Two- and three-dimensional photonic crystals made of macroporous silicon and liquid crystals

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(Received 4 June 2003; accepted 6 August 2003)

Variations of the refractive index can be utilized in order to shift the stop band in periodic structures, such as photonic crystals. We report on investigations about three-dimensional macroporous silicon structures that are filled with a liquid crystal. Fourier transform infrared measurements indicate that a shift of the photonic band edge can be induced by changing the temperature. The director field in macropores within the silicon structure is investigated by ²H-NMR spectroscopy and compared to director field simulations. The latter method indicates a preferred parallel orientation of the director in the nematic state. Based on this finding, we analyze the optical properties. © 2003 American Institute of Physics. [DOI: 10.1063/1.1614000]

Photonic crystals are structured materials that show a spatially periodic variation of the dielectric permittivity. If the lattice constant is of similar magnitude as the wavelength of electromagnetic radiation, these structures can not only show Bragg reflection, but even a complete photonic band gap: an interval of frequencies within which no radiation of the respective frequency can propagate. High amplitude of the variation of the dielectric constant and a proper shape of the Brillouin zone of the structure are necessary for a photonic band gap. Photonic crystals are of high fundamental interest due to the analogy between the propagation of light in these structures and the propagation of electrons in semiconductors. In addition, they are potential key materials for integrated optical elements, including optical waveguides, inductors. In addition, they are potential key materials for interconnects and switches, miniaturized interferometers, integrated optical filters, resonant cavities, and lasing structures. For practical applications, it may be desirable to tune the photonic band structure by changing the lattice constants, the symmetry or the dielectric contrast. Liquid crystals (LCs) are suitable for this purpose. Here, we describe the first example of a three-dimensional (3D) structure consisting of macroporous silicon filled with a LC. The photonic properties for light propagation along the pore axes (1) and the director field of the LC were studied by Fourier transform infrared (FTIR) spectroscopy and deuterium-nuclear magnetic resonance (²H-NMR), respectively.

A two-dimensional hexagonal array of pores with a lattice constant \( a = 1.5 \, \mu m \) [Fig. 1(a)] was produced by electrochemical etching of an n-doped Si wafer, pre-structured with photolithography. Along the pore axis, each pore is periodically modulated with a lattice constant \( b = 2.6 \, \mu m \). This modulation leads to a 3D lattice. The radius of the pores varies with the depth from \( R_{\text{min}} = 0.38 \pm 0.05 \, \mu m \) to \( R_{\text{max}} = 0.63 \pm 0.05 \, \mu m \). The pores were filled with the nematic LC 4-cyano-4’-pentylbiphenyl (5CB) which shows a clearing temperature of \( T_c = 34 \, ^\circ C \). ²H-NMR measurements were performed using two-dimensional structures of pores with constant radius \( R = 0.45 \, \mu m \) and \( R = 1.00 \, \mu m \), respectively, filled with 5CB deuterated in the \( \alpha \)-position of the alkyl chain.

For light propagation along the pore axes, the FTIR transmission spectrum of the silicon–air structure [Fig. 1(b)] shows a stop band centered at \( \lambda = 10.5 \, \mu m \). The variation of \( R_{\text{min}} \) and \( R_{\text{max}} \) with position due to slight inhomogeneities in the electrochemical etching process causes a variation of the center wavelength of \( \approx 0.5 \, \mu m \). Filling the pores with 5CB decreases the dielectric contrast to silicon and results in a shift of the stop band to \( \lambda = 12 \, \mu m \). The band edge at lower wavelengths corresponds to electromagnetic modes where maximum intensity is located in the LC regions. This “liquid crystal band” (in analogy to the air band of nonfilled structures) can be tuned by more than 140 nm while heating the LC from the nematic phase (24 °C) to the isotropic state (40 °C). Fig. 1(c) shows the polarization dependence of the incident light. Here, the center wavelength is at \( \lambda = 12.5 \, \mu m \). Rotation of the sample with respect to the plane of polarization causes a shift of the LC band edge by \( \Delta \lambda \approx 152 \, nm \). The different central wavelengths in Figs. 1(b) and 1(c) are due to small variations of the pore radius.

The shift of the photonic band edge towards larger wavelengths indicates an increase of the effective refractive index with increasing temperature. In order to explain this behavior, it is necessary to know the director field of the LC inside the pores. Figure 2(a) shows some possible director configurations which were calculated using the alignment tensor

\[
a_{\mu \nu} = \langle n_{\mu} n_{\nu} \rangle - 1/3n_x n_y \delta_{\mu \nu},
\]

and solving the corresponding relaxation equation

\[
\tau (\delta a_{\mu \nu}/\delta t) - \xi_0 \Delta a_{\mu \nu} + \Phi_{\mu \nu} - F_{\mu \nu} = 0.
\]
Kilian and Hess\textsuperscript{11} have developed an algorithm for the numerical relaxation of a system which is discretized in space [step size $d_l$] and time [step size $\delta t = \gamma_l \delta t^2/(2dK)$]. The coordinates of the director after a time step $\delta t$ are given by\textsuperscript{11}

\begin{equation}
n^\text{new}_\mu = \lambda \{ n^\mu n_v + \mu_0 \chi_6 \delta t^2/(2dK) \} H_\mu H_v n_v.
\end{equation}

where brackets indicate averaging of the neighboring positions (at distance $d_l$), $n^\mu$ and $n_v$ are the initial director coordinates, $\gamma_l$ the rotational viscosity, $\chi_6$ the anisotropy of the magnetic susceptibility, $d$ the dimension of the system ($d = 3$), $K$ an effective elastic coefficient, and $H_\mu, H_v$ the components of an external magnetic field. Depending on the anchoring conditions at the pore wall, the director field may have a parallel (P), escaped radial (ER), or planar polar (PP) configuration.

\begin{figure}[ht]
\centering
\includegraphics[width=\linewidth]{figure1}
\caption{(a) Scanning electron microscope images (top and side view) of a 3D photonic crystal made of macroporous silicon with modulated pore radius. (b) Transmission spectra of the LC-filled photonic crystal in $\Gamma$–A direction. Solid line: pores filled with air. Dotted lines: spectra of pores filled with 5CB. The shift of the band edge by 144 nm towards larger wavelength is induced by an increase of the temperature from 24 to 40 $^\circ$C. (c) Polarization dependence. Measurements were made with a Bruker IFS 55 infrared spectrometer. The legends 0$^\circ$ and 90$^\circ$ represent the direction of the electric field.}
\end{figure}

\begin{figure}[ht]
\centering
\includegraphics[width=\linewidth]{figure2}
\caption{(a) Calculated director fields ($K = 10^{-11}$ N, $\gamma_l = 0.1$ Pa s, $H = 0$) and corresponding $^2$H-NMR spectra (in the lower-left corner of the respective diagram). P: uniaxial director field, parallel to the cylinder axis. PP: Planar polar director field. ER: escaped radial director field. Strong anchoring parallel (P and PP) or perpendicular to the Si surface (ER) was assumed, respectively. (b) $^2$H-NMR spectra. Solid line: experiment for $\alpha$-deuterated 5CB in macroporous silicon (pore radius $R = 1.0 \mu m = \text{const}$). Dashed line: calculated spectrum for a uniform parallel director field [type P in (a)]. Dotted line: calculated spectrum for an ER structure. In the latter case, the dependence of the polar angle $\theta$ of the director on the radial distance $r$ from the central axis of the cylinder is described by the function $\theta(r) = 1.294(v/r) - 0.288(v/r)^2$ which corresponds to the ER director field with weak anchoring described in Ref. 5.}
\end{figure}
configuration [Fig. 2(a)]. A very sensitive experimental tool to measure the orientational distribution is the quadrupolar splitting of the $^2$H-NMR signal

$$\Delta \nu = \frac{1}{2} \Delta \nu_0 (3 \cos^2 \vartheta - 1),$$

where $\vartheta$ is the angle between the local director and the magnetic field.\(^{12,13}\) The intensity distribution of the $^2$H-NMR signal indicates the orientational distribution $f(\vartheta)$, averaged over the sample volume. As model systems, we investigated hexagonal arrays of unmodulated pores with constant radii $R=0.45 \mu m$ and $R=1.00 \mu m$, respectively, to obtain qualitative results. Comparison between our NMR results and the calculated spectra [Fig. 2(b)] indicates a parallel alignment of the director along the pore axis.

For this uniform parallel alignment, the effective refractive index of the nematic component corresponds to the ordinary refractive index of 5CB. Thus, an increase of the temperature from $T<T_C$ to $T>T_C$ causes an increase of the average dielectric constant $\varepsilon_{av}$ of the heterogeneous structure, and thus a shift of the stop band towards larger wavelengths [Fig. 1(b)]. The value $\varepsilon_{av}$ can approximately be obtained from the Maxwell–Garnet relation\(^ {14}\)

$$\frac{(\varepsilon_{av} - \varepsilon_{Si})}{(\varepsilon_{av} + 2\varepsilon_{Si})} = \xi (\varepsilon_{LC} - \varepsilon_{Si}) (\varepsilon_{LC} + 2\varepsilon_{Si})^{-1},$$

where $\xi$ is the volume fraction of the LC ($\xi=0.423$ for a hexagonal array ($a=1.5 \mu m$) of cylindrical pores with a modulation of the pore radius $R$ between $R_{min}=0.38 \mu m$ and $R_{max}=0.63 \mu m$). For $\varepsilon_{Si}=(3.4)^2$, we expect that an increase of $\varepsilon_{LC}$ from $(1.5)^2$ to $(1.55)^2$ leads to an increase of the average refractive index and consequently the central wavelength of the stop band shifts by about 0.65%, as observed. The calculation of the dispersion relation using a plane wave approach\(^ {15}\) allows a more precise analysis (Fig. 3). The calculation confirms the considerable spectral shift of the “LC band,”\(^ {13}\) while the shift of the “silicon band” is negligible. The pore cross sections are squares with rounded edges. This symmetry breaking explains that the transmission of linearly polarized light depends on the plane of polarization.\(^9\) Our experimental result [Fig. 1(c)] is qualitatively confirmed by calculations for pores with a quadratic cross section of modulated width between 0.76 and 1.26 $\mu m$ (Table I, Fig. 3). Note that this polarization dependence appears even if the dielectric materials composing the photonic crystal are isotropic. The shift observed in the theoretical calculations is larger than in the experiment, because in the band structure calculation the pores were assumed to be perfect squares, so that the effect of symmetry breaking is more important than it is experimentally, and the volume fraction of the LC is slightly overestimated.

In summary, our results indicate that the liquid-crystal director in our silicon pores shows a uniform parallel alignment, and that the high-frequency band edge can be remarkably shifted by changing the temperature (1.23 meV) or the plane of polarization (1.61 meV). Both results are in good agreement with theoretical calculations. It is interesting to note that Leonard et al.\(^ {5}\) have reported results that can be explained by an escaped radial structure. Since the director configuration is very sensitive to the surface anchoring, it is very challenging to vary the surface properties systematically in forthcoming experiments. Due to computer simulations [Fig. 2(a)], we predict the appearance of a periodic array of defects in the ER director configuration for pores with modulated radius.

The authors would like to thank the Deutsche Forschungsgemeinschaft (Schwerpunktprogram 1113 “Photonic Crystals”) for financial support of the physical investigations and the National Science Foundation Science and Technology Center (ALCOM) DMR89-20147 for financial support of the synthesis effort at Kent State University.

### Table I: Experimental and theoretical values of the “LC band” edge for different polarizations of the incident IR radiation and different mesophases of the liquid crystal.

<table>
<thead>
<tr>
<th>Polarization</th>
<th>Phase</th>
<th>$\lambda^{-1}$ (Experiment) (cm$^{-1}$)</th>
<th>$\lambda^{-1}$ (Theory) (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0^\circ$</td>
<td>Nematic</td>
<td>894</td>
<td>932</td>
</tr>
<tr>
<td>$0^\circ$</td>
<td>Isotropic</td>
<td>885</td>
<td>918</td>
</tr>
<tr>
<td>$90^\circ$</td>
<td>Nematic</td>
<td>882</td>
<td>897</td>
</tr>
<tr>
<td>$90^\circ$</td>
<td>Isotropic</td>
<td>871</td>
<td>885</td>
</tr>
</tbody>
</table>

FIG. 3. Comparison of the calculated band structure (left) to the measured transmittances (right) dependent on temperature and polarization.

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