

Alignment of liquid crystal E7 in composite photonic crystals based on single crystal silicon

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ABSTRACT

The orientation of nematic liquid crystal (LC) E7 on the surface of (111) silicon wafers and in the channels of grooved silicon structure has been investigated. Grooved Si is a periodical structure obtained by wet anisotropic etching of deep and narrow grooves in (110) Si using an alkaline solution. This structure can serve as a one-dimensional (1D) photonic crystal. Composite structures obtained from grooved Si infiltrated by LC are promising candidates for electro-optic application. LC E7 was infiltrated into the channels of grooved Si and into the bulk Si cells. IR spectroscopy and capacitance-voltage characteristics under DC electric field were applied to investigate LC orientation. It is shown that the E7 liquid crystal in grooved silicon exhibits a weak planar orientation with respect to the silicon walls.

Keywords: 1D photonic crystals, silicon, liquid crystals, infrared spectroscopy.

1. INTRODUCTION

Silicon-based photonic bandgap (PBG) structures have received much attention in the research community as an established technology for fabricating high-performance optical elements¹⁻⁵. Fabricating the structures on a silicon substrate provides the advantage of easier integration with current semiconductor processing technology. It has been shown recently^{6,7} that a periodic array of silicon stripes and air spaces (so called grooved Si) fabricated by wet anisotropic etching on (110) oriented Si wafers can serve as a one-dimensional (1D) photonic crystal (PC). Depending on the lattice constant, A , grooved Si structures possess a main photonic bandgap in the region of $\sim 10\text{-}30\ \mu\text{m}$ and a number of secondary bandgaps extended to the near infrared range of the spectrum. Composite materials with optical properties different to the original matrix can be more easily obtained by infiltrating the grooves with liquid crystal. The optical properties of such composites can be tuned by altering the refractive index of the liquid crystal (LC) by any means. However the initial optical properties of the starting composite material will depend on the type and quality of LC alignment on the surface of Si walls which formed the stripes in a grooved Si structures. Despite the existence of the considerable number of papers on investigation of the crystalline surface influence on the alignment of various type of liquid crystals^{8,9}, there are little data on the influence of different crystallographic planes of crystalline Si on LC alignment.

The aim of this study was to analyze how the director of a nematic liquid crystal (LC) E7 is oriented on the (111) Si surface in the bulk LC cells and in the channels of grooved silicon matrix. The results were compared with data obtained recently¹⁰ on the orientation of liquid crystals in the pores of macroporous silicon matrix with a regular triangular lattice which served as two-dimensional photonic crystal (2D PC). The influence of the Si surface treatment of the alignment of liquid crystal E7 is also investigated.

2. EXPERIMENT

Each liquid-crystal cell was fabricated from two 1-mm-thick Czochralski-grown n-Si (111) wafers with resistivity of 30 Ohm-cm. The silicon windows for LC cell (sample C in Table 1) were treated by chemical etching of (111) Si wafer in a hot alkali solution, which simulated the process of anisotropic etching (see Refs.^{6,7} for details). To obtain a required thickness of LC cell Teflon spacers of thickness $d=5\ \mu\text{m}$ were used between (111) oriented Si windows. The cell was clamped and glued with an epoxy adhesive from two opposite sides. The cells and the periodic grooved structures were

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Table 1. Parameters of the samples studied.

Sample name	Type of structure	Surface pretreatment	Conditions of filling with LC	Orientation of the director with respect to the silicon walls	$N_o = D_0/D_{90}$ at 2220 cm^{-1}	Magnitude of the electro-optic effect as indicated by the dichroic ratio $N_V = D(0)/D(V)$
C	Bulk silicon cell	KOH solution $T=65^0\text{ }30\text{ min}$	$T=25^0\text{ }C$	Planar homogeneous	2.78	1.75 ($U=6V$)
J	Bulk silicon cell	3% PVA, , 4000-rpm centrifuge, annealing at $80^0\text{ }C$, 30 min.	$T=25^0\text{ }C$	Planar heterogeneous or isotropic	1	1.6 ($U=6V$)
Gr29A	Large-area grooved silicon $l=45\mu\text{m}$	Hydrophilization by RCA-clean +0,5% PVA, , annealing at $100^0\text{ }C$ for 30 min	$T=76^0\text{ }C$ + gradual cooling, removal of LC from the surface with another wafer	Isotropic or weakly planar	Enhancement of all bands at P perpendicular to the grooves	
Gr29B	Large-area grooved silicon $l=45\mu\text{m}$	Hydrophilization by RCA-clean, chromolan, annealing at $120^0\text{ }C$ for 60 min	$T=76^0\text{ }C$ + gradual cooling, removal of LC from the surface with another wafer, surface is poorly wettable	Isotropic or weakly planar	Enhancement of all bands at P perpendicular to the grooves	
Gr29D	Large-area grooved silicon $l=45\mu\text{m}$	Hydrophilization by RCA-clean	$T=90^0\text{ }C$ + removal of LC with a flow of compressed nitrogen	Isotropic or weakly planar	Enhancement of all bands at P perpendicular to the grooves	

filled with nematic LC by means of the capillary effect at different temperatures, T (see Table 1). The ordinary LC cells were filled at $T > T_c$ (where T_c is the transition temperature of LC from the nematic to the isotropic phase). The cells were then gradually cooled down to the room temperature in the course of three hours. A well-known liquid crystal mixture E7, which is based on cyanobiphenyls and possess a positive anisotropy of the dielectric constant, $\Delta\epsilon > 0$, and high anisotropy of the refractive index in the IR spectral range, $\Delta n = 0.20$ ^{11,12}, was used for our investigations. The basic characteristics of this mixture are listed in Table 2.

The alignment of rod-like LC molecules was determined from IR transmission spectra measured with light beam incidence perpendicular to the silicon windows for bulk cells or to the substrate of grooved silicon as shown in Fig. 1, configuration *a*. The spectra were recorded with a Digilab 6000 FTIR Fourier spectrometer or Specord-75 spectrophotometer. To study the photonic properties (photonic band gaps for instance) of grooved Si + LC composite structure the light beam was directed in parallel to the substrate plane, i.e., perpendicularly to the silicon walls as shown in Fig. 1, configuration *b*. In this case, the light beam was focused onto the Si walls of height $\sim 50\mu\text{m}$ with a UMA-500 IR microscope and the reflection/transmission spectra were recorded. The experimental procedure was described in more details in Refs.^{6,7}.

3. RESULTS AND DISCUSSION

3.1 Bulk cells

Figure 2 shows an optical transmission spectrum of the LC cell C, obtained for two mutually perpendicular polarizations of light. The spectrum clearly shows the absorption bands of a mixture of cyanobiphenyls published

previously in Ref.¹³. The band assignment and their orientation with respect to the long molecular axis are given in Table 3.

Table 2. Parameters of the liquid-crystal mixture E7¹².

Parameter	Designation of the parameter	Value of the parameter	Value of the parameter
Temperature of transition from nematic to isotropic phase	T_c	58°C	
Anisotropy of the dielectric constant (20°C, 1 kHz)	$\Delta\epsilon$ ϵ_{\parallel} ϵ_{\perp}	+13.8 19.0 5.2	
Optical anisotropy (20°C)	Δn $n_e(\parallel)$ $n_o(\perp)$	0.2253 1.7464 ($\lambda=589\text{ nm}$) 1.5211 ¹³	0.20 1.69 ($\lambda=10.6\ \mu\text{m}$) 1.49 ¹¹
Threshold voltage (20°C)	V_{10}	1.41 V	
Saturation voltage (20°C)	V_{90}	1.99 V	

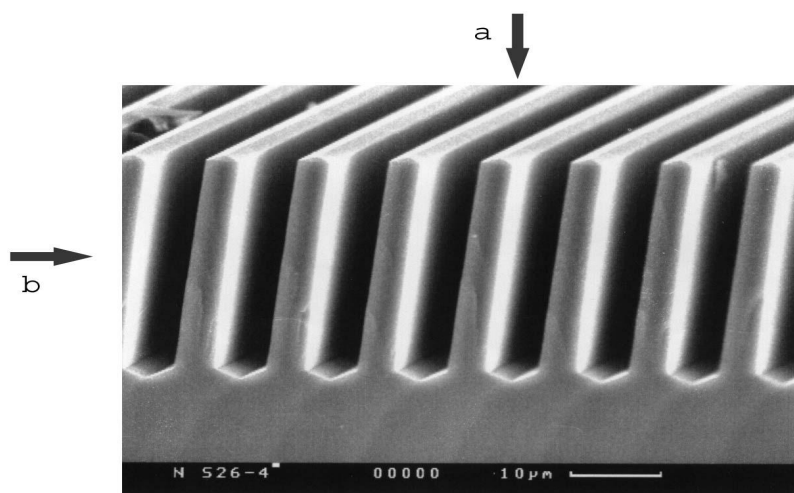


Figure 1: SEM image of grooved silicon sample. Arrows in configurations *a* and *b* show the direction of the incident light in the case of optical (LC alignment and birefringes) and photonic (band gap) properties measurements, respectively.

The magnitude of the absorption peak depends on the relative orientation of the LC director, *L*, and the polarization vector, *P*. It can be seen from the spectra shown in Fig. 2 that the magnitude of the absorption bands varies with the light polarization. This means that there exists a preferential orientation of the director in the plane of the silicon wafers. The degree of orientational ordering (called order parameter, *S*) in the Si windows plane can be estimated from the

absorption band at $\nu = 2220 \text{ cm}^{-1}$, which belongs to C-N stretching vibrations with transition dipole moment oriented parallel to the long axis of E7 molecules. The parameter S was found using the dichroic ratio $N = A_z/A_x = 2.78$, where A_z and A_x are the peak intensities of the chosen vibrational band for two mutually perpendicular directions of light polarization, P_z and P_x . The order parameter was found from N by using the following well known expression ¹⁴:

$$S = \frac{N - 1}{N + 2} = 0.373$$

The obtained value of S is significantly lower than that normally obtained for nematic LC ($S = 0.67$) contained between two windows coated with an orienting agent. The orientation of the LC director L can also be roughly estimated from the ratio of intensities of the absorption bands at 2220 and 817 cm^{-1} . The absorption of the former band is at a maximum at $L \parallel P$, and that for the later one is maximal at $L \perp P$ ¹³. When infrared measurements performed at oblique incidence of light, the information on the orientation of aforementioned bands in the plane perpendicular to the windows plane can be obtained ¹⁵. The normal and oblique IR measurements performed in this study for bulk LC cells allow us to conclude that the alignment of the LC director on the Si (111) surface treated with a hot alkali is a weak planar.

Table 3. Spectral positions of the absorption bands of E7 LC

N	ν, cm^{-1}	$\lambda, \mu\text{m}$	Type of vibration	orientation with respect to the long molecular axis
1	2960	3.38	(-C-H)	\perp
2	2920	3.42		\perp
3	2840	3.52		\perp
4	2220	4.50		\parallel
5	1600	6.25	$\nu(\text{C}\equiv\text{N})$	\parallel
6	1400	7.14	$\nu(\text{C}-\text{C})$	\parallel
7	1240	8.06	$\nu(\text{C}-\text{C})$	
8	1200	8.33	$\delta(\text{C}-\text{H})$	
9	1000	10.0		
10	817	12.24		\perp

A study of the Frederiks S-effect under applying a DC voltage, U , ranging from 0 to 6 V has been carried out by measuring the optical density of both vibrational bands, $\nu_1 = 2220 \text{ cm}^{-1}$ and $\nu_2 = 817 \text{ cm}^{-1}$ and the capacitance (at a frequency $f = 1 \text{ kHz}$) versus U . These investigations demonstrated that the reorientation of the director alignment from planar to homeotropic upon application of an electric field has been occurring. Furthermore, the effect of the aligning agent, which is commonly used in combination with mechanical rubbing of the window's surface for obtaining a homogeneous planar alignment of LC, was also investigated. Obviously, this type of the surface treatment is not applicable in the case of grooved silicon, and, therefore, other methods of surface treatment were used in this particular case. The coating of silicon wafers with 3% polyvinyl alcohol (cell J) resulted in heterogeneous planar alignment of LC, viz. the intensity of the absorption band at 2220 cm^{-1} was the same in both polarizations of light. The peak intensity of this band was decreased by only a factor of 1.6 on applying a rather high voltage to the bulk LC cell. Comparison with the magnitude of the electro-optic effect in cell C indicates that the using of polyvinyl alcohol as an orienting agent does not improve LC alignment, which was originally weakly homogeneous planar.

3.2 Grooved Si

Grooved silicon structures were obtained by means of wet anisotropic etching of Si (110) wafers with a resistivity of 5 Ohm cm. The structures and the procedures used for their fabrication are described in more details in ^{6,7}. Measurements in configuration a (Fig.1) were carried out on samples with a lattice period $A = 7 \mu\text{m}$. The vertical silicon walls of

thickness $D_{Si} = 2.3 \mu\text{m}$ alternate with air gaps of width $4.7 \mu\text{m}$. The groove depth is $l = 30\text{-}45 \mu\text{m}$ at a total thickness of the wafer equal to $200 \mu\text{m}$.

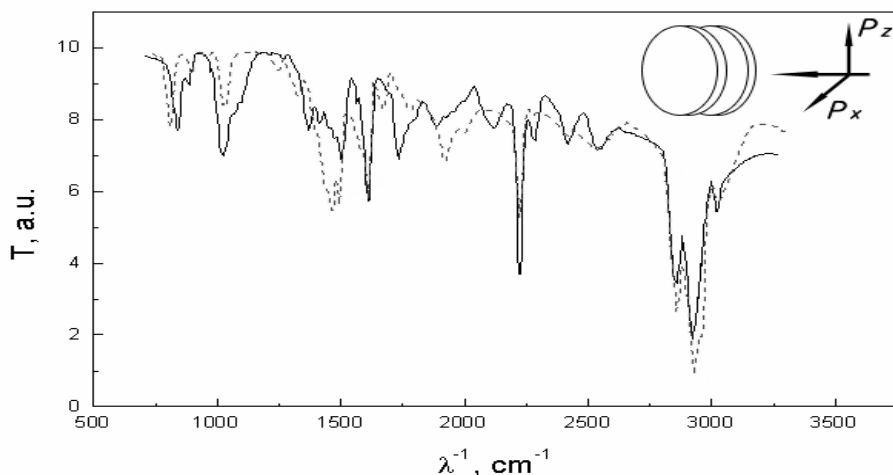


Figure 2: The transmission spectra of LC in silicon cell C at two mutually perpendicular polarizations of light P_x (solid line) and P_z (dashed line). The inset shows the experimental configuration: the horizontal arrow indicates the direction of light propagation, and the arrows P_x and P_z , the direction of optical polarization.

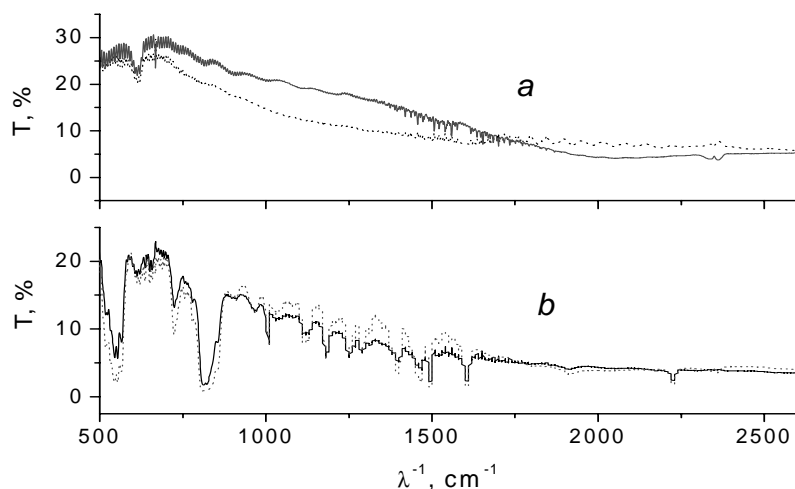


Figure 3: Transmission spectra of an empty (sample Gr29D, spectrum a) and infiltrated with LC E7 (spectrum b) matrix of grooved Si in two orthogonal polarizations of light: perpendicularly to the grooves (dashed line) and parallel to the grooves (solid line). Configuration “a” shown in Fig. 1 for the light incidence was used in this experiment.

Samples of grooved silicon were washed with a standard peroxide-ammonia solution (RCA-clean). Various orienting agents (orientants) were tested for creating a certain alignment of LC. These orientants were deposited onto the surface of the silicon walls in the grooved Si structure by (i) coating of the walls with a film of polyvinyl alcohol (PVA) with a subsequent annealing at $T = 100^\circ\text{C}$ or (ii) treatment of the grooved Si samples in a chromolan solution¹⁶. After the

surface treatment for each case the LC was deposited onto the surface following by sample being kept at room temperature for 10 min for capillary filling of grooves to occur. The excess amount of LC was removed from the surface by centrifugation or with a flow of compressed nitrogen. A study of the absorption spectra of samples treated with these orientants demonstrated that they do not exert any noticeable influence on the height of the absorption peaks associated with the LC.

Figure 3a shows polarized transmission spectra of grooved Si before (Fig. 3a) and after the LC infiltration (Fig. 3b). A characteristic feature of the obtained spectra is the very low transmittance at short wavelengths and an increase in transmittance at wavelengths λ comparable with the lattice period, A , of the structure. A similar behaviour is observed in infrared spectra of macroporous silicon (*maSi*). Note that the starting silicon wafer from which the grooved Si samples were fabricated is transparent in this spectral range. Therefore, the low optical transmission of grooved and macroporous silicon at short-wavelengths is presumably due to a strong scattering on silicon walls¹⁷. Although the calculations in¹⁷ were performed for another shape of scattering particles, their results are qualitatively applicable to the Si matrices under consideration. If the wavelength exceeds the size of scattering particles (grooves or pores), the intensity of the light scattering decreases and the transparency increases.

The transmission spectra of the samples infiltrated with LC show all the absorption bands characteristic for E7 (Fig. 3b). It can be seen from Fig. 3b that the intensities of all these bands are somewhat higher for light polarized perpendicularly to the grooves, although the heights of peaks must vary in antiphase for vibrations occurring along and across the long axis of the molecule. In the other words, a rise in the height of the peak at $\nu_1 = 2220 \text{ cm}^{-1}$ must be accompanied by a decrease in the intensity of the peak at $\nu_2 = 817 \text{ cm}^{-1}$ and vice versa. Therefore, a comparison of the absorption spectra of LC in grooved silicon for two orthogonal polarizations of light gives no way of making a conclusion as to whether the alignment of LC molecules with respect to the silicon walls is planar or homeotropic. If the relative heights of the peaks at ν_1 and ν_2 in the grooved and macroporous matrices are compared with their heights in the bulk-type cell, it can be seen that all the short-wavelength absorption peaks of LC are weakened. The intensity of the ν_1 band is nearly an order of magnitude lower than that of the ν_2 band, whereas their ratio in the cell is less than two. This effect was first observed in a study of the behaviour of other LCs (discotics and ferroelectrics) in macroporous silicon with a period $A = 12 \mu\text{m}$ ¹⁰ and was interpreted as being due to an increase in the absorption coefficient for long-wavelength bands. The absorption coefficients of the LC E7 for the bulk cell and for the several samples of grooved and macroporous silicon were calculated with their porosity taken into account. The results obtained are summarised in Table 4. It can be seen from the table that the absorption coefficient for the short-wavelength peak ν_1 is always substantially lower than that for the bulk cell, but for the long-wavelength peak ν_2 , this difference is not so pronounced. Therefore we can conclude that the periodic matrix suppresses the intensity of short-wavelength peaks, rather than enhances the intensity of the long-wavelength peaks.

Qualitatively, this can be attributed to the waveguide effect, for which a decrease in wavelength to the value smaller than the structure period, A , leads to a displacement of light into a region with a high dielectric constant (silicon walls of the grooved matrix or regions between pores in macroporous silicon)¹⁸. This is equivalent to a decrease in the intensity of light transmitted through the LC. The redistribution of the light flux is manifested as a decrease in the absorption of the LC.

The IR reflection spectra of grooved silicon were measured in configuration *b* on samples with seven silicon walls separated by grooves. No orientants were used for these samples. Figure 4 shows a reflection spectrum of a sample of grooved silicon with a period $A = 4 \mu\text{m}$ and thickness of silicon wall $D_{\text{Si}} = 2.3 \mu\text{m}$ infiltrated with LC.

High-reflectance regions in the reflection spectrum correspond to the photonic band gaps of this 1D PC. When the grooves are filled with LC, the photonic band gaps are shifted to longer wavelengths and become narrower, which is due to a decrease in the refractive index contrast. For illumination with H-polarized light (parallel to the z -axis in the inset), the band at around $\lambda \approx 9 \mu\text{m}$ is shifted to longer wavelengths, compared with the case of E-polarization (parallel to the x axis in the inset). The experimental reflection spectra were compared with those calculated by the characteristic matrix method described in¹⁹. The best agreement between the experimental and calculated spectra was achieved at $n_{\text{LC}} = 1.52$ and $1.67 (\pm 0.01)$ for the E- and H-polarizations, respectively. As the higher refractive index corresponds to a

polarization of light in parallel to the optical axis, it can be stated that the LC director is oriented in the samples studied along the z-axis, i.e. planar alignment with respect to the silicon walls and homeotropic alignment with respect to the bottom of the grooves.

Table 4. Absorption coefficients of E7 LC at 817 and 2220 cm^{-1} in bulk cell, in grooved Si (GrSi) and in macro-porous Si maSi matrixes.

Type of structure	Sample no.	Absorption coefficient at $\nu_2=817\text{cm}^{-1}$, cm^{-1}	Absorption coefficient At $\nu_1=2220\text{cm}^{-1}$, cm^{-1}
Bulk cell	C	10^3	$1.4 \cdot 10^3$
GrSi*	De29(7)A	$6 \cdot 10^2$	$2 \cdot 10^2$
GrSi	De29(7) B	$7.6 \cdot 10^2$	$1.8 \cdot 10^2$
GrSi	De29(7) C	$5.3 \cdot 10^2$	$3.2 \cdot 10^2$
GrSi	De29(7)D	$6.2 \cdot 10^2$	$1.3 \cdot 10^2$
GrSi	grSi 10	$9.3 \cdot 10^2$	$2.5 \cdot 10^2$
maSi	2J12N	$2.62 \cdot 10^2$	9
maSi	2M28N2	$1 \cdot 10^2$	15
maSi	2A12N14	89	4

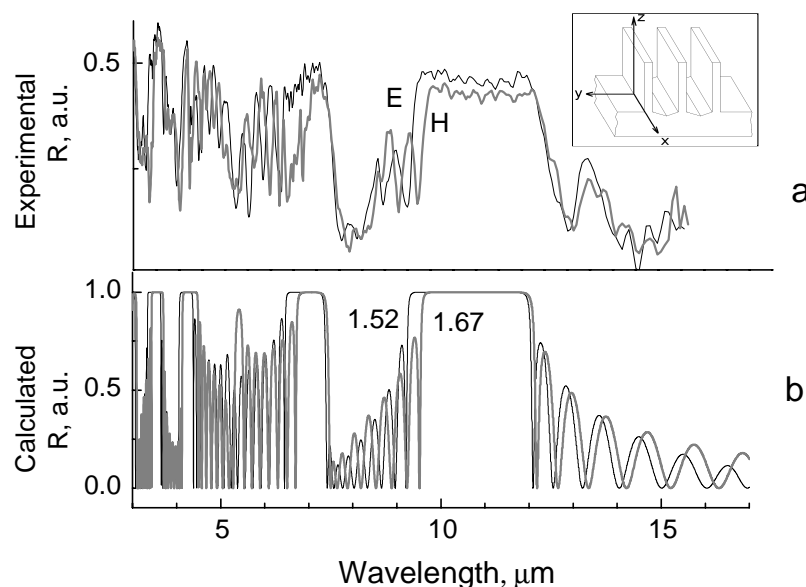


Figure 4: a) Experimental and b) calculated reflection spectra of grooved silicon infiltrated with LC E7 obtained at different polarization of light, E and H. The schematic of different polarization orientation with respect to the grooves is shown in insert. The numbers in b) correspond to the values of the refractive index used for calculations. Configuration “b” shown in Fig. 1 for the light incidence was used in this experiment.

It should be noted that, for part of samples (~50%), no difference was observed between the spectra measured for the light polarized in two mutually perpendicular directions (E- and H-polarization). The shift of the band gaps after filling of a sample with LC, obtained by comparing the experimental and calculated spectra, corresponded to an average refractive index $n_{LC} = 1.6 \pm 0.02$. Apparently, the orientation of LC molecules with respect to the silicon walls was isotropic in these samples.

4. CONCLUSION

Based on the results obtained for bulk liquid crystal cells it was established that the adhesion of E7 liquid crystal molecules to (111) Si plane, obtained by etching in a hot alkali, is weak. As a result, nematic liquid crystal in composite photonic crystals based on grooved silicon have a weakly pronounced planar alignment with respect to the silicon walls, and this alignment cannot be improved with the orienting agents used in this study.

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