Optical characterization of porous silicon layers by spectrometric ellipsometry in the 1.5–5 eV range, *Solid State Commun.* 84 (1992) 293–296.
- [19] L.H. Qin, Y.D. Zheng, R. Zhang, S.L. Gu, H.T. Shi, D. Feng, Ellipsometric studies of porous silicon, *Appl. Phys. A* 58 (1994) 163–165.
- [20] P. Basmaji, G. Surdutovich, R. Vitlina, J. Kolenda, V.S. Bagnato, Anisotropy investigation and photoluminescence properties of porous silicon, *Solid State Commun.* 91 (1994) 649–653.
- [21] I. Mihalcescu, G. Lerondel, R. Romestain, Porous silicon anisotropy investigated by guided light, *Thin Solid Films* 297 (1997) 245–249.
- [22] S. Zangoie, R. Jansson, H. Arwin, Investigation of optical anisotropy of refractive-index-profiled porous silicon employing generalized ellipsometry, *J. Mater. Res.* 14 (1999) 4167–4175.
- [23] M.E. Kompan, J. Salonen, I.Yu. Shabanov, Anomalous birefringence of light in free-standing samples of porous silicon, *J. Exp. Theor. Phys.* 90 (2000) 324–329.
- [24] O.G. Sarbey, E.K. Frolova, R.D. Fedorovich, D.B. Dan'ko, Birefringence of porous silicon, *Phys. Solid State* 42 (2000) 1240–1241.
- [25] J. Diener, N. Kunzner, D. Kovalev, E. Gross, V.Yu. Timoshenko, G. Polisski, F. Koch, Dichroic Bragg reflectors based on birefringent porous silicon, *Appl. Phys. Lett.* 78 (2001) 3887–3889.
- [26] D. Kovalev, G. Polisski, J. Diener, H. Heckler, N. Kunzner, V.Yu. Timoshenko, F. Koch, Strong in-plane birefringence of spatially nanostructured silicon, *Appl. Phys. Lett.* 78 (2001) 916–918.
- [27] R.C. Weast, *CRC Handbook of Chemistry and Physics*, 1st Student Edition, CRC Press, Boca Raton, FL, 1988, p. c-267 and -295.