EFFECT OF SURFACE ALIGNMENT LAYER ON ELECTRO-OPTICAL PROPERTIES OF FERROELECTRIC LIQUID CRYSTAL DISPLAYS

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Chapter 1
Introduction and background

1.1 Liquid crystalline materials

Nowadays, almost everybody has heard the words ‘Liquid Crystal’, mostly in the context of the ‘Liquid Crystal Display’. Although it has been 120 years since Austrian botanical physiologist Dr. Friedrich Reinizer discovered the liquid crystalline phase\(^1\) and, soon after that, the term ‘liquid crystal’ was introduced by Otto Lehnman\(^2\), liquid crystals have received particularly close attention since liquid crystal displays were invented in the 1960s. Since that time, a huge amount of research and engineer work has been done, which eventually led to the current situation in the world display market: at this time (2008), the vast majority of devices with a display uses liquid crystal technology.

Liquid crystals are substances that exhibit a phase of matter (usually called mesophase) that has properties between those of a conventional liquid (e.g., it flows), and those of a solid crystal (e.g., it exhibits optical anisotropy). In simplest liquid crystalline phases, there is no long-distance positional ordering of the molecules, but instead there is long-distance orientational ordering. There are two basic types of liquid crystalline phases with the regard to the conditions required for their occurring. *Thermotropic* liquid crystals have mesophase in certain temperature range, while *lyotropic* liquid crystal consists of two or more components that exhibit liquid-crystalline properties in certain concentration ranges. In this work, we only consider thermotropic liquid crystals.
Thermotropic liquid crystals consist of molecules that have anisotropic shape. Usually they are rod-like (calamitic liquid crystals) or disc-like (discotic liquid crystals), although some other more exotic molecular shapes have been discovered to create liquid crystalline phases, such as, for example, banana-shaped (bent-core) liquid crystals.

There are many liquid crystalline phases, from which the most widely used are nematic and smectic phases (Figure 1.1). Nematic liquid crystals are used in the vast majority of all liquid crystal display devices that are currently present at the market. In nematics, all molecules tend to align directed along one selected direction that is called director, \( \vec{n} \).

Smectic phases consist of layers of molecules. In smectic A, molecules are aligned perpendicular to the boundaries between layers; in smectic C molecules are tilted with respect to the layer normal.

### 1.2 Overview of liquid crystal displays

The vast majority of applications of liquid crystals are Liquid Crystal Displays (LCD). In these devices, thin layers of liquid crystals are usually sandwiched between two glass plates with transparent electrodes. The work of the display is based on the electro-optical response of the liquid crystal, when its molecules reorient under the action of the electric field and change optical properties (e.g., transmission or reflectance) of the device.
Figure 1.1. Liquid crystalline phases: (a) nematic; (b) smectic A; (c) smectic C
Besides liquid crystals, LCDs also consist of various optical elements, such as polarizers, retardation films, color filters, etc. Specific design of the display device including distribution of liquid crystal director inside the cell and design of the optical elements depends on the type of the display and required characteristics of the device.

There exist various types of Liquid Crystal Displays. Two main types of LCDs are defined by the type of driving of the device (switching of display’s pixels): passive-matrix displays and active-matrix displays.

In passive-matrix displays pixels are addressed one at a time by row and column addresses. It is called ‘passive matrix’ because the pixel must retain its state between refreshes without the benefit of a steady electrical charge. As the number of pixels (and, correspondingly, columns and rows) increases, this type of display becomes less feasible. This type of displays usually utilizes the STN (super-twisted nematic) mode.

Active-matrix displays usually contains, besides liquid crystal and polarizers, a matrix of thin-film transistor (TFT). These devices store the electrical state of each pixel on the display while all the other pixels are being updated. This method provides a much brighter, sharper display than a passive matrix of the same size. Most common LC modes used in active-matrix displays are Twisted Nematic (TN), Electrically-controlled Birefringence (ECB), In-plane Switching (IPS), Vertical Alignment (VA), etc.

LCDs are characterized by few parameters, among which probably the most important ones are response time and contrast ratio. Response time is the time needed to switch LCD pixel from the dark state to the bright state. Contrast ratio is the ratio of light
intensities of the dark and the bright states. These characteristics of the display play the most important roles in the quality of the output image.

Also, LCDs can work in either transmissive, reflective or transflective (combination of the first two) modes. Choice of the particular mode is dictated mostly by the application of the display device. While direct-view LCD TVs, laptop screens, etc. work in a transmissive mode, wrist watches and Rear-Projection LCD TVs are reflective. In particular, LCOS (Liquid Crystal on Silicon) devices are widely utilized in a "micro-projection" or "micro-display" technologies used in Rear-Projection TVs. In LCOS devices, liquid crystals are applied directly to the surface of a silicon chip coated with an aluminized layer, with some type of reflective passivation layer. Finally, devices intended for outdoor and indoor use are typically designed to work in both modes (transflective displays).

There is separate class of displays (not limited to LCDs) that are bistable. It means that these devices have two states (dark and bright) which do not require energy to be kept in its state. Such devices are perfect low power consumption solutions for applications that do not need frequent refresh of an image, such as electronic books. Moreover, bistable displays utilize passive matrix and therefore they are easy and cheap to produce.

At another side of the wide display devices spectra, there are analog displays (also called V-shaped devices due to the shape of their electro-optical response) with
grey-scale capability within single pixel. In these devices, one can gradually change each pixel transmission from dark to bright.

At this time, most of all above-mentioned LCD devices use nematic liquid crystals. However, there are displays that are based on cholesteric, smectic and other liquid crystalline phases. In this dissertation we focus on devices that utilize chiral smectic C liquid crystals (SmC*), both analog and bistable.

### 1.3 Surface alignment of liquid crystals

In order to utilize electro-optical properties of liquid crystals, it is usually needed to align liquid crystal, e.g. to obtain homogeneous samples of the liquid crystal, so that the director is points along one chosen direction in the whole sample. Typically liquid crystals are aligned by the surfaces inside the cell by surface alignment layers. These surfaces are characterized by anisotropic interaction with the liquid crystal molecules. Such interaction is characterized by an ‘easy axis’, which corresponds to the distribution of the director on the surface with the minimal elastic energy.

Traditionally liquid crystal alignment if achieved by unidirectional mechanical rubbing of thin polyimide films deposited on the electrode surfaces. Depending on the type of polyimide, liquid crystal and parameters of rubbing, it is possible to obtain various types of alignment: planar (director lies in the plane of the cell), homeotropic (director is perpendicular to the cell’s surface) and tilted alignment. This method is widely used in the manufacturing process of LCDs.
However, along with advantages (ease of process, good alignment quality, low cost), rubbing is a mechanical contact process, which produces a lot of particles and causes defects on the polymer surface. There exist other methods of alignment which do not require rubbing, such as photo-alignment\(^3\) (where photosensitive polymer deposited on the substrates is illuminated by the polarized UV-light) and alignment by obliquely evaporated inorganic materials, such as silicon oxide (SiO\(_x\)), first demonstrated by John Janning in 1971\(^4\). More details of alignment of liquid crystal by obliquely evaporated SiO\(_x\) are discussed in Chapter 3.

Besides non-contact process and other advantages, it was found that these non-conventional alignment methods are actually preferable for some applications. In particular, photo-alignment technique is very promising for very large displays used in LCD manufacturing (for 6\(^{th}\) generation matrices it is already pretty difficult to obtain uniform alignment by rubbing). On the other hand, it is extremely hard to align miniature devices, such as waveguides, by rubbing, so here photo-alignment might be the only possible way to align liquid crystal in such devices. Also, if complicated director distributions are required, e.g. for optical processing devices, photo-alignment is arguably the most convenient and reliable way to achieve these goals as well.

Obliquely evaporated inorganic materials, such as SiO\(_x\) provide high pretilt angle and are excellent alignment layers for bistable chiral smectic C (SmC\(^*\)) devices (see chapter 1.4). A large part of this dissertation is dedicated to the effect of the deposition parameters of SiO\(_x\) on the electro-optical characteristics of such devices.
1.4 Ferroelectric liquid crystal displays

Ferroelectricity is a physical property of a material which exhibits a spontaneous electric polarization, the direction of which can be switched between equivalent states by the application of an external electric field. Ferroelectric phenomenon was first discovered in the solid state (Rochelle salt) in 1920 by J. Valasek. The experimental evidence for this domain switching is a hysteresis loop (Figure 1.2).

In 1975, Robert Meyer has shown that specially constructed chirally asymmetric molecules can form chiral Smectic C structure with macroscopic permanent dipole moment, \( P_s \), directed perpendicularly to \( \vec{n} \). However, chirality of the molecules also makes them form helical structure. Figure 1.3a shows how within one pitch \( (P) \) of the helix, \( P_s \) rotates by 180°, adding all \( P_s \) vectors to be equal to zero.

In 1980, Clark and Lagerwall proposed to use ferroelectric liquid crystal in the geometry that suppresses the helix (Figure 1.4). They demonstrated that if the cell gap is smaller than the helical pitch of the material (typical cell gap is \( \sim 1-2 \mu m \)), the helix gets suppressed. Such structure was named Surface-Stabilized Ferroelectric Liquid Crystal (SSFLC). A new kind of bistable display device was proposed based on this effect. In this device, ferroelectric liquid crystal is filled in the cell with alignment layers that constrain the director to lie in the plane of the surface, making smectic layers perpendicular to the cell’s substrates (bookshelf geometry). For this geometry, two stable homogeneously aligned domains with opposite ferroelectric polarization coexist in the cell. Projections of the liquid crystal director on the plane of the cell in these two domains are at the angle of
approximately \(2\theta_c\) with respect to each other (\(\theta_c\) is the cone angle of the FLC, as shown in Figure 1.3b). If \(2\theta_c\) is close to 45°, then optically between crossed polarizers these two domains will correspond to the dark and the bright states of the device, as shown in Figure 1.4c. By applying positive or negative DC electric pulse, one can switch between states due to the polar coupling between electric field and ferroelectric polarization of the liquid crystal. Figure 1.4 demonstrates work of the SSFLC display device.

Soon after the initial discovery of the SSFLC devices, Reiker and Clark demonstrated that in most SSFLC devices due to the layer shrinkage occurring near the SmA-SmC* phase transition, chevron or tilted structures are formed instead of bookshelf (Figure 1.5). Chevron structures are most widely used and are discussed in more detail in Chapter 3.

Among advantages of the SSFLC devices are fast switching time (~100µs, which allows usage of time sequential grayscales), relatively low driving voltage due to coupling between ferroelectric polarization and electric field, and good viewing angle and contrast ratio characteristics due to in-plane switching. One of the issues for wide manufacturing and application of SmC* SSFLC displays is alignment of the smectic phase. It was shown before\(^9,28\) that thin layers of obliquely evaporated silicon oxide (SiO\(_x\)) work great due to high pretilt (elimination of zigzag defects which occur if two types of chevron are present; high pretilt eliminates one of them), non-contact deposition method (possibility to achieve defect-free alignment) and excellent bistability.
Figure 1.2. Hysteresis of polarization in ferroelectric materials
Figure 1.3. (a) Helical layer structure of a SmC* liquid crystal; vector $P_s$ is rotated by $180^\circ$ over the helical pitch; (b) molecule inside a cone structure. $P_s$ is normal to the director $\vec{n}$ and tangential to the circle of the cone, $\vec{c}$ -director is pointing from center of the circle to the $\vec{n}$ -director.
Figure 1.4. Bookshelf geometry of a SSFLC device and its switching; (a) dark state; (b) bright state; (c) liquid crystal texture showing domains of the opposite polarizations.
Switching of SSFLC devices is characterized by some threshold voltage, below which the device is not switching between its states. On the contrary, so-called V-shaped or analog, or threshold-less display devices are not bistable. In 1995 Fukuda et al\textsuperscript{10} and later Inui et al\textsuperscript{11} have discovered that for some SmC* liquid crystal, the electro-optic response to the triangular waveform was a symmetric, linear and threshold-less. The name “V-shape switching” came from the form of the electro-optical response resembling the letter “V” (Figure 1.6). This effect attracted a lot of attention because of possibility to use it in truly analog display devices with intrinsic grayscale capability together with high speed, low operating voltages and great viewing angle characteristics. There are several modes of V-shaped switching, but in this dissertation we will focus on ‘electrostatic model’, introduced by Clark et al\textsuperscript{12,77}. In this model, materials with very high spontaneous polarization (>100 nC/cm\textsuperscript{2}) are ‘stiffened’, i.e. the FLC’s director structure becomes spatially uniform and maintains its arrangement while switching. Surface anchoring energies are comparable to the distortion energy of the bulk director configuration and affect switching behavior of the FLC.

As in the case of bistable SSFLC, performance of the V-shaped device depends on the surface alignment layers. In Chapter 5 the effect of the surface alignment layer on electro-optical response is discussed.
Figure 1.5. Layer structures of the SSFLC device: (a) bookshelf; (b) chevron; (c) tilted;
Figure 1.6. Example of V-shaped electro-optical response to the triangular waveform
1.5 Focus of this dissertation

Here I present brief chapter-by-chapter overview of the work presented in this dissertation.

In Chapter 2 I describe implementation of the computer program that simulates dynamics of the SSFLC cell switching. It is later used to explain experimental results of bistable and analog switching of SSFLC cells, which are discussed in Chapters 3 and 5.

In Chapter 3 I focus on optimizing the surface alignment layer for bistable SSFLC displays to achieve low voltage threshold. SiO$_x$ is used as the alignment layer, and its properties and effect of its deposition parameters on the electro-optical response of the SSFLC device are studied. The question being answered is what properties of the surface define bistability and threshold voltage of the SSFLC device. Besides experimental studies, I present results of the simulation that models switching of the SSFLC device depending on the properties of the cell’s surfaces.

In Chapter 4 I report on the experimental technique of obtaining aligned samples of high-polarization SmC* materials that have I-SmA-SmC* phase sequence and are designed for V-shaped display devices.

In Chapter 5 I report on the study of the effect of surface alignment layer on the analog V-shaped switching of the I-SmA-SmC* materials that were aligned using the technique described in Chapter 4. From experimental results and with the help of computer simulation I explain the effect of surface aligning layer properties such as
dielectric capacitance, anchoring energy, pretilt, easy axis gliding and surface melting of
the smectic phase, on the V-shaped electro-optical response of the cell.

Finally, in Chapter 6 I summarize my dissertation and formulate the conclusions.

In Appendix I discuss my work on characterizing of the surface memory effect in
the nematic liquid crystal cells. This effect occurs due to adsorption/desorption processes
of the liquid crystal molecules on the surface. The same effects are responsible for so-
called ‘gliding’ of the easy axis (preferable director orientation on the surface) and may
play a role in the switching of SSFLC devices.
Chapter 2

Computer simulation of SSFLC cell electro-optical response

2.1 Motivation and description of the method

Electro-optical response of SSFLCs is a complicated function of many parameters, such as elastic and electric properties of the FLC, pretilt, surface anchoring energy (polar and non-polar), capacitance of alignment layers, frequency of driving waveforms, etc. Depending on its features, SSFLC can work in bistable modes characterized by steep threshold or in analog threshold-less hysteresis-free mode. In this dissertation, I study effects of surface alignment layer on the work of both kinds of SSFLC devices. To explain experimental results and to better understand effect of the alignment layer, I wrote a computer program that simulates switching of the SSFLC cell taking into account parameters of the FLC and the surface.

In this chapter I describe a method for the numerical simulation of the dynamics of the electro-optical switching of the ferroelectric liquid crystals. In the following chapters I demonstrate application of this program to the studied SSFLC cells.

The computer program that I wrote utilizes numerical method developed by Sergei Palto\textsuperscript{13,14}. This method is based on the relaxation of the smectic director to the lowest energy state by numerically solving dynamic equations for the director coupled with the electric current equations. It can be used for other liquid crystalline phases as
well by modifying formulation of the elastic free energy of the phase. It is discussed in
details in reference [14]. Although Palto’s approach of the FLC description is not the
only one, I have chosen it because of the possibility to relatively easy apply numerical
methods for the calculations. My implementation included some simplifications along
with the inclusion of the effects that were not considered in the original method, which I
discuss below.

The dynamics of the electro-optical switching of FLC cells depends on many
parameters, including electric field, bulk elastic, viscous and electric properties, surface
anchoring conditions, properties of aligning layers, etc. A surface stabilized FLC cell is
considered with the aligning surfaces located in the XY-plane. Smectic layers with a
fixed layer normal \( \mathbf{k} = (k_x, k_y, k_z) \) form an arbitrary angle with the XY-plane, the
molecules are tilted at angle \( \Theta \) (cone angle) with respect to the smectic normal \( \mathbf{k} \). FLC
molecules at the surfaces are defined by the surface boundaries conditions with variable
zenithal and azimuthal anchoring energies. Aligning layers have finite capacitance, which
plays an important role in the electro-optical switching. Euler-Lagrange equations for the
FLC bulk are considered in the absence of flow. They include the elastic, electric and
viscous torques.

**Elastic energy**: the elastic energy is taken in the form

\[
F_1 = \frac{1}{2} \left( K_{11} (\nabla \cdot \mathbf{n})^2 + K_{22} (\mathbf{n} \cdot \text{curl} \mathbf{n} + q_0)^2 + K_{33} (\mathbf{n} \times \text{curl} \mathbf{n} - \mathbf{b})^2 + K_4 (\cos \Theta - \mathbf{n} \cdot \mathbf{k})^2 \right)
\]  

(1)
where \( K_{ii} \) are Frank elastic constants, \( K_4 \) describes compressibility of smectic layers related to a change in the cone angle \( \Theta \) (it is frequently denoted as \( B \) and has typical values of \( \approx 10^6 \div 10^7 \, N / m^2 \)) \(^{15} \), \( q_0 \) and \( \vec{b} = \beta \vec{k} \times \vec{n} \) describe correspondingly spontaneous twist and bend of the director \( \vec{n} \).

**Electric energy:** If the charge is fixed at the boundaries of a FLC, the electric contribution to the free energy density is positive \( F_2 = \vec{D}_i \vec{E}/2 \). Here \( \vec{D}_i \) is a field-induced contribution to the total displacement \( \vec{D} = \vec{D}_0 + \vec{D}_i = \vec{P}_z + \vec{E} \), \( \varepsilon \) is the dielectric permittivity tensor which, for a uniaxial medium, defines dielectric anisotropy \( \Delta \varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} \), \( \vec{P}_z \) is spontaneous polarization. For \( \vec{E} = (0,0,E_z) \), \( \vec{D}_i = (D_{ix},D_{iy},D_{iz}) \) and \( d \) the cell gap, one obtains the for electric free energy density and voltage on the FLC:

\[
F_2 = \frac{D_{iz}E_z}{2} = \frac{(D_{iz} - P_{z\parallel})^2}{2\varepsilon_{\perp} \left( 1 + \frac{\Delta \varepsilon}{\varepsilon_{\perp} n_z^2} \right)} \quad \text{and} \quad U_{LC} = \int_0^d D_{iz} - P_{z\parallel} \quad d_iz,
\]

where \( P_{z\parallel} = P_0 \left[ (k \cdot n)(k \times n) \right]_z \), \( P_0 = P_z / \cos \Theta \sin \Theta \).

**Surface anchoring energy:** the surface anchoring is determined by the balance of two torques—the elastic torque of a FLC and the surface torque due to anchoring, by the equation of the torque balance:

\[
\pm \frac{\partial F}{\partial \vec{n}} - \frac{\partial W}{\partial \vec{n}} = 0,
\]
where the sign depends on the surface (z=0 or z=d).

The surface anchoring energy is written in the Papoular-Rapini\textsuperscript{16} form, which in the problem’s geometry becomes

\[
W = \frac{1}{2} W_a \left( n_z \sin \varphi - n_y \cos \varphi \right)^2 + \frac{1}{2} W_z \left( n_z \sin \theta - n_x \cos \varphi \cos \theta - n_y \sin \varphi \cos \theta \right)^2,
\]

where \( W_a \) and \( W_z \) are azimuthal and zenithal anchoring energy coefficients, \( \theta \) and \( \varphi \) are angles that define easy axis at the surfaces (correspondingly zenithal and azimuthal).

**Viscous torque:** as the mass transfer is disregarded, only the second rank rotational viscosity tensor is considered. In the local system corresponding to the SmC* symmetry the tensor \( \gamma \) has three different principal components \( \gamma_1, \gamma_2 \) and \( \gamma_3 \). Component \( \gamma_2 \) determines friction along the director normal to the plane of vectors \( \vec{k} \) and \( \vec{n} \), and usually determines the viscosity for director motion over the cone. \( \gamma_1 \) and \( \gamma_3 \) correspond to the so-called ‘soft mode’ of the director motion, usually denoted as \( \gamma_\theta \). After applying the similarity transformation \( \gamma = R \gamma \gamma R^{-1} \), where \( R \) is the rotation matrix, one can find the viscosity tensor in the laboratory frame and the corresponding viscous torque.

**Taking into account elements of the electric circuit:** the considered equivalent circuit is shown in Figure 2.1. Two aligning layers can be treated as one capacitor \( C \) and
resistor $R$ connected in parallel. The resistance of electrodes $R_0$ is in series with the output resistance of the voltage source. For the current and voltages in the circuit one can get:

$$\frac{dU_C}{dt} + \frac{1}{C} \left( \frac{1}{R} + \frac{1}{R_0} \right) U_C = \frac{1}{CR_0} (U - U_{LC})$$

$$\frac{U_{LC}}{R_{LC}} + A \frac{dD_z}{dt} = I,$$  \hspace{1cm} (5)

$$U_{LC} = U - IR_0 - U_C$$

Here $A$ is the electrode overlapping area; $U_C$ and $U_{LC}$ are voltages across the electrodes, aligning layers and FLC; $I$ is the current from the source; $D_z$ is the $z$-component of the electric displacement in a FLC with constant ohmic resistance $R_{LC}$.

The last system of equations together with the boundary conditions and general vector-form expression for the balance of elastic, electric and viscous torques

$$\gamma \dot{n} = -\frac{\partial \tilde{F}}{\partial \tilde{n}} + \frac{d}{dz} \frac{\partial \tilde{F}}{\partial \tilde{n}} + \lambda \dot{n},$$

$$\tilde{F} = \tilde{F}_1 + \tilde{F}_2,$$  \hspace{1cm} (6)

where $\lambda$ is Lagrange multiplier (introduced for satisfying condition $n^2_x + n^2_y + n^2_z = 1$) presents the full set of equations which allows the calculations of time and spatial dependencies of the director components at any voltage.
Figure 2.1. Equivalent electric scheme of a LC cell (from [14])
2.2 Modifications and numerical implementation

For the sake of simplicity, some assumptions were done to simplify general Palto’s model\textsuperscript{14}.

- Normal to the smectic layers is along $x$-direction: $k = (1,0,0)$
- One Frank elastic constant approximation: $K_{11} = K_{22} = K_{33} = K$
- $q_0 = 0$ (inverse pitch), $b = 0$ (modulus of spontaneous bend)

- Isotropic viscosity tensor: $\gamma_L = \begin{pmatrix} \gamma & 0 & 0 \\ 0 & \gamma & 0 \\ 0 & 0 & \gamma \end{pmatrix}$ (components of the viscosity can be reduced to the rotational viscosity of the director motion on the cone, if we consider small compressibility of the smectic layers; in this case, director is effectively confined to the motion on the cone only).
- Zero dielectric anisotropy: $\Delta \varepsilon = \varepsilon_\parallel - \varepsilon_\perp = 0$
- Resistance of the capacitor $R$ is infinite; the series resistance of the ITO electrodes $R_0$ is zero.

The equation of the torque balance is written in the terms of the torques components:
Taking into account simplifications, expressions for torques components are written down as following (primes correspond to the spatial derivatives of the director with respect to the $z$-axis):

\[ M_{1x} = K(n_x n_x'^2 + n_x''') + 4n_x' n_y' n_y - n_x n_y'^2 \]  
\[ M_{1y} = K(-n_y n_y'^2 + 2n_x n_x' n_y' + n_y n_y'^2 + n_y'' + 2n_z n_y'^2 n_z'^2) \]  
\[ M_{1z} = K(-n_z n_z'^2 + n_z'^2 n_x'^2 + n_z'') \]

\[ M_{2x} = \frac{D_z n_y P_0}{\varepsilon_\perp}, \quad M_{2y} = \frac{D_z n_x P_0}{\varepsilon_\perp}, \quad M_{2z} = 0, \]

where \( D_y(z) = D_z - P_0 n_x n_y \), and \( D_z = \frac{\int_0^d \varepsilon_\perp U_{LC} + P_0 n_x n_y \, dz}{d} \).
Surface boundary conditions on two cell substrates \((z=0, d)\) are defined by the derivatives of the director on the surfaces (here condition for the FLC director \(n_x^2 + n_y^2 + n_z^2 = 1\) is taken into account):

\[
\begin{align*}
\frac{\partial n_x}{\partial z} \bigg|_{z=0,d} &\equiv G_x = n_x \frac{W_z \cos^2 \theta_a}{K} - n_z \frac{W_z \cos \theta_a \sin \theta_a}{K} \\
\frac{\partial n_y}{\partial z} \bigg|_{z=0,d} &\equiv G_y = -n_x \frac{W_a \sin \theta_a}{K} + n_y \frac{W_a}{K} \\
\frac{\partial n_z}{\partial z} \bigg|_{z=0,d} &\equiv G_z = -n_x \frac{W_z \cos \theta_a \sin \theta_a}{K} + n_z \frac{W_a \sin^2 \theta_a}{K}
\end{align*}
\]

(10)

**Capacitance of the alignment layers:** if we ignore conductivity of the FLC material (which is good approximation unless we study specific dynamic effects, which are discussed in Chapter 5), then we only take into account capacitance of the alignment layer in the simplified case (we have a capacitor in series with the FLC cell, resistance of the FLC material and of the capacitor is infinite, series resistance of the electrodes and wires is zero). Voltage on the FLC will be the difference between total voltage applied to the electrodes and voltage drop on alignment layers:

\[
U_{LC} = U - U_c
\]

The current going through the LC is the same as is going through the capacitor, so one can say that \(U_c = I_{LC} X_c\), where \(X_c\) is the reactance of the capacitor \(X_c = 1/i\omega C\). The current going through the LC is
\[ I_{LC} = \frac{U_{LC}}{X_{LC}} = \frac{U_{LC}}{i \omega C_{LC}} = \frac{U_{LC} i \omega (D_z A / U_{LC})}{i \omega D_z A}, \]

taking into account that \( C_{LC} = \varepsilon A / d = D_z A / Ed = DA / U_{LC} \) (here \( A \) is the area of the LC electrodes and \( D_z \) is the \( z \)-component of the electric displacement in the FLC cell).

From here, \( U_c = D_z A / C \) is the voltage drop on the alignment layers and
\[ U_{LC} = U - D_z A / C \] (11)
is the voltage on the FLC.

Now I describe introduction of two factors that were not included in the original Palto’s model: surface gliding and nematic layer at the surface.

**Surface gliding:** Surface gliding is described in details in Appendix A. I include it in the model to investigate if surface gliding may affect bistable switching of the FLC cell. Surface gliding is introduced into the model the following way. Surface gliding is the drift of the easy axis which minimizes the anchoring energy.

Specifically, the easy axis will move to lower the energy \( W = W_a \sin^2 \Delta \phi \), where \( \Delta \phi \) is the difference between the azimuthal director at the surface and the azimuthal easy axis (defined by \( \varphi_a \)). One may say that the torque on the easy axis due to the anchoring energy \( 2W_a \sin \Delta \phi \cos \Delta \phi \) is balanced by a ‘viscous’ torque \( \gamma_s \frac{d\phi}{dt} \):
\[ 2W_a \sin \Delta \phi \cos \Delta \phi = \gamma_s \frac{d\phi}{dt} \] (12)
Here \( \gamma_s \) is some effective ‘surface viscosity’, for which various physical mechanisms may be responsible (such as adsorption/desorption of the LC molecules on/from the surface; the value of \( \gamma_s \) actually represents time constant of this process).

Change of the easy axis position \( d\phi \) is calculated from this torque balance, and the speed of the gliding is related to the value of surface viscosity \( \gamma_s \).

**Nematic layer on the surface:** as mentioned in Palto’s work\(^{14}\), the derived equations are universal and work not only for ferroelectric liquid crystals, but also for other liquid crystalline phases with higher symmetries. In particular, after simplifications I already did, simply setting \( K_4=0 \) will effectively turn smectic C* into nematic (in this case the form of elastic energy density (1) will be valid for the nematic phase). Moreover, it is easily possible to have both smectic and nematic phases in the cell simultaneously by setting \( K_4(z)=0 \) in the regions of the cell with no smectic ordering. The reason for doing this is to be able to have smectic order ‘melted’ near the surfaces as we predicted before due to the seeming impossibility for the smectic layers at the substrates to accommodate to the rough surface of SiO\(_x\).

In the end, our problem is narrowed down to solving the system of differential equations
\[ \gamma \dot{n}_x = M_{1x} + M_{2x} + \lambda n_x, \]
\[ \gamma \dot{n}_y = M_{1y} + M_{2y} + \lambda n_y, \]
\[ \gamma \dot{n}_z = M_{1z} + M_{2z} + \lambda n_z, \]
\[ n_x^2 + n_y^2 + n_z^2 = 1 \]

Together with boundary conditions and equations for the electric field inside the FLC.

We solve the above equations for director components using finite difference method. The cell is divided into \( N \) layers, and for each layer \( n_x, n_y \) and \( n_z \) can be calculated that causes director dynamic equations above to be satisfied. In finite difference approximations these equations have the following form (\( \Delta t \) is infinitesimal time step):

\[ \gamma \frac{n_x^{\text{new}} - n_x^{\text{old}}}{\Delta t} = M_{1x} + M_{2x} + \lambda n_x \]
\[ \gamma \frac{n_y^{\text{new}} - n_y^{\text{old}}}{\Delta t} = M_{1y} + M_{2y} + \lambda n_y \]
\[ \gamma \frac{n_z^{\text{new}} - n_z^{\text{old}}}{\Delta t} = M_{1z} + M_{2z} + \lambda n_z \]

Spatial derivatives in the expressions for the elastic and electric torques are written as

\[ \frac{dn_x}{dz} = \frac{n_x^{i+1} - n_x^{i-1}}{2\Delta z}, \quad \frac{dn_y}{dz} = \frac{n_y^{i+1} - n_y^{i-1}}{2\Delta z}, \quad \frac{dn_z}{dz} = \frac{n_z^{i+1} - n_z^{i-1}}{2\Delta z}, \]
where $\Delta z = d / N$, $i$ is layer number.

Second spatial derivatives are written as

$$
\frac{d^2 n_x}{dz^2} = \frac{n_x^{i+1} + n_x^{i-1} - 2n_x^i}{\Delta z^2}, \quad \frac{d^2 n_y}{dz^2} = \frac{n_y^{i+1} + n_y^{i-1} - 2n_y^i}{\Delta z^2}, \quad \frac{d^2 n_z}{dz^2} = \frac{n_z^{i+1} + n_z^{i-1} - 2n_z^i}{\Delta z^2}.
$$

So, for each layer in the cell we can write

$$
n_x^{new} = n_x^{old} + \frac{\Delta t}{\gamma}(M_{1x} + M_{2x}) + \lambda n_x,
$$

$$
n_y^{new} = n_y^{old} + \frac{\Delta t}{\gamma}(M_{1y} + M_{2y}) + \lambda n_y,
$$

$$
n_z^{new} = n_z^{old} + \frac{\Delta t}{\gamma}(M_{1z} + M_{2z}) + \lambda n_z.
$$

Again, $\lambda$ is Lagrange multiplier introduced to take into account the constraint on the director unit vector length: $n_x^2 + n_y^2 + n_z^2 = 1$. It is calculated from the following considerations. For the $i$'s component of the director dynamic equation of the torque balance is written as following:

$$
\gamma \frac{\Delta n_i}{\Delta t} = M_{1i} + M_{2i} + \lambda n_i
$$

From this we find a new value of $n_i$, $n_i'$:

$$
n_i' = n_i + \Delta n_i = n_i + \frac{\Delta t}{\gamma}(M_{1i} + M_{2i}) + \lambda' n_i
$$

(15)
Here $\lambda'$ includes the factors of $\gamma$ and $\Delta t$. We can call the first two terms on the right side $n_i^*$, so $n_i' = n_i^* + \lambda' n_i$

Then from the condition $n_x^2 + n_y^2 + n_z^2 = 1$

$$n_x^2 + n_y^2 + n_z^2 = 1 = Tr + \lambda'^2 + 2\lambda' (n_x^* \cdot n_x + n_y^* \cdot n_y + n_z^* \cdot n_z),$$

where $Tr = n_x^*^2 + n_y^*^2 + n_z^*^2$. We can assume that $n_i^* \cdot n_i = (n_i + \Delta n_i) n_i = n_i^2$, so we can say $(n_x^* \cdot n_x + n_y^* \cdot n_y + n_z^* \cdot n_z) = 1$ and $\lambda'^2 = 0$. Therefore, $Tr + 2\lambda' = 1$ and $\lambda' = \frac{1 - Tr}{2}$. The new normalized value of the director is $n_i' = n_i^* + \frac{1 - Tr}{2} n_i$

**Surface anchoring:** to take into account surface boundary conditions, a little bit different algorithm is needed. I show it for the example of the first surface ($z=0$).

Writing down expressions for the spatial director derivatives at the surfaces (expressions (31)-(33) from [14]), one obtains

$$\frac{\partial n_x}{\partial z} \bigg|_{z=0,d} = G_x = G_{xx} n_x + G_{xy} n_y + G_{xz} n_z = n_x \frac{W_z \cos^2 \theta_a}{K} - n_z \frac{W_z (\cos \theta_a \sin \theta_a)}{K}$$

$$\frac{\partial n_y}{\partial z} \bigg|_{z=0,d} = G_y = G_{yx} n_x + G_{yy} n_y + G_{yz} n_z = -n_x \frac{W_x \sin \theta_a}{K} + n_y \frac{W_a}{K}$$

$$\frac{\partial n_z}{\partial z} \bigg|_{z=0,d} = G_z = G_{zx} n_x + G_{zy} n_y + G_{zz} n_z = -n_x \frac{W_z \cos \theta_a \sin \theta_a}{K} + n_z \frac{W_z \sin^2 \theta_a}{K} \quad (16)$$
Presenting derivatives as finite differences, one gets

\[
\frac{\partial n_x}{\partial z} \bigg|_{z=0,d} = G_x = \frac{n_i^2 - n_i^1}{\Delta z}
\]

\[
\frac{\partial n_y}{\partial z} \bigg|_{z=0,d} = G_y = \frac{n_i^2 - n_i^1}{\Delta z}
\]

\[
\frac{\partial n_z}{\partial z} \bigg|_{z=0,d} = G_z = \frac{n_i^2 - n_i^1}{\Delta z}
\]  
(17)

Here \( n_i^1 \) and \( n_i^2 \) are values of the director at the surface (1\textsuperscript{st} layer) and the first bulk layer (2\textsuperscript{nd} layer). From here,

\[
n_i^2 = n_i^1 (G_{xx} \Delta z + 1) + n_i^1 G_{xy} \Delta z + n_i^1 G_{xz} \Delta z
\]

\[
n_i^2 = n_i^1 G_{yx} \Delta z + n_i^1 (G_{yy} \Delta z + 1) \Delta z + n_i^1 G_{yz} \Delta z
\]  
(18)

\[
n_i^2 = n_i^1 G_{zx} \Delta z + n_i^1 G_{zy} \Delta z + n_i^1 (G_{zz} \Delta z + 1)
\]

Or, in the matrix form,

\[
\begin{pmatrix}
\hat{n}_y \\
\hat{n}_x \\
\hat{n}_z
\end{pmatrix}
= \begin{pmatrix}
\hat{G}_{xx} & \hat{G}_{xy} & \hat{G}_{xz} \\
\hat{G}_{yx} & \hat{1} + \hat{G}_{yy} & \hat{G}_{yz} \\
\hat{G}_{zx} & \hat{G}_{zy} & \hat{1} + \hat{G}_{zz}
\end{pmatrix}
\begin{pmatrix}
\hat{n}_y \\
\hat{n}_x \\
\hat{n}_z
\end{pmatrix}
\]

(19)

We know \( n_i^2 \) and \( \hat{G} \), so from here we calculate \( n_i^1 \).
Similarly to the case of the bulk, we use Lagrange multipliers to normalize values of the director on the surface:

\[ n_i^{\text{normalized}} = n_i^1 + \lambda n_i^1 = n_i^1 + \frac{1}{2} Tr n_i^1, \]

where \( Tr = (n_i^1)^2 + (n_j^1)^2 + (n_k^1)^2. \)

Since we have \( N \) grid points, we loop through from point 2 to N-1. At each grid point the torques \( \dot{M}_1 \) and \( \dot{M}_2 \) are evaluated, and new values \( n_x, n_y \) and \( n_z \) are obtained using dynamic equations. These new values are stored in a temporary array until we have scanned through the whole cell. At this point the older array of \( n_x, n_y \) and \( n_z \) variables is overwritten and the process continues until the difference in the new and old values reaches a certain tolerance (at that point the system is considered to be in equilibrium) or until some specific time set in the program.

**Effect of polarization stiffening:** I would like to show that in the Palto model spontaneous polarization leads to spatially uniform distribution of the dipole moments in the cell (so-called ‘polarization stiffening’). Free energy density due to the electrostatics is defined as \( F_z = D_z E_z / 2 = (D_z - P_{z0})^2 / 2 \epsilon_\perp \) (if we set \( \Delta \epsilon = 0 \)), where \( D_z \) is the z-component of the induced displacement. If we for simplicity consider the case of the zero voltage across the FLC and layer normal directed along x-axis, then from equations (25) and (26) from the reference [14], \( D_z = (P_{z0} / d) \int_0^d \sin \phi(z) dz - P_{z0} \sin \phi(z) \) (\( \phi \) is the angle of
the dipole rotation on the cone). It is easy to see from here that

\[ D_{z} = D_{z} - P_{z} = \left( P_{z0} / d \right) \left( \int_{0}^{d} \sin \phi(z) dz - d \sin \phi(z) \right) \]

is minimized when \( \sin \phi(z) \) is constant, so the expression in the brackets becomes zero. This means that minimum of the electric part of the free energy is minimized for the case of uniform dipole distribution throughout the cell, which explains the effect of polarization stiffening.

**Surface gliding:** after discretizing torque balance at the surface, one obtains

\[ 2W_{a} \sin \Delta \phi \cos \Delta \phi = \gamma^{*} \frac{\Delta \phi}{\Delta t} = \gamma^{*} \frac{\phi_{\text{new}} - \phi_{\text{old}}}{\Delta t}, \]

from which \( \phi_{\text{new}} \) is evaluated:

\[ \phi_{\text{new}} = \phi_{\text{old}} + \frac{\Delta t}{\gamma^{*}} 2W_{a} \sin \Delta \phi \cos \Delta \phi. \]

In the next chapters I demonstrate application of this simulation technique to bistable and analog (V-shaped) ferroelectric liquid crystals.
Chapter 3

Bistable SSFLC device: role of surface alignment layer

3.1 Overview of bistable SSFLC devices

First, I would like describe basic physics of ferroelectric chiral smectic (SmC*) liquid crystals and electro-optical performance of Surface Stabilized Ferroelectric Liquid Crystal (SSFLC) devices. It was Robert Meyer who discovered ferroelectricity of chiral smectic liquid crystals in 1975\(^7\). As I briefly discussed in section 1.4, in chiral smectic liquid crystals molecules are arranged in liquid-like smectic layers. Each smectic layer can posses an in-plane spontaneous polarization as shown in Figure 1.3. By symmetry, spontaneous polarization is only allowed in a direction normal to the molecular tilt (this value of spontaneous polarization corresponds to the particular value of the SmC* cone angle; spontaneous polarization as defined in (2) is more general):

\[
\vec{P}_s = \pm \vec{P}_0 \hat{z} \times \vec{n}
\]

The director \(\vec{n}\) is coupled to \(\vec{P}_s\) and is constrained to rotate around the cone, preserving its angle \(\theta_c\) with the symmetry axis. Because chirality of the phase makes director \(\vec{n}\) twist around the symmetry axis, vector of spontaneous polarization also rotates with the director (Figure 1.3). Within a pitch of the smectic helix, all polarization vectors sum up to zero and as a bulk, chiral smectic liquid crystal is not polarized.
In 1980, Clark and Lagerwall published their method of suppressing the director helix, thus breaking the spontaneous polarization symmetry and making SmC* macroscopically polar. If FLC cell gap is smaller than the pitch, helical structure becomes suppressed by the interaction between the FLC and boundary plates, which allows ferroelectrical properties of the SmC* phase to show. This structure is called 'Surface Stabilized Ferroelectric Liquid Crystal' (SSFLC) and it stabilizes two director states, which can be switched via the electric field with different polarity (section 1.4). Electric field is coupled with the vector of spontaneous polarization, which results in very fast switching speeds\textsuperscript{17,18}:

\[ \tau^{-1} \sim \frac{\vec{P}_s \cdot \vec{E}}{\gamma}, \]

where \( \gamma \) is a characteristic rotational viscosity of the SmC* liquid crystal.

When SSFLC was discovered, it was first considered that in this geometry SmC* has so-called ‘bookshelf’ geometry, as shown in Figure 1.5a. However, as it was shown by Reiker with X-Ray diffraction experiments\textsuperscript{19} and in other works\textsuperscript{20,21,22}, due to layer shrinkage near SmA-SmC phase transition most frequently two types of structures may form: it is either ‘chevron’ structure (Figure 1.5b), or ‘tilted’ structure (Figure 1.5c), depending on surface alignment conditions. For bistable SSFLC, chevron layer structure is preferred. All of our experiments in this chapter will relate to chevron FLC cells.

Actual layer structure and distribution of the molecules inside layers of the chevron SSFLC is a little more complicated and depends on variety of factors, such as
material cone angle, layer tilt angle (or chevron angle), alignment direction and pretilt, character of interaction of FLC with the aligning surfaces, etc\cite{23,24,25}. Two types of chevron (C1 and C2) may occur in the SSFLC cell\cite{26,27}. C1 is the structure when the chevron apex is pointing opposite to the rubbing direction; C2 is the structure when the chevron apex is pointing towards the rubbing direction. If C1 and C2 chevron coexist in the cell, it leads to appearance of zigzag defects, which cause light leakage and their growing and expansion in the SmC* during switching degrade the performance of the device. Using high pretilt SiO$_x$ alignment layer suppresses C2 chevron\cite{28}, thus eliminating zigzag defects.

The chevron interface is a non-polar boundary, which acts as a third boundary condition in the cell. At the chevron interface, the director $n$ wants to be parallel to the boundary surfaces, no matter how the director configuration varies through the rest of the cell. Although the director $n$ is continuous across the chevron interface, the polarization vector $P_s$ makes a jump at the interface. The Z-component of $P_s$ is continuous across the chevron interface. If the solid surface boundary is polar ($P_s$ wants to be directed from the surface into the FLC, or from the FLC to the surface), it will lead to splay state of $P_s(z)$ corresponding to a splay-twist in the director field\cite{17}. With a chevron, the splay is taking place in the upper or lower half of the cell when it is in UP or DOWN state, respectively. This splay-twist structure in the director field is most often called twist state. The optical properties of these configurations will be numerically modeled using Extended Jones $2 \times 2$ method in section 3.8.
Development of SSFLC display technology has been challenging due to the issues related to intrinsic chevron structure of SSFLCs and difficulties of liquid crystal alignment. Recently, a defect-free bistable C1 SSFLC device that used obliquely evaporated SiO$_x$ layers was demonstrated$^{28}$; it allowed the design of a doubled-brightness ferroelectric LCoS projection microdisplay device$^{29}$. SiO$_x$ films obliquely deposited at shallow angles (~5° with respect to the cell’s plane) have been shown to provide defect-free, large memory angle due to its favorable properties, such as high pretilt that helps to suppress C2 chevron structure and eliminates zigzag defects. Besides high pretilt, relatively weak surface anchoring energy helps to achieve excellent bistability.

Further improvement of these devices require decrease in the threshold switching voltage of the device. In this chapter, I describe experimental and computer simulation study of the effect of surface alignment layer on the threshold voltage of SSFLC devices.

3.2 Study of threshold voltage dependence on evaporation parameters of SiO$_x$

It is well known that inorganic thin films deposited onto a substrate at oblique angles exhibit anisotropic electrical, optical, magnetic and mechanical properties, and the magnitude of the anisotropies depends strongly on the angle of incidence between the normal to the substrate surface and the direction of evaporation$^{30,31,32,33,34,38}$. Most often, silicon monoxide or silicon dioxide are used to create thin SiO$_x$ or SiO$_2$ film on glass substrate, which is widely used in many applications, including high pretilt high quality alignment layer for liquid crystals$^{35,36,37}$. 
In 1971 John L. Janning published first results on using of obliquely evaporated SiO films for alignment of nematic liquid crystals 5CB and MBBA. Soon after that it was discovered that actual molecular composition of vacuum-deposited films are not exactly SiO, but SiO\textsubscript{x}, where \( x \) is in the range from 1 to 2. Parameters of deposition (film thickness, pressure in the vacuum chamber, but most of all angle of deposition) define topography and, as a result, aligning properties of the SiO films. For example, shallow angles of deposition (<10° with respect to the direction of the evaporating beam) lead to highly topographical film and typically high pretilt alignment of liquid crystals in the plane of the evaporation beam. Large angles result in smoother surfaces that make liquid crystal align homogeneously in the plane perpendicular to the evaporation direction.

Using SiO\textsubscript{x} as alignment layers has advantages compared to conventional rubbed polyimides. First, unlike rubbing of polymers, deposition of SiO\textsubscript{x} is much cleaner process which leads to generation of smaller amount of particles that contaminate surface of the device. Due to specifics of the deposition process, SiO\textsubscript{x} is not suited for very large substrates and therefore are typically used in microdisplay applications. For microdisplays and other applications, importance of defect-less alignment is crucial for the performance of the device.

The technique proposed by Janning is based on direct deposition of the material by thermal evaporation. There also exist indirect methods, such as ion-beam sputtering and e-beam deposition, where deposited materials are being evaporated by high-energy beam of ions or electrons. Because of higher temperatures, silicon dioxide is used as the source of evaporation and the resulting film is SiO\textsubscript{2}. In my experiments, I mostly used the
method of direct thermal evaporation to obtain SiO$_x$ alignment film. Also, I prepared SiO$_2$ films using e-beam deposition technique, which were used mostly for comparison to SiO$_x$.

### 3.3 Deposition of SiO$_x$/SiO$_2$ films

SiO$_x$ films were prepared by evaporating silicon monoxide powder by Kurt J. Lesker Company heated by electric current in a vacuum chamber ($\sim 10^{-6}$ torr). Substrates were inclined with respect to vertical evaporation direction by an arbitrary angle (typically $<10^\circ$ from the evaporation direction). Film thickness was measured in-situ by an oscillating quartz crystal thickness monitor. The deposition rate was controlled to be 4~5Å/sec. The Scheme of the SiO$_x$ evaporation setup (manufactured by Kurt J. Lesker Company) is shown in Figure 3.1.

To deposit SiO$_2$, I used GenVac e-beam deposition setup on glass substrates using the specially designed holder, as shown in Figure 3.2a. Substrates are attached with the tape vertically to the holders that are arranged on the circle around the center of the base plate. The radius of this circle defines deposition angle of SiO$_2$, $\theta$. The plate is located above the source so that plate center is directly above the center of the crucible containing SiO$_2$ material. The illustration of this configuration is shown in Figure 3.2b (this illustration shows another type of L-bracket that is shown in the Figure 3.2a).
Figure 3.1. Schematic illustration of the setup for obliquely evaporated SiO\textsubscript{x} alignment and R. D. Mathis’s design of multi-heat-baffled, tantalum boat source for SiO deposition

(*re-drawn from [9]*).
Figure 3.2. (a) Photograph of cell holder for oblique deposition of SiO$_2$; (b) Illustration of deposition geometry: $\theta$ is the angle of evaporation.
Usually the thickness of the deposited film is controlled by the measuring crystal that is located approximately at the height of the plate and a little off-centered. To achieve a more collimated SiO$_2$ beam, we focus the electron beam to the center of the crucible, so the SiO material would melt and evaporate only from the center of the crucible which is around 1 inch in diameter. The effective surface area where SiO$_2$ material is being melted is around 0.7 cm$^2$. As a result, the e-beam burns a crater in the material. On the one hand, it gives us collimated SiO$_2$ beam, but on the other hand, most of the SiO$_2$ does not get to the crystal. It leads to the wrong SiO$_2$ thickness value showed by the meter. To measure SiO$_2$ film thickness, we attached silicon wafer horizontally on the plate and then measured the film thickness using ellipsometry.

### 3.4 Characterization of SiO$_x$ films by SEM imaging

It has been shown in numerous works that evaporation of SiO$_x$/SiO$_2$ at glancing incident angles ($>80^\circ$), leads to film with a highly porous structure consisting of tilted columns. I attempted to present an approximate model description of SiO$_x$ film evaporated at $5^\circ$ based on my measurements and SEM imaging, as well as on previous experimental and theoretical work. The main mechanism responsible for columnar structure of SiO$_x$ films is self-shadowing: random nuclei on the substrate prevent particles in the vapor stream from reaching substrate in the geometric shadow of each nucleus. As evaporation proceeds and the growth deposits increase in size, vacant regions are left in film and individual columns create 2-D array on the surface.
Another mechanism that plays an important role is surface diffusion. SiOx particles after hitting the surface may reflect, scatter or adsorb onto the surface, which effectively can be considered as diffusion of SiOx particles after hitting the surface. Overall, there are many parameters of the deposition process that define final SiOx structure: parameters deposition rate, the angular distribution of the incident vapor flux, the film and substrate temperature, the energy of the surface-substrate interface, and the partial pressure of residual gases in the deposition chamber. Most of them are kept constant for all our depositions but some, such as temperature, can change. The parameters of the deposition that we control are the evaporation angle, film thickness and the pressure in the chamber.

Since obliquely evaporated SiOx was shown to be an excellent liquid crystal aligning material, a lot of experimental and theoretical work was done to better understand its properties. Group in the University of Alberta has used the simulation software GROFILMS to demonstrate the growth of obliquely evaporated films as an effect self-shadowing and surface diffusion, showing excellent agreement with the experimentally obtained images of such films\textsuperscript{40}. Earlier, Monkade et al have used transmission electron microscopy to explore cross-section of the SiOx film and show the dependence of deposition parameters on surface topography\textsuperscript{41}.

We conducted Scanning Electron Microscope (SEM) imaging of SiOx/SiOx films to better understand the topographical structure of the film and, consequently, figure out how the deposition parameters of SiOx influence its characteristics as the surface alignment layer in the liquid crystal cell. I worked on Electron Microscope Hitachi S4500
that belongs to Swagelok Center for Surface Analysis of Materials at Case Western Reserve University (Cleveland, OH). This scanning electron microscope is equipped with a field-emission gun, two secondary electron detectors, a backscatter detector, and an infrared chamber scope. The microscope is capable of operating at a spatial resolution of less than 1.5 nm at 15 kV energy. It also performs well at reduced beam energies (1 kV), facilitating the observation of highly insulating materials and of producing micrographs that emphasize the near-surface structure of the specimen.

Sample preparation for SEM imaging:

1) ITO-covered glass substrates were scribed from the non-ITO side using manual glass scriber. Then substrates are washed following our cleaning standard procedure (for details, please refer to section 3.5).

2) Thick SiO$_x$ film (~500 nm) is deposited on the ITO side of the substrate, following the standard procedure (as described in section 3.3).

3) After that, the substrate is broken along the scribed line and the sample is inserted in the SEM chamber such way so that electron beam would be directed at the straight edge with SiO$_x$ layer on top of the glass. Right before inserting sample in the SEM’s chamber, it is covered with conductive layer (Pd) around 5 nm thick.

We have looked at SiO$_x$ films deposited at the angle of 5° and 2°. Typical SEM images are presented in Figures Figure 3.3-Figure 3.5. The picture obtained in the SEM is actually an ‘image’ of the secondary electrons scattered from the surface of the sample.
after bombarding the surface with high-energy ‘primary’ electrons, so this image does not exactly correspond to how the sample surface really is, but it rather needs some interpretation. For example, changing energy of the primary electrons leads to changes in the picture, with different resolution and depth of view.

At such small scales we are working at the limits of SEM’s capabilities. In particular, 5 nm-thick palladium layer adds some unwanted details on the picture (I believe that what makes SiO$_x$ columns look grainy; we also think that cauliflower-like heads of columns are due to palladium layer). I found that it makes sense to work only with thick SiO$_x$ layers, as with thinner films the features we are interested in get lost in the palladium coating (as seen in Figure 3.6). On the other hand, some images (such as presented in Figure 3.8) reveal more realistic images in areas that were not heavily covered with palladium layer.
Figure 3.3. SEM image of 5° SiOx taken at 90° with respect to the cell substrate and estimated angle of the columns tilt.
Figure 3.4. SEM image of 2° SiOx taken at 90° with respect to the cell substrate
Figure 3.5. SEM image of 5° SiOx taken at 45° with respect to the cell substrate
Figure 3.6. SEM image of thin 5° SiOx taken at 90° with respect to the cell substrate
I estimated geometrical parameters from the SEM images, which are denoted in Figure 3.7: columns height ($l$), thickness ($a$), column tilt angle ($\gamma$) and distance between shadowed regions ($d$). Accurate estimation was difficult due to the palladium coating on top of SiOx columns make them look considerably thicker, so we used image with uncovered parts of the columns. To estimate distance between shadowed regions $d$, I measured distance between the columns that shadow one another.

I compared my estimates with the results of computer simulations of the University of Alberta group (Figure 3.9 taken from [40]). This simulation made for deposition parameters that are very similar to ours (4° evaporation angle) and has good agreement with our data (except tilt angle of the columns).

So, estimating geometrical parameters for the SiO$_x$ film for the evaporation angle of 85° and detector reading of film thickness of 1000Å, I get: $a$~30 nm, $\gamma$~45°, $d$~300 nm, $h$~50 nm. From the SEM image it may look that distance between columns is much shorter, as they are packed more densely. However, as also discussed in [40] (see Figure 3.9), on a SEM image one can see a superposition of the rows of columns. Because of random character of nucleation, columns do not have good positional ordering in the direction perpendicular to the evaporation direction. Therefore, instead of ordered rows, one can observe rather chaotic distribution of the closely packed columns along this direction. This model for the SiO$_x$ films also suggests that thin films (<10 nm) consist of little hills rather than columns (Figure 3.11), leaving large areas of exposed ITO surface.
Figure 3.7. Estimating geometrical parameters of SiOx columns from the SEM image
Figure 3.8. Estimating thickness of SiOx columns from the SEM image
Figure 3.9. (From [40]) (a) Simulated image of a completed oblique deposition (evaporation angle is 4°); (b) Overlay plot of six such simulations to simulate the effect of three-dimensional layering.
One more parameter that is used in the simulation is average diffusion length, $\Lambda$. This is the parameter that defines degree of surface diffusion. It depends on temperature and plays important role in columns thickening. In most of cases for highly oblique evaporation, including these simulations, we consider this parameter to be pretty small (i.e. surface diffusion is small). It is also considered that all (or almost all) of the molecules coming to surface stick to it, i.e. sticking coefficient is close to 1.

Another issue is column length and overall SiO$_x$ film thickness associated with it. During deposition of the film, crystal deposition rate detector is used to measure film thickness. The crystal is located perpendicularly to the evaporation direction, so it measures thickness of SiO$_x$ film that is solid, not porous. When evaporating at oblique angles, same amount SiO$_x$ material gets into columns, therefore making them longer compared to the value of solid film multiplied by cosine of evaporation angle. Simple calculation shows that effective thickness of SiO$_x$ film $h$ is

$$ h = \frac{\sin \gamma}{a} \left( d h_0 \cos \theta - \frac{a^2}{\tan \gamma} \right) $$

Here $h_0$ is thickness of film on crystal detector; $\theta$ is evaporation angle (85° in our case). Using estimated parameters $a$ and $d$, we get the tooling factor $k$ ($d_{\text{real thickness}} = k \cdot d_{\text{crystal reading}}$) to be ~0.6. SEM image gives us $k$~0.35-0.5. This is pretty close, especially taking into account that SiOx molecules coefficient may actually be lower than 1.
Last aspect of the SiOx model is asymmetric shape of the heads of the columns. Due to usage of palladium this is hidden from the view on SEM pictures, but it is clear from geometrical considerations. As evaporation proceeds, the nucleus grows along the substrate towards the deposition source until the advancing edge of the nucleus reaches the shadow of the second nucleus (as shown by the dashed line in Figure 3.11). Once the first nucleus reaches the shadow of the second one, growth along the substrate in the plane of incidence stops and then the growth of the first nucleus proceeds approximately parallel to the shadow side of the second one which is parallel to its own shadow side.

Obtained results can help better understand specific properties of highly topographical 5° SiOₙ films. As suggested by Monkade et al⁴¹, morphology of the film leads to strong decrease of nematic liquid crystal order parameter in the close vicinity of the surface (surface melting). Melting of smectic phase at the rough surfaces is studied less, although it was shown that in many cases effective decrease of smectic ordering occurs in confined geometries⁴²,⁴³ and at the rough surfaces⁴⁴,⁴⁵,⁴⁶. In particular, Durand has predicted a decrease of surface order for strong surface disorientation and discussed roughness-induced surface transitions⁴⁵. This allows us to suggest for the smectic phase in the close vicinity of very rough surface the possibility of a strong decrease (or elimination) of the smectic order parameter and a decrease of the nematic order parameter.
Figure 3.10. Geometrical parameters of SiOx columns: columns thickness $a$, height $h$, tilt angle $\gamma$, length $l$ and distance between columns $d$.

Figure 3.11. Illustration of self-shadowing mechanism of SiO$_x$ column growth which leads to asymmetrical shape of the columns’ heads.
Another question that better understanding of SiO\textsubscript{x} morphology allows to answer is how to estimate dielectric properties of the SiO\textsubscript{x} film which, in addition to serving as an alignment layer, serves as voltage divider, affecting threshold voltage of the device. Typically capacitance of alignment layer is calculated using standard expression for the capacitance of the dielectric: $C = \varepsilon_0 \varepsilon A / d$, where $\varepsilon_0$ is vacuum permittivity, $\varepsilon$ is permittivity of the dielectric of area $A$ and thickness $d$. For porous dielectric material of a capacitor, one may assume some effective value of dielectric permittivity $\varepsilon$ that is estimated knowing dielectric permittivity of SiO\textsubscript{x} and the liquid crystal and distribution of the substrate’s surface area among them.

### 3.5 Cell assembly and experimental details

In this section we briefly describe experimental technique of measurements of threshold voltage in bistable SSFLC cells. For best results, the cell gap for these experiments usually must not exceed 1.5 µm (however, using thicker cells for bistable SSFLC devices were also reported, e.g. in the work by Jákli et al\textsuperscript{47}), so the cell assembly procedure was performed in the clean room of class 1000.

*Substrate preparation and cell assembly:* for each cell two types of substrates were prepared. One type was photolithographically etched and cut using Mask #106, as shown in Figure 3.12a. Another type of substrate had etched channels, as shown in Figure 3.12b, just like the substrates we used for monodomain alignment of stiffened SmC*
materials (Chapter 4). Such substrates were chosen for the purpose of convenience, ease of cell filling and conservation of FLC materials. After etching, substrates were thoroughly cleaned and alignment layers were deposited.

UV-sensitive glue (Norland 68) was dispensed onto one of the substrates using automated XY dispenser. Cell gap was controlled by 1.2 µm spacers that were sprayed over both substrates and also mixed in the glue (5% weight concentration). Dispense pressure was 50 psi, distance from the needle to the substrate was 0.002’. Then two substrates were put together so that SiO$_x$ deposition directions on both substrates were parallel, as shown in Figure 3.12 (c). After that, cells were placed on the vacuum plate, pressed down with the plastic film and cured by UV irradiation for 7 minutes.

**Cell gap measurements:** when cells were assembled, their reflection spectrum was taken by the OceanOptics setup. Obtained spectrum was fit to the modeling program utilizing Berreman method$^{48}$. Typical calculated cell gap was ~1.2-1.3 µm.

**Cell shortage removal:** if the assembled cell was shorted, we applied 60V voltage to the cell for a very short time. This removed the shortage. In most cases, this did not seriously disrupt ITO layer over large areas, since shorted area was usually very small.

**Cell filling:** cells were filled in the vacuum chamber (pressure ~50 militorr) in the isotropic phase and then slowly cooled to the SmC* phase. We found that using channel substrates was very useful for filling process. With regular cells, it was very hard to achieve homogeneously filled cell without air bubbles probably due to the rough topography. Profile of the channel cells make LC homogeneously fill in into the grooves.
Figure 3.12. Schematical drawings of two substrate types used to assemble SSFLC cells
**Cell characterization:** we connected electrodes to the cell and applied bipolar waveform (Figure 3.13) using BosLab EOM software. The cell is placed in the polarizing microscope between crossed polarizers. On the top of the microscope, we place camera for taking texture pictures or photodiode to register light signal. Oscilloscope with floppy disk drive for data output is connected to the computer’s National Instruments board output and to the photodiode. The result of the measurement is the optical response of the FLC cell to the applied waveform.

### 3.6 Threshold voltage measurements

Typical electro-optical response of the bistable SSFLC cell is shown in Figure 3.14. Here electro-optical response is plotted along with the applied waveform. We find threshold voltage from the condition of saturation of the response, which corresponds to full latching of the director and maximum memory angle. In the example electro-optical response, threshold voltage corresponds to the solid line on the response curve ($V=10.5$ volts). The curves of the electro-optical response the lower applied voltages ($V=9.5$ and 10 volts) correspond to the case of partial latching. Microscopic observations of the FLC textures during switching at these voltages have shown that the FLC texture is not fully uniform, but consists of many small domains.
Figure 3.13. Bipolar waveform applied to the SSFLC cell. Time of pulse: 1 millisecond; time of rest: 19 milliseconds
Some of the domains are latched, and some are not, which reduces the overall electro-optical effect, turning the FLC texture grayish instead of black or white. We connect this to the non-ideal uniformity of the SiO$_x$ surface. I have studied effect of angle of deposition and film thickness of SiO$_x$ on threshold voltage. Range of tested deposition angles was 2° to 11.5°, thickness range was 5 nm to 180 nm. Figures 3.15-3.21 shows measured threshold voltage as function of the film thickness for various deposition angles. For most of the cells we measured pretilt angle of the thick (20 µm) anti-parallel cell with equivalent alignment layers filled with nematic liquid crystal 5CB. Magnetic null method was used for measurements; the measured values of pretilt are denoted at the plots in Figures 3.15-3.21. The summary of the results along with the parameters of the measured cells are presented in Table 1.
Figure 3.14. Characteristic electro-optical response of the bistable SSFLC cell. Curve on the top is shape of applied waveform, curves on the bottom are intensities of light behind crossed polarizers for different amplitudes of the applied waveform.
Table 1 Results of measurements of threshold voltage in SiOx SSFLC cells

<table>
<thead>
<tr>
<th>SiO&lt;sub&gt;x&lt;/sub&gt; evap. angle, °</th>
<th>SiO&lt;sub&gt;x&lt;/sub&gt; film thickness on crystal (actual thickness), Å</th>
<th>Deposition pressure, torr</th>
<th>Cone angle (memory angle), °</th>
<th>Overall Alignment Quality (1-5)</th>
<th>Threshold Voltage, Volts</th>
<th>Pretilt, °</th>
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<td>39(34)</td>
<td>4</td>
<td>4.5</td>
<td>31</td>
</tr>
<tr>
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<td>9&lt;sup&gt;-10&lt;/sup&gt;</td>
<td>40(38)</td>
<td>4.5</td>
<td>7</td>
<td>28</td>
</tr>
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<td>2</td>
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<td>40(39)</td>
<td>4</td>
<td>8.5</td>
<td>28</td>
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<tr>
<td>2</td>
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<td>10&lt;sup&gt;-10&lt;/sup&gt;</td>
<td>40(39)</td>
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Figure 3.15. Threshold voltage depending of SiOx film thickness for the evaporation angle of 2°
Figure 3.16. Threshold voltage depending of SiOx film thickness for the evaporation angle of 3°
Figure 3.17. Threshold voltage depending of SiOx film thickness for the evaporation angle of 4°
Figure 3.18. Threshold voltage depending of SiOx film thickness for the evaporation angle of 5°
Figure 3.19. Threshold voltage depending of SiOx film thickness for the evaporation angle of 6.5°
Figure 3.20. Threshold voltage depending of SiOx film thickness for the evaporation angle of 8.5°
Figure 3.21. Threshold voltage depending of SiOx film thickness for the evaporation angle of 11.5°
From these results, it is clear that thinner SiO$_x$ films lead to lower threshold voltage values. This result at first seemed to suggest that the main reason for increase of threshold voltage with increase of SiO$_x$ thickness was the voltage drop on alignment layers. However, we noticed that the tendency for appearance of twist states in SSFLC strongly depended on the thickness of SiO$_x$. These twist states are known to form in the SSFLC under the influence of polar, or dipole-dipole interactions between FLC molecules and surfaces$^7$. Uniform states of the SSFLC (when dipole moments of the molecules point to the same direction on both surfaces) are energetically favorable if only smectic elasticity is considered. Polar surfaces makes vector of spontaneous polarization $\vec{P}_s$ point into (or out from) the surface on both substrates, leading to splayed configuration of $\vec{P}_s$ throughout cell’s thickness and twisted director configuration. Twisted structures for typical SSFLC cell gaps have bluish coloring, if the cell is between crossed polarizers. More details on molecular structures of uniform and twisted states are discussed in the section 3.8.

We studied uniform and twist states of our cells in more detail to have a better understanding about the effect of polar interaction on the switching behavior. It is well known that SSFLC cell with chevron structure effectively has three boundaries (two solid surfaces and the chevron interface). During switching, director can switch on any of these surfaces. Optically surface and chevron switching look different between crossed polarizers due to the shapes of switching domains and the colors of the FLC texture.
At zero field states, before any voltage is applied to the cell since it has been cooled to the SmC* phase from the isotropic phase, stable configurations of the SSFLC cells depended on the thickness of the SiO$_x$ aligning layer (Figure 3.22). For thin SiO$_x$ layers (<25 nm), the uniform structure is stable (Figure 3.22a). For thick cells (>100nm) the twisted structure is stable (Figure 3.22c). For intermediate thicknesses both uniform and twisted structures coexist in the cell (Figure 3.22b).

We wanted to understand the character of all switching transitions that we are observing in our SiO$_x$ cells (either it is surface or chevron). We started out by looking at switching by slow triangular waveform ($f=0.05$ Hz) to look at domain shape and texture color as a function of the SiO$_x$ layer thickness (polarizers are aligned along one of the memory states). Diagrams of these transitions are shown in Figure 3.23 as the examples of three particular cells. Figure 3.23a shows transitions for the SSFLC cell with SiO$_x$ aligning film evaporated at 5° and 20 nm thick, Figure 3.23b - 6.5° and 90 nm thick, Figure 3.23c - 6.5° and 180 nm thick. Dots on the waveform correspond to the transition points between two uniform states ‘UP’ and ‘DOWN’, and twist state if it is observed.

For thin SiO$_x$ layers (<25 nm, Figure 3.23a), no twisted structure ever appears in the cell. Applying a triangular waveform leads to the following transitions: UNIFORM UP (bright) $\rightarrow$ UNIFORM DOWN (dark).

For intermediate SiO$_x$ layers (>25 nm, Figure 3.23b), the twist structure is initially present in the cell, but after switching of the cell to the uniform state, it stays uniform.
Figure 3.22. Typical textures of uniform and twisted states of the SSFLC at zero field for different thicknesses of SiO$_x$ alignment layers: (a) 20 nm; (b) 40 nm; (c) 180 nm.
Figure 3.23. Diagram of structural transitions in SSFLC cell. (a) Thin SiO$_x$ alignment layer: 20 nm film evaporated at 5°; (b) intermediate alignment layer: 90 nm film evaporated at 6.5°; (c) thick SiO$_x$ alignment layer: 180 nm film evaporated at 6.5°. Dots on the triangular waveform represent transitions between different SSFLC states.
Applying triangular waveform leads to the following transitions: UNIFORM UP (bright) $\rightarrow$ TWISTED (blue) $\rightarrow$ UNIFORM DOWN (dark).

For thick SiO$_x$ layers (>100 nm, Figure 3.23c) twisted state is stable and even though FLC director is latching on the surfaces, after turning the field off, it slowly (within seconds) goes back to twist structure. Applying triangular waveform leads to the following order of structures in the cell: UNIFORM UP (bright) $\rightarrow$ TWISTED (blue) $\rightarrow$ UNIFORM DARK (dark).

As SSFLC can switch both on solid surfaces and on the chevron interface, it is useful to understand what kind of switching is taking place at the given transition. Usually two types of cells are distinguished from the point of view of surface versus chevron switching: low-pretilt PI cell and high-pretilt SiO cells$^{49,50}$. Appearance of the domains is different for these two types of cells. It was observed that for low pretilt and high anchoring cells (usually with PI as alignment layer), chevron switching occurs with lower voltages, characterized by high contrast and distinctive smooth boat-shaped domains. At higher voltages, FLC-solid interface transition occurs via surface domains which are more irregular in shapes$^{19,51,52}$. For high pretilt and low anchoring cells (usually with SiO as alignment layer), low-voltage chevron switching occurs via irregularly-shaped domains characterized by low contrast, while high-contrast surface switching occurs via smoother domains with shoe-resembling shape$^{49,53}$. More details on the shape of the switching domains depending on the cell type can be found in the references [49] and [50].
In section 3.8, we demonstrate the results of our computer simulation that describes optical effect of the surface and the chevron switching for the high-pretilt cell. These results help us to explain observed structural transitions in the cells, which are described below.

First, in high-pretilt cells all high-contrast transitions are surface transitions. They can be transition between *two uniform* states (Figure 3.24a) or between *uniform and twisted states* (Figure 3.24b). Chevron interface transitions are characterized by very low contrast.

They can be transitions between *two twisted states* (Figure 3.24c) or between two states, one of which *is uniform* and another one of which is *uniform with switched chevron interface* (Figure 3.24d). In Figure 3.24d, both the latter kind of transition (corresponding to the low-contrast gray areas) and surface transition between two uniform states (high contrast black areas) can be seen. All the transitions that are denoted with the dots in Figure 3.23 are the surface transitions.

A little more ambiguous question is the shape of domains. For the cells with thin SiO₃ shapes of the domains are typical for the surface transitions in high-pretilt SiO cells (Figure 3.24a). However, for cells with thick SiO₃ aligning film, we observed two slightly different types of domains at two different transitions: from uniform to twist (Figure 3.25a) and from twist to uniform (Figure 3.25b). The first type of domains is smoother, which is typical for surface transitions; the second one has a rougher shape, resembling chevron transitions (it is still a surface transition because of its high contrast).
Figure 3.24. Structural transitions in the SSFLC cells: (a) surface switching between two uniform states; (b) surface switching between twist and uniform state; (c) chevron switching between two twisted states; (d) chevron and surface switching between two uniform states.
Our hypothesis is that at the second transition, chevron and surface are switched virtually simultaneously, and surface switching is ‘led’ by chevron switching, thus affecting the shape of the domains.

Finally, we measured dependence of threshold voltages of different transitions (e.g. uniform to twisted, twisted to uniform, uniform to uniform) on SiO$_x$ thickness (Figure 3.26). For this measurement, the waveform applied to the cell was chosen in such way that before the testing pulse was applied, a large pulse of the opposite polarity had fully switched SSFLC. This allowed us to make sure that all the transitions start from the same uniform state (dark state for the polarizers configuration used in the experiment). Two pulses of the same amplitude but opposite polarity were applied to avoid accumulation of the ions double layers on the surface. The threshold voltage corresponds to the value of the applied voltage when 50% of the viewing area have switched. One can see that for the cells with thin SiO$_x$ aligning layers due to the absence of twist states, only one kind of transition is observed (dark state to the bright state). For thicker alignment layers, one can see two transitions (dark state to the twist state and twist state to the bright state).
Figure 3.25. Shape of domains during transitions (a) from uniform to twist state; (b) from twist to uniform state.

Figure 3.26 Threshold voltage of transitions in the SSFLC cell as a function of $\text{SiO}_x$ thickness. Angles of $\text{SiO}_x$ evaporation are denoted for each cell at the plot. Evaporation angle for the films thinner than 500Å was 5°, for the other films - 6.5°.
3.7 Simulation of the bistable electro-optical response

To quantitatively analyze the effect of the voltage drop on alignment layers, surface anchoring energy and other parameters on threshold voltage, we have done computer simulation of the bistable switching of our SSFLC cells. We have implemented simulation method developed by Palto described in Chapter 2.

We have used parameters of the cell and the FLC material that were used in experiment: cell thickness $d=1.2 \ \mu m$, FLC spontaneous polarization $P_s=10 \ \text{nC/cm}^2$, elastic constant of the FLC $K_{11} = K_{22} = K_{33} = 5 \text{pN}$, FLC viscosity $\gamma=0.1 \ \text{Pa}\cdot\text{s}$, cone angle of the material $\Psi=20^\circ$, dielectric constants of the FLC $\varepsilon_\parallel = \varepsilon_\perp = 5$, electrode area $A=0.3 \ \text{cm}^2$, electric resistance of electrodes $R_0=0$, orientation of the smectic layer normal $(k_x, k_y, k_z) = (1,0,0)$, compressibility module $K_4=1 \ \text{MPa}$. Other parameters, such as surface zenithal and azimuthal anchoring energies $W_z$ and $W_a$ and capacitance of alignment layers $C$ were varied according to conditions of experiment and simulation.
Figure 3.27. Characteristic pulse waveform applied to the simulated SSFLC cell
First, I calculate voltage drop on the alignment layers to find actual voltage on the FLC layer. The simulation program calculates FLC response to the short voltage pulse (shown in Figure 3.27). Only one polarity of the pulse is considered; negative pulse results in exactly symmetrical response of the FLC. The capacitance of SiO$_x$ alignment layer is estimated as described in section 3.4. Assuming approximately 50% coverage of the SiO$_x$ on the substrate surface, $\varepsilon_{\text{SiO}}=2$, $\varepsilon_{\text{FLC}}=5$, we estimate capacitance of SiO$_x$ alignment layer using the expression $C = \varepsilon_0 \varepsilon^* A/d$, where $\varepsilon^* \approx 3.5$ is effective dielectric constant.

Figure 3.28 shows threshold voltage as function of the alignment layer thickness. On the plot, along with actual applied voltage that causes latching of the director to the bright uniform state (corresponding to the results shown in Figure 3.26), we show voltage on the FLC layer, calculated at the time of the pulse application.

In Figure 3.29 I demonstrate simulated response of the FLC to the pulse waveform as a function of waveform amplitude for three sets of surface anchoring energies. Figure 3.29a shows dynamical response of the FLC as orientation of molecular dipoles for an extreme case of zero anchoring energy. Figure 3.29b shows the same simulation calculated for the zenithal anchoring energy $W_z=10^{-5}$ J/m$^2$ and azimuthal anchoring energy $W_a=5\times10^{-6}$ J/m$^2$. These values of surface anchoring energies approximately correspond to the reported values for the thin SiO$_x$ films measured for nematic liquid crystals$^{54,55}$. Figure 3.29c shows the simulation results for the equal values of energies $W_z=W_a=10^{-5}$ J/m$^2$ (approximately corresponding to the thicker SiO$_x$ films).
The value of alignment layer capacitance was 50 nF. As seen from comparison of these plots, the effect of anchoring energy is very small on the threshold voltage. The simulated value of threshold voltage is around 4 volts for the parameters of the actual SSFLC cell with thin SiO\textsubscript{x} alignment layer, which is in a good agreement with the experimental results.

As pretilt angle is defined by the alignment layer and may change with the thickness of the SiO\textsubscript{x} film, we simulated the effect of the pretilt angle for the fixed value of surface anchoring energy ($W_s=10^{-5}$ J/m\textsuperscript{2}, $W_a=5\times10^{-6}$ J/m\textsuperscript{2}). Dynamics of the FLC director for the pretilt of 5° and 10° (Figure 3.30) are compared to the zero pretilt case (Figure 3.29b). Alignment layer capacitance is 50 nF. The results suggest that there is an effect of the pretilt on the memory angle, but not on the threshold voltage.

Another possible mechanism that can affect dynamics of FLC’s director switching is possible decrease of the smectic ordering near the surface. Usually it was considered that smectic ordering does not change in the proximity of the surface. While this approximation may work on very smooth surfaces, it was shown that in many cases effective surface melting of the smectic phase occurs.\textsuperscript{44,45,46} Theoretical\textsuperscript{42} and experimental\textsuperscript{43} works on smectic phase in confined geometries allows us to suggest that a likely scenario for the smectic phase in the close vicinity of the rough surface is elimination of the smectic order parameter and serious decrease of nematic order parameter. For this model, we assume that a thin nematic layer exists between aligning surface and the smectic bulk of the cell.
Figure 3.28. Voltage drop of the alignment layers as a function of SiO\textsubscript{x} thickness.
Figure 3.29. Simulated dynamics of the director in the center of an LC cell depending on amplitude of the applied 1 ms pulse. Simulation was done for the different values of the surface anchoring energies: (a) $W_z=W_a=0$; (b) $W_z=10^{-5}$ J/m$^2$, $W_a=5*10^{-6}$ J/m$^2$; (c) $W_z=W_a=10^{-5}$ J/m$^2$. Alignment layer capacitance is 50 nF.
Figure 3.30. Simulated dynamics of the director in the center of an LC cell: effect of the pretilt angle on the threshold voltage: (a) pretilt angle is 5°; (b) pretilt angle is 10°. Alignment layer capacitance is 50 nF, surface anchoring energies are \( W_z = 10^{-5} \) J/m\(^2\), \( W_a = 5 \times 10^{-6} \) J/m\(^2\).
To study the described effect, we repeated simulations with included thin nematic layer at the surfaces of various thicknesses. This is realized by eliminating compressibility module $K_4$ (which is responsible for maintaining of the smectic ordering) for the layers next to the surfaces. However, the realistic thicknesses of nematic layer (<100 nm) does not affect the values of the threshold voltage. In fact, values of the nematic layer due to surface melting proposed in the literature are smaller (<10 nm), so we can conclude that surface melting does not considerably affect the dynamics of the SSFLC cell, or that this effect is adequately taken into account by the lowered values of the surface anchoring energy.

3.8 Optical modeling of Chevron SSFLCs

In this section I present the results on optical modeling of chevron SSFLCs. I used open-source software ‘Memory Angle Calculation of SSFLC Device, Version 3.0’ written by Chenhui Wang and Philip J. Bos\(^9\). Details of the calculation are thoroughly described in the reference, here I briefly overview the physical model of the SSFLC cell used in this simulation.

The basic chevron layer structure of SSFLC is shown in Figure 3.31 and Figure 3.32. The two boundary plates are equally treated and the SiO$_x$ evaporation directions of two plates are parallel. I only consider symmetric C1 chevron structure (chevron apex is pointing opposite to the SiO$_x$ evaporation direction).
In the system of coordinates associated with the cone \((x,y,z)\) and in the laboratory system of coordinates \((X,Y,Z)\) director can be written as following (here \(\theta\) is cone angle, \(\delta\) is chevron angle, \(\Phi\) is rotation angle of the c-director in the cone, \(\theta_p\) is pretilt angle, \(\psi\) and \(\gamma\) are twist and tilt angles of the n-director in the \(XYZ\)-system):

\[
n(x,y,z) = (\sin \theta \cos \Phi, \sin \theta \sin \Phi, \cos \theta), \quad (20)
\]

\[
n(X, Y, Z) = \begin{pmatrix}
\sin \theta \cos \Phi \\
\sin \theta \sin \Phi \cos \delta - \cos \theta \sin \delta \\
\sin \theta \sin \Phi \sin \delta + \cos \theta \cos \Phi
\end{pmatrix}. \quad (21)
\]

The tilt angle \(\gamma\) and twist angle \(\psi\) of \(\vec{n}\)-director are expressed as:

\[
\gamma = \sin^{-1}(\sin \theta \sin \Phi \cos \delta - \cos \theta \sin \Phi); \quad (22)
\]

\[
\psi = \tan^{-1}\left(\frac{\sin \theta \cos \Phi}{\sin \theta \sin \Phi \sin \delta + \cos \theta \cos \Phi \delta}\right). \quad (23)
\]

Calculations were done in steps. First, we calculate director structure in the cell as twist and tilt angles across the cell: \(\gamma(z)\) and \(\psi(z)\). Then for these configurations we calculate dependence of light transmission vs angle between polarizer and SiO\(_x\) evaporation direction. Half of difference between two darkest states (minimums of the transmission curve) is the memory angle of the cell. Then, with the polarizer direction along memory direction, we calculate transmission spectra of the dark and bright states of the cell.
Figure 3.31. (redrawn from \textsuperscript{56}). Coordinate systems of the chevron SSFLC cell. Y and Z represent the cell and the smectic layer normal, z is the central axis of the cone.

Figure 3.32. (redrawn from \textsuperscript{56}). Scheme of the director at the surface.
The following parameters of the SSFLC were used: chevron angle=17°, cone angle=19°, pretilt=25°, cell gap=1.2 microns, $n_o$=1.4, $n_e$=1.6. We were considering the following transitions: (a) UNIFORM OFF-STATE $\rightarrow$ UNIFORM ON-STATE, (b) UNIFORM $\rightarrow$ UNIFORM with chevron switched and (c) TWISTED $\rightarrow$ TWISTED with chevron switched. Schematic diagrams of these structures are shown in Figure 3.33.

Calculated dependences of light transmission vs angle between polarizer and SiO$_x$ evaporation direction for uniform structure, uniform structure with chevron switched and twist structure are shown in Figure 3.34. One can see that first two uniform structures can be brought to extinction, and the twisted structure cannot.

Finally, calculated transmission spectra for the ON and OFF-states (when chevron is switched and when it is not) of the uniform, double-splay, and twisted structure are calculated when the polarizer direction is at memory angle with respect to the SiO$_x$ evaporation direction (Figure 3.35 and Figure 3.36). It is easy to see that spectra of the ON and OFF states of the uniform structures suggest black and white textures, and gray texture for the double-splay structure. Switching of chevron in uniform configuration does not change color of the texture. At the same time, twist states show no full extinction and spectra with maximum around 430 nm, which corresponds to bluish texture between crossed polarizers at the dark state. Switching of chevron in twisted structure does not change its color and the contrast between ON- and OFF-states is low.
Figure 3.33. Schematic diagrams of SSFLC structural states under consideration: (a) uniform state; (b) uniform state with chevron switched (double splay); (c) twist state; (d) twist-state with chevron switched.
Figure 3.34. Transmittance of the SSFLC cell vs position between polarizer and $\text{SiO}_x$ evaporation direction: (1) uniform structure; (2) uniform structure with chevron switched (double splayed); (3) twist structure.
Figure 3.35. Transmission spectra of the ON- and OFF-states of the uniform and double-splay SSFLC structures. Polarizer direction is at memory angle with respect to the SiO$_x$ evaporation direction.
Figure 3.36. Transmission spectra of the ON- and OFF-states of the twist SSFLC structures. Polarizer direction is at memory angle with respect to the SiO$_x$ evaporation direction.
3.9 Discussion

I answer the question: what parameters of the surface affect threshold voltage of the SSFLC cell with obliquely evaporated SiO\textsubscript{x} aligning surface? My initial assumptions based on previously obtained results suggested that there are four main factors: pretilt angle, voltage drop on alignment layers, non-polar surface anchoring energy and polar FLC-surface interactions. Results of the experiment and computer simulations allow to estimate effect of these factors quantitatively or qualitatively and propose ways to further decrease threshold voltage.

**Pretilt angle.** Our measurements have shown that only for very thin SiO\textsubscript{x} films (<4nm) pretilt angle is substantially smaller (<20°) than for thicker films. For thicker films, pretilt angle does not strongly depend on SiO\textsubscript{x} thickness and is in the range of 26° to 37° without any obvious correlation to the threshold voltage value. Low pretilt angle leads to appearance of C2 chevrons and therefore to characteristic zigzag effects. Also, memory angle of the SSFLC cell is substantially decreased, so, although threshold voltage can achieve low values of ~3 volts, low pretilt cells are not well suitable for the practical applications. Computer simulations have shown that effect of pretilt more affects memory angle, but not threshold voltage.

**Voltage drop on alignment layers.** As simulation results confirmed, there is substantial voltage drop on alignment layers, which increases with the thickness of SiO\textsubscript{x} aligning film. We subtracted voltage drop from the measured value of applied voltage and then plotted voltage on FLC layer as a function of SiO thickness (Figure 3.28). The
obtained curve saturates when SiO\textsubscript{x} films are thicker than 50 nm. It is also seen from this curve that the effect of voltage drop is not significant for thin SiO\textsubscript{x} films.

**Non-polar surface anchoring energy.** Non-polar part of surface anchoring energy frequently written as Rapini-Papoular potential plays an important role in the work of SSFLC device. Anisotropic and low surface anchoring of obliquely evaporated SiO\textsubscript{x} has made it perfect candidate for usage in bistable SSFLC devices. The results of the simulations has shown that despite increase of the azimuthal anchoring energy with increase of the SiO\textsubscript{x} thickness, as shown by experiment, this change in the surface conditions does not significantly affect threshold voltage of the device. Even modeling the situation with unphysical zero surface anchoring energy does not eliminate the threshold.

**Polar FLC-surface interactions.** SSFLCs are characterized by non-compensated spontaneous polarization $\vec{P}_s$ (unlike, for example, nematic liquid crystals) that interacts with polar surfaces. Energy of this interaction depends on energy of dipole-dipole interaction between molecules of the surface and the liquid crystal. Polar anchoring leads to splay of the polarization vector and consequently to the twist of the director in the cell. Our experiments have unequivocally shown that for the thickness of SiO\textsubscript{x} film that is above some threshold value, twist states are stable in SSFLC cells, which probably means increase of the polar interaction strength. The experimental results shown in Figure 10 suggest that polar interactions play important role for the cells with thicker SiO\textsubscript{x} film that promote twist states in the cell.
Although SiO$_x$ material itself is not very polar, it is known to easily pick up molecules of water from the air which are strongly polar. If we assume that strength of polar anchoring depends on the number of water molecules on the surface of SiO$_x$, then it is easy to visualize that the polar anchoring will be related to the height of SiO$_x$ columns, or equivalently, SiO$_x$ film thickness. Inclusion of polar surface anchoring in the model for the simulation of SSFLC is the subject of future work and should provide more clear and quantitative explanation of threshold voltage dependence on SiO$_x$ film thickness.

In the end, as we try to understand what limits threshold voltage for the thinnest SiO$_x$ films, my study suggests that the threshold is not limited by the surface, but rather by properties of the FLC itself. The dependence of threshold voltage on rotational viscosity of the FLC (Figure 3.37) shows that the surface viscosity is probably responsible for the threshold when other factors such as surface anchoring, polar FLC-surface interactions and the voltage drop on the alignment layers are small.

In conclusion, in this chapter I presented results of the study of effect of deposition parameters of obliquely evaporated SiO$_x$ on threshold voltage of bistable SSFLC display devices. The lowest values of threshold voltage (~4 volts) were obtained for thin SiO$_x$ films (~5 nm). Increase of threshold voltage with increase of SiO$_x$ thickness is mostly related to the voltage drop on SiO$_x$ film that acts as a voltage divider and to polar dipole-dipole interactions between surface and FLC molecules, which are thought to increase with thickening of the SiO$_x$ film. However, for thin SiO$_x$ aligning layers, as effects of voltage divider and polar interaction are strongly reduced, I have shown that the factor that is holding threshold voltage is the rotational viscosity of the FLC.
Figure 3.37. Threshold voltage of the SSFLC cell as a function of FLC’s rotational viscosity. The value of the threshold voltage corresponds to the amplitude of the pulse of the certain width (1 ms in our case) which fully switches bistable SSFLC cell.
Chapter 4

Obtaining of aligned SmC* samples without regard to surface alignment layer

4.1 Introduction

Most applications of smectic liquid crystals require aligned samples of the smectic phase. Therefore, alignment of smectic liquid crystals is of a great practical interest due to their numerous display applications. In particular, ferroelectric liquid crystal (FLC) displays utilizing chiral smectic C materials have many attractive features such as fast response time and bistability. Most FLCs used in displays possess an I-N-A-C phase sequence (Isotropic–Nematic–Smectic A–Smectic C) and are usually aligned in their nematic phase using conventional surface-treatment methods such as rubbed polymer surfaces, obliquely deposited SiO$_x$ surfaces, and photo-aligned polymer surfaces.

However, there is a class of FLCs with unique characteristics such as large cone angles and reduced layer shrinkage having I-A-C phase sequences. Conventional alignment methods do not work well for these materials due to the absence of the nematic phase. Several methods have been proposed for aligning I-A-C liquid crystals. They include using rubbed nylon as the alignment layer$^{57}$, gentle shearing in the smectic A phase$^8$, application of a magnetic field during cooling from isotropic to smectic A phase$^{58}$, guided backflow method$^{59}$ and the spatial gradient cooling technique$^{60,61}$, which
relies on cooling the liquid crystal from its isotropic phase is the presence of a thermal
gradient in the plane of the cell and perpendicular to a nucleating wall. According to this
method, as a cell is cooled the SmA–I transition-temperature contour line moves parallel
to the nucleating wall and out into the liquid crystal to grow a band of smectic-phase out
from the wall. Use of this technique and I-A-C materials has the advantage, suggested by
Fukuda, that the cell surface treatment can be chosen for its effect on the director in the
smectic phase of interest without regard to how it aligns a nematic liquid crystal. For
example, as we show in Chapter 4, it is possible to make a smectic C* device with a
bookshelf layer geometry on surfaces that promote homeotropic director alignment.

The gradient cooling technique has proven useful; however in the discussed case
where the director aligns parallel to the nucleation wall the alignment of the smectic
layers is often imperfect. Perhaps improved layer alignment could be achieved if the
layers were aligned parallel to the nucleating wall and perpendicular to the applied
gradient, as in this case the nucleation wall will tend to promote smectic ordering, and the
gradient direction is along a symmetry direction of the layered structure (Figure 4.1).
While the use of walls that promote homeotropic alignment of the director (parallel
alignment of the smectic layers) has been previously proposed it has not yet been
demonstrated\textsuperscript{60,61}. In the case of homeotropic aligning wall it is especially important that
this wall be smooth at the molecular size level, otherwise one can expect many defects in
the smectic phase (Figure 4.1c). Air surface is perfect for the role of nucleation wall: it is
known to promote homeotropic alignment of the liquid crystalline molecules\textsuperscript{63} and makes
a molecularly smooth wall.
Figure 4.1. Growth of smectic layers from the nucleation wall: (a) nucleation wall promotes planar alignment of liquid crystal molecules; (b) perfectly smooth nucleation wall promotes homeotropic; (c) rough homeotropic wall leads to smectic layer defects.
Here we demonstrate a spatial-gradient cooling alignment technique that utilizes an air bubble as the nucleating wall. Along with the advantages of this technique we discuss the problems found in applying this method, and their solutions.

### 4.2 Experimental method and results

#### 4.2.1 Experimental set-up

To explore the use of bubbles as the nucleating wall we constructed an experimental set-up where an elongated air bubble, defined and contained by a lithographically etched channel in the cell substrate, is aligned normal to a temperature gradient in the plane of the cell, as shown in Figure 4.2a. Channels were etched into ITO-coated glass using photo-patterned resist and hydrofluoric acid. Upon completion of photolithography process, the substrates were thoroughly washed and the surface treatment, if any, was deposited.

To investigate the effect, or lack of effect, of surface treatments on the smectic layer alignment we made cells with each of the following: clean ITO, SiO$_x$ deposited at 5° (85° incidence angle to surface normal), SiO$_x$ deposited at 30°, Glymo (3-glycidoxypropyltrimethoxysilane), Nissan PI 7511 and its analog PI 1211, and Dupont PI 2555 polyimide. When assembling the cell, it is possible to use two substrates with channels, as shown in Figure 4.2a, or one substrate with channels and one plain ITO substrate. While it may be expected that the first case will yield a more symmetric air-LC interface, we found that in most cases the simpler second case also works well. The cell
gap was defined by powder spacers that were mixed in the UV-sensitive glue which held two substrates together. We measured the empty cell gap by the optical interference method. For most of our alignment experiments the cell gap was about 4 µm, although some experiments were done with thinner cells (cell gap about 1.5 µm). The cells were filled with liquid crystal in isotropic phase using the capillary filling method so that only the spaces between the channels were filled with liquid crystal, leaving the channels to contain only air. To prevent liquid crystal from filling air channels, we limited amount of the liquid crystal. We used the following liquid crystal materials, all without nematic phase: 10CB (I - 51°C – SmA), 12-S5 (4'-Pentylbenzenethiol-4-dodecyloxybenzoat, I - 90°C - SmA - 87°C – SmC - 60°C - K) and Displaytech MX10498 (I - 95°C - SmA - 86°C - SmC - 30°C - K). All gave similar results in our experiments. A rough drawing of the thermal gradient set-up is shown in Figure 4.2b. The liquid crystal cell was placed between four metal plates (two at each side) to direct a thermal gradient across the channels. The distance between the plates was about 6 mm. We used ceramic heating elements and a refrigerated circulating water bath (Brookfield TC602), both with thermocouple sensors and under computer control, to set the temperatures of the hot side and cold side, respectively. Thermocouple sensors were tightly secured between metal plates to ensure good thermal contact, as shown schematically shown in Figure 4.2b. We put this set up on the stage of a polarizing microscope to observe the alignment process. The photograph of the experimental setup is presented in Figure 4.3.

With the cell between the plates we set the temperature of both sides so that the whole sample would become isotropic, and then started slowly cooling the cold side. The
thermal gradient when the cold side was cooled sufficiently to cause the SmA-I transition line to be at the spatial location of the air/liquid-crystal interface was approximately 10 K/mm. As we continued to cool the cold side, the thermal gradient value gradually increased to about 20 K/mm when the SmA-I transition line had moved across the area of liquid crystal to be aligned. Depending on temperatures phase transitions of the liquid crystal, steep thermal gradient sometimes resulted in co-existence of more than one liquid crystalline phase over 1 mm area (usually SmA and SmC), which, however, did not disturb the alignment process.

4.2.2 Alignment process

Initially we observed a mono-domain, defect-free smectic-A layer nucleate and grow from the air/liquid-crystal interface as shown in Figure 4.4a. The dark area to the right of the bright stripe of the smectic-A band contains air, while the dark area to the left of the stripe contains isotropic liquid crystal. However, when the smectic stripe reached a particular width we observed a dramatic structural change as seen in Figure 4.4b. The typical value of this threshold width was about 20 µm. Before this change smectic molecules were uniformly aligned normal to the nucleation edge. In Figure 4.4a this structure is shown with nucleation edge at 45° to the crossed polarizer and analyzer. Had the polarizer been parallel to the nucleation edge the smectic mono-domain would have appeared dark and undistinguishable from the background. After the structural transition the smectic phase has the appearance shown in Figure 4.4b.
Figure 4.2. (a) Design of liquid crystal cell (not drawn to scale). Channel substrates were made by photolithographic etching of standard ITO-coated glass with hydrofluoric acid; (b) Scheme of gradient heater. Liquid crystal cell is placed between cooled and heated metal plates elements to create a spatial thermal gradient along the cell.
Figure 4.3. Picture of the gradient heater experimental set-up
Figure 4.4. Growth of smectic A band from air bubble wall: (a) uniformly aligned band below critical width; (b) band with defect structure above critical width; (c) and (d) Smectic A – Isotropic interface after further cooling. Top-view of the cell with Displaytech MX 10498 on alignment layer of Nissan 7511 polyimide is shown in this and further photographs in this section, unless otherwise noted.
After further cooling to allow the width of the smectic-A stripe to grow, it acquires the appearance shown in Figure 4.4c. Surprisingly, the effect of the defects at the SmA-I interface has weakened and a nearly uniform texture is seen along the right (cooler temperature) side of the smectic band. We initially thought that the structural transition apparent in Figure 4.4b would prevent attainment of uniform alignment over wider bands, but we subsequently found that with extremely slow cooling rates (~0.05 μm/s) good alignment could be obtained due to the annealing effect seen in Figure 4.5. At the onset of cooling, before the smectic stripe had reached its critical thickness, as shown in Figure 4.4a, the cooling rate could be relatively high. Uniform smectic layers grew as a mono-domain as long as the cooling rate was lower than 1 K in 2 minutes. However, after the structural transition the critical cooling speed had to be less than around 1 K per 20 minutes, corresponding to a growth rate of the smectic band of about 0.05 μm/s. Faster cooling rates typically produced a cascade of defects, with appearance depending on the cooling rate, as seen in Figure 4.6. If the cooling rate produced growth of the smectic band exceeding our very slow rate of around 0.05 μm/s elongated bâtonnets start to “shoot out” from the interface, as seen in Figure 4.6a. Further cooling-rate increase to produce smectic-band growth of around 0.1 μm/s caused bâtonnets to form in the isotropic phase close to the interface, as seen in Figure 4.6b. Such defects disrupt the mono-domain alignment, as seen in Figure 4.5a, but they can be removed by heating the sample up a little to the point where the defects melt, and then resuming cooling, with results shown in Figure 4.5b. With low cooling rates we found it possible to grow a fully aligned 1-mm wide mono-domain, as shown in Figure 4.7.
Figure 4.5. Annealing of defects formed in smectic A: (a) initial appearance after nucleation of defects; (b) appearance after melting and cooling again—defects disappeared.

Figure 4.6. Alignment defects appearing at different growth rates: (a) 0.1 µm/s; (b) 0.2 µm/s.
Although our channel pattern limited the width of the smectic band to 1 mm, it is clear that this method using an air interface for layer nucleation, a high thermal gradient, and a very slow cooling rate could be used to obtain arbitrarily large smectic-A domains.

Figure 4.8 shows the results of alignment obtained on different surfaces. In Figure 4.8(a) and Figure 4.8(c), texture of Displaytech MX10498 is shown; in Figure 4.8(b), the liquid crystal is 12-S5. These pictures have different colors due to variation of the cell gaps and difference in the liquid crystalline materials birefringence. Using alignment layers of Glymo, $5^\circ\text{SiO}_x$ and $30^\circ\text{SiO}_x$ gave very similar results. We present them here to show that the quality of the smectic-A layer alignment was not influenced by the choice of cell-substrate surface treatment. We obtained good alignment with all the surface treatments we tried. The quality of alignment did not depend much on the surface layer, but rather on experimental conditions related to the temperature profile in the cell. We found the alignment quality was very sensitive to temperature fluctuations, such as of the heater and cooler, or even air movements near the cell. The value of temperature gradient was also very important to obtaining mono-domain alignment. A high gradient was required to stabilize the SmA-I interface and prevent bâtonnets from forming ahead of the interface. When the gradient was not steep enough focal conics tended to nucleate on the interface, disrupting the mono-domain. We found that thermal gradients of 10–20 K/mm were sufficient.
Figure 4.7. Uniform alignment across full smectic band width. Due to thermal gradient the left side of the picture is in the smectic A phase, and the right side is in the smectic C phase.

Figure 4.8. Alignment results on different surfaces: (a) Dupont polyimide 2555; (b) clean ITO; (c) Nissan polyimide 1211. Crossed polarizers are at 45° with respect to the layer normal.
I would also like to mention possible problems that may occur during described alignment process and how to avoid them.

\textit{a) Choice of photomask:} two most frequently used types of photomasks used in the photolithographic processes are emulsion on film masks and chrome on glass masks\textsuperscript{62}. The first one is cheaper, but only suitable for critical dimensions down to 20-50 µm. Chrome on glass masks are more expensive, more durable and are suitable for smaller feature sizes. Photomask used in described method must be able provide smooth edge of the channels (jaggedness of the edge must be at least of sub-micron size). In our case, chrome on glass works fine; emulsion on film mask does not. In Figure 4.9 we show SEM images of channel edges prepared using (a) chrome on glass mask and (b) emulsion of film mask. Jagged edge of the channel in the case of emulsion of film photomask prevents smectic layers from homogeneous nucleating at the air wall.

\textit{b) Spacers usage:} it is crucial for the quality of alignment to have clean surface of the substrates. Any relatively large defects (>0.5 µm) may disrupt layer growth. Typically during cell assembly spacers are sprayed evenly over the substrate to ensure uniform cell gap. However, in our case this would cause numerous defects, as shown in Figure 4.10. Therefore, spacers must be used in the cell exclusively mixed with the glue. To improve cell gap uniformity, it is useful to have several glue lines across the cell, not only at the edges.

\textit{c) Thermal stability of gradient heater:} in our method we usually keep the hot side of the gradient heater at constant temperature and cool the cold side. Cold side is temperature is controlled by refrigerating bath, and hot side is heated by ceramic heaters
connected to the power supply. Refrigerating bath due to large amount of water is quite inertial and therefore thermal stability is good and sufficient for our needs. However, ceramic heaters temperature stability may become an issue, as it is important to maintain stable temperature of both sides if the gradient heater. Initially we used simple DC power supply (made by Varian); then when we switched to OMEGA DC power supply with feedback feature. In Figure 4.11 we show difference between temperature stabilities the gradient heater’s hot side using these power supplies. We obtained considerably better results (less number of alignment defects) with more stable temperature of the hot side of the heater.

\[\text{d) Flatness of the air bubble/liquid crystal interface:}\] in the ideal case the air/liquid crystal interface should be flat; however, in our experiment this interface is probably somewhat curved. We have observed that if channels on both substrates are aligned reasonably well with respect to each other, then curvature of the air/liquid crystal interface does lead to the defects appearance at the interface.

\subsection*{4.3 Discussion}

The method described above nucleates smectic layers parallel to a molecularly smooth interface formed by an air bubble in the liquid crystal. The main difficulty in obtaining uniform large-area alignment with this method arises from focal conic defects that spontaneously appear at the smectic-A/isotropic interface after the width of the smectic band exceeds some critical value, similar to a phenomenon previously observed by Fournier, Dozov, and Durand\textsuperscript{63}. Fournier, et al. considered a smectic-A liquid crystal
sample floating on an isotropic droplet, with a temperature gradient across the thickness of the sample. They pointed out that at the air/smectic-A interface the smectic layers prefer to align parallel to the interface (liquid crystal molecules are aligned homeotropically at the interface), while at the smectic-A/isotropic interface the layers tend to align perpendicularly to the interface (planar alignment of the liquid crystal molecules).

These antagonistic boundary conditions produce texture distortions, involving both layer dilation and curvature\textsuperscript{63}, which, in turn, lead to the appearance of focal conic defects at the interface, as observed for the first time in 1910 by Friedel and Grandjean\textsuperscript{64}, as well in more recent works\textsuperscript{65}. We conclude the smectic band in our experiments has a structure similar to that shown in Figure 4.12. However, we have observed under the polarizing microscope that some regions never appear dark between crossed polarizers, regardless of the sample orientation with respect to the polarizers’ axis, implying some twisting of the layer structure through the thickness of the cell, and that the exact layer configuration may be more complex than shown in Figure 4.12.
Figure 4.9. SEM images of the channels’ edges in the cell prepared by photolithographic process using (a) chrome on glass photomask and (b) emulsion on film photomask.
Figure 4.10. Defects of the smectic phase due to spacers in the area of the channel
Figure 4.11. Thermal stability of hot side of the gradient heater for two types of power supplies
Subsequent study by Fournier, Warenghem, and Durand\textsuperscript{66} of the growth dynamics of the smectic slab found that a critical growth rate for their system was about 25 µm/s, above which growth instabilities of the smectic-A/isotropic interface led to nucleation of focal conic domains. By analogy with a Mullins-Sekerka instability\textsuperscript{67}, where growth velocity was limited by the diffusion of impurities, they estimated a threshold cooling rate of 50 µm/s, in a good agreement with their experimental results.

We found that once defects begin to cascade, as shown in Figure 4.6, it was not possible to continue the growth of a uniformly aligned smectic-A domain. However, our experiments show that if the cooling rate is drastically decreased, to about 0.05 µm/s, uniform layer formation is possible even in smectic bands thicker than the threshold thickness for defect formation. We suggest that at growth rates low enough that the distorted focal conic structure can relax to a uniform undistorted one flat smectic layers continue to form, as depicted in Figure 4.13. In their study of the focal-conic structure of smectic-A bâtonnets, Fournier and Durand\textsuperscript{68} argue that permeative flow in the smectic A phase increased the persistence of structural irregularities they called sailles to times on the order of 0.3 hour, consistent with our finding that very slow cooling is required in order for defects to anneal away.
Figure 4.12. Proposed structure smectic-A layers at onset of defect formation.
Figure 4.13. Annealing from focal conic distorted structure to uniform, undistorted structure during slow cooling.
4.4 Summary

I have demonstrated an alignment method that does not rely on surface treatments for aligning liquid crystal materials that have a smectic-A/isotropic phase transition. It uses an air bubble, located by a photolithographically-defined channel, to create a smooth wall for nucleation of smectic layers and to induce perpendicular molecular orientation for liquid crystal molecules. However, antagonistic boundary conditions lead to nucleation of focal-conic defects in the growing smectic-A region, once it attains a threshold size of a few tens of microns. These focal-conic defects persist unless the smectic-A is grown in the presence of a large temperature gradient and at a cooling rate slow enough that the smectic-A growth velocity is low (~0.05 µm/s), in which case the focal conic regions to anneal to a uniform structure. We obtained very good quality of smectic layer alignment over large areas regardless of a variety of different surface treatments. Future use of more-localized heating, such as could be provided by a scanned laser, will allow the whole cell to be maintained at a temperature close to the SmA-I transition temperature with only a thin line heated to the isotropic phase. This should decrease the focal-conic relaxation time, allow faster motion of the interface line, and make the alignment method more convenient for industrial applications.
Chapter 5
Effect of surface alignment layer on V-shaped switching of stiffened SmC* materials

5.1 Overview of V-shaped display devices

The first SmC*-based devices were bistable, therefore binary. Two stable states of the display are the dark and bright states\(^8\). Gray states for such displays are achieved using special techniques, such as amplitude-controlled gray levels\(^69,70,71\), spatial dither technique\(^17\), temporal dither technique\(^17\), etc. All these methods are based on averaging between two states, dark and bright. However, there is a possibility of obtaining true grayscale without the need of averaging over space or time. For example, as shown by Jákli et al, achievement of grayscale switching is possible using the deformed helix method\(^47\). Bistable devices are binary, or digital by their work principle. An opposite, analog operation of the device with the V-shaped electro-optical response can be achieved if one can continuously switch between two opposite extreme states. To make that possible, specific configurations of the SmC* devices and materials parameters are required. Such devices, in contrast to the bistable FLC displays, are hysteresis-free and threshold-free, allowing them to be driven by smaller voltages. Both ferroelectric and anti-ferroelectric (the main difference between FLC and AFLC devices is that in the
AFLC phase, the director is tilted in opposite direction in alternate layers) liquid crystals are capable of V-shaped switching.

This effect has received a lot of attention due to the great display application potential, so a lot of work has been done in the area of V-shaped devices; however, the nature of this mode is not yet completely understood.

V-shaped switching was first discovered in 1995 by Fukuda et al\(^{10}\) and later Inui et al\(^{11}\). They found that for some three-component mixture with an anti-ferroelectric SmC* phase, the characteristic hysteresis loop has changed into linear response. This discovery immediately attracted great interest, because it was possible to use thresholdless switching mode with analog grayscale in AFLC display that possess attractive features such as excellent viewing angle because of bookshelf geometry and very high switching speed due to coupling between electric field and spontaneous polarization of the material. Display prototypes were demonstrated soon after discovery of the effect.

Generally, the term ‘V-shaped switching’ relates only to the shape of the electro-optical response in the specific configuration of the polarizers (which are crossed and polarizer’s plane is parallel to the smectic layers) and does not specifically describe physics of the effect. The common thing for all V-shaped modes is using intermediate states between extreme dark and bright ones.

In *Twisted Smectic Mode*\(^{72}\) splayed mode is realized (surfaces make dipoles on both surfaces look into the surface, thus creating 180°-twisted structure of the director
throughout the cell. Applying intermediate voltages allows one to partially unwind the twist and change polarization state of the light at the output of the cell.

*Continuous Director Rotation mode*\(^7\) utilizes materials that have I–N\(^*\)–SmC\(^*\) phase sequence. Such devices are monostable with lowest energy state of the director parallel to the rubbing direction. Application of a field opposite to the aligning field gradually rotates the molecules, leading to gray levels in the transmission. It does not work the other way around, so it leads to the asymmetric *half V-shape mode*.

*Polymer Stabilized V-shaped switching*\(^7\) is realized by doping FLC with photocurable monomer and consequent photo-polymerization of the monomer. This leads to removal of alignment defects and enables thresholdless grayscale operation. Electro-optical response can be symmetric or asymmetric, depending on the parameters of the photocure.

Recently Blinov *et al* proposed a new approach to V-shaped switching\(^7\). The basic idea of this approach lies in the assumption that V-shaped switching is actually an apparent effect which happens only in very narrow frequency range and is due to *dynamic voltage divider*\(^7\) formed by an the alignment layers of the liquid crystal cell. Depending on frequency and capacity of alignment layers, the same ‘V-shaped’ FLC cell may as well have threshold and normal or inverse hysteresis. Authors claim that V-shaped switching actually has a threshold and normal hysteresis, if the optical transmission is plotted as a function of the voltage over the FLC, not as a function of the total voltage over the cell.
A separate model was developed for the case of FLC materials that are characterized by very high values of spontaneous polarization (>100 nC/cm²). This model was introduced by Noel Clark and is commonly called ‘electrostatic model’\textsuperscript{12}. Generally, it predicts that that under for large values of spontaneous polarization, the FLC’s director structure becomes spatially uniform (‘stiffened’). In this case, V-shaped switching cells are also surface stabilized (helix free), planar and have bookshelf structure, as shown in Figure 5.1 (a). For no voltage applied, polarization of the incident light is parallel to the layer normal, which, in the ideal case and with crossed analyzer behind the cell, leads to no light at the output. Application of electric field causes spatially uniform director to rotate around direction of the layer normal, effectively rotating cell’s optical axis, changing cell’s transmittance, leading to V-shaped electrical response in the case of triangular voltage waveform, as shown in Figure 5.1 (b). In this chapter, I consider this mode of analog SSFLC switching.

In Figure 5.2 I present several FLC configurations that describe the switching process in the FLC cell. Smectic phase is viewed with the layer parallel to the plane of the page (layer normal is directed towards the reader). Usually in this geometry FLC is characterized by the angle $\phi$ which is the azimuthal orientation of $P$-vector (arrows in the figures) around layer normal on the tilt cones (circles) and by $c$-director (little T’s).

Generally, director distribution in FLC cells is defined by bulk nematic director deformation energy (which is lowest when $P$ is uniform everywhere in the cell) and of an effective surface anchoring energy. Usually surface anchoring energy can be modeled as
\[ U(\phi) = U_p \cos \phi_s - U_{np} \cos^2 \phi_s, \] where \( \phi_s \) is director orientation at the surface, and \( U_p, U_{np} \) are correspondingly polar and non-polar interaction coefficients. Additionally, \( U_p \) depends on the orientation of the \( P \)-vector relative to surface normal directed into the liquid crystal. Depending on the character of the surface and its interaction with liquid crystal, values of these coefficients may vary; however, it is common for polar surfaces that the preferred orientation of the \( P \)-vector is \textit{out} of the liquid crystal normally to the surface.

In Figure 5.2 some possible configurations of liquid crystal in the FLC cell are shown. Completely uniform SSFLC state (usually called UP are DOWN, depending on direction of the \( P \)-vector) are realizable in the conditions of non-polar surface and low \( P_s \), or under the action of the strong electric field. Uniform UP-state is depicted in the in Figure 5.2a.

For polar surface, surface anchoring lowest when \( P \) is directed out of the cell, which leads to the splay of the \( P \) vector, as shown in Figure 5.2b. Such structure is seen in the low-\( P_s \) materials, when the surface interaction is strong enough to overcome the bulk elasticity. For higher \( P_s \), director with the same surface boundary conditions looks like in the Figure 5.2c: director is uniform everywhere in the cell except \( P \)-twisted surface domains. Further increase of \( P_s \) will lead to completely uniform stiffening of the director, including the surfaces.
Application of an electric field to the stiffened FLC cell will cause an immediate torque \( \vec{P} \times \vec{E} \neq 0 \), no matter how small \( E \) is, which means threshold-less switching mode. Intermediate voltages induce a torque, turning \( P \) continuously and resulting in linear electro-optical response.

Even though for high-\( P \) materials surface forces often become overwhelmed by bulk elastic forces, insulating surface alignment layers still play a key role in the work of the device. It appears that if the high-\( P \) FLC cell has no alignment layers, the overall orientation of the \( P \)-vector is controlled by only surface interaction and the cell will be effectively bistable. The reason for it is that surface polarization charges caused by the rotation of \( P \)-vector are cancelled by the free charges at the surface (Figure 5.3a).

However, if there is an insulating alignment layer, surface polarization charges and free charges are separated. If voltage \( V \) is applied to the cell (Figure 5.3b), dipoles in the FLC bulk rotate to decrease electric field in the FLC. This process continues until electric field inside of the FLC is \( E = 0 \). In this case, all the voltage applied to the cell is dropped on the alignment layers. This voltage drop is given by the following\(^77\):

\[
V = \frac{2t_a P_s \cos \varphi}{\varepsilon_0 \varepsilon_a},
\]

where \( t_a \) and \( \varepsilon_a \) are thickness and dielectric constant of the alignment layer.
Figure 5.1. (a) Bookshelf FLC smectic layers, the orientation of the FLC dipoles $P$, and the director/index ellipsoid axis $n$ (from O’Callaghan\textsuperscript{77}); (b) Sketch of ideal ‘V-shaped’ response of the stiffened FLC cell
Figure 5.2. Schematic drawings of the FLC configuration in the cell. Smectic layers are parallel to the plane of the page (layer normal is directed towards the reader). (a) Uniform UP-configuration; (b) Splayed configuration (for low-$P_s$ materials); (c) Splayed configuration (for stiffened high-$P_s$ materials); (d) Rotation of the director under the action of electric field in high-$P_s$ materials.
Figure 5.3. Two cases of bistable and analog switching of high-$P_s$ FLC materials for a cell: (a) without alignment layers; (b) with alignment layers.
This relation predicts that the voltage dependence of a high-$P_s$ FLC’s optic axis is defined by only three parameters: FLC’s spontaneous polarization $P_s$, the alignment layer’s thickness $t_a$ and its dielectric constant $\varepsilon_a$.

A lot of attention has been paid to the role of the surface alignment in the high-$P_s$ FLC cells. First, one of the biggest problems was alignment of such materials which often lack nematic phase. Chapter 4 of this dissertation is dedicated to solving this problem.

However, there is still no complete understanding of the role of the alignment layer in V-shaped switching. It appears that some alignment layers allow smooth, uniform switching of the director over the whole area of the cell, while others stimulate inhomogeneous, domain-like switching. In this chapter I present results of the study of how different surface alignment layers affect character of switching of the high-$P_s$ FLC cell.

5.2 Motivation

As we already mentioned, surface stabilized ferroelectric liquid crystals show a steep threshold that is very useful for bistable display devices, but undesirable for a fast analog switching driven by an active matrix. Certain FLC materials demonstrate threshold-less and hysteresis-free switching, when a triangular impulse is applied to the cell with bookshelf smectic structure. Electro-optical response acquires V-shaped form and has analog character. An 1-D electrostatic model of such materials that assumes
uniform director distribution in the plane of the cell was developed to explain its analog switching properties\textsuperscript{12,77}. The model predicts that large spontaneous polarization leads to the director structure of the FLC being spatially uniform, or ‘stiffened’. Surface anchoring energies are comparable to the distortion energy of the bulk director configuration and affect switching behavior of the FLC.

Besides displays, FLCs can be used to provide high speed phase retarders that can be used in beam steering and waveform control applications. For these applications, the FLC cell is configured to be a half-wave phase retarder where the optic axis can be effectively rotated in the plane of the cell\textsuperscript{78}. As with AC-driven display devices, it is required that the director field be uniform though the cell so that the projector of the director field on the plane of the cell provides a well defined effective optic axis orientation for light normally incident on the cell. To achieve AC-operation of the device with good contrast, V-shaped response must be symmetrical with respect to the zero field state and have very low transmission in its minimum near zero.

Detailed 1-D numerical simulation of electro-optical response of FLC cells has been done taking into account compressibility of smectic layers, finite surface anchoring, dielectric properties of alignment layers and external elements in the cell’s electric circuit\textsuperscript{14}. The results of this simulation has demonstrated the effect of surface anchoring energy anisotropy on the character of electro-optical switching (bistable or analog) and importance of external electric elements for hysteresis-free V-shaped switching. These results together with experimental work\textsuperscript{75} have shown that it is possible to remove
switching hysteresis by proper choice of external capacitors and resistors connected to the cell. Another, and, perhaps, preferable way of achieving threshold-less V-shaped switching is using charge drive instead of voltage drive, as suggested by M. O’Callaghan et al.\textsuperscript{79}

Our goal was to study in more detail the effect of alignment layer on the character of V-shaped switching device. For practical applications, we wanted to obtain analog switching in devices that can be operated using V-shaped switching effect and achieve continuous uniform rotation of the director by optimizing surface alignment layer of the FLC cell.

Previously achieving uniform analog hysteresis-free switching was complicated by difficulties in aligning of FLC materials that possess favorable features, such as reduced layer shrinkage, high cone angle and high spontaneous polarization. In Chapter 4 I described alignment technique that relies on growing of smectic phase from the isotropic phase in the presence of spatial thermal gradient from smooth nucleating wall. This allowed me to use wide variety of surface alignment layers in the high-polarization FLC cells. Such alignment layers may promote homeotropic or degenerated planar alignment of liquid crystals, while structure of layers in the cell remains bookshelf with layer normal being perpendicular to the plane of the cell. This opened possibility to further explore effect of the surface on the characteristics of the V-shaped switching device and improve understanding of the analog switching.
5.3 Experiment

Most conventional FLC materials exhibit layer shrinkage when cooled in the SmC phase, which leads to appearance of chevron structure and, therefore, to a bistable director orientation at the chevron interface at the cell midlayer\textsuperscript{17}. These materials demonstrate INAC (isotropic – nematic – SmA – SmC) phase sequence. For such materials, alignment of smectic phase is defined by alignment of the nematic phase, which in turn is defined by the alignment layer.

In our experiments, we used FLC materials that exhibit the IAC phase sequence (isotropic – SmA – SmC) and have reduced layer shrinkage\textsuperscript{80}. This feature is necessary for analog switching at the cell midlayer. IAC materials also can be aligned by vertical wall in the cell\textsuperscript{61} that allows us to obtain smectic alignment, independent of the surface alignment layer.

The main idea of our alignment method is using gradient cooling from isotropic to SmA phase. A smooth edge of the liquid crystal slab created by molecularly smooth LC-air interface allowed growing of smectic layers from this interface without defects creating SmA mono-domain. As quality of the smectic layers structure does not depend on properties of surface alignment layer, we were able to use aligning materials that induce high pretilt and homeotropic alignment, or not to use alignment layer at all. For every aligning materials used we obtained uniform bookshelf structure in the SmA phase.

The obtained smectic layer structure in the SmA phase is approximately preserved when the FLC is cooled down to the SmC\* phase. Since material that we used has reduced
layer shrinkage, we obtained a structure in the SmC\* phase that we assume is nearly bookshelf.

We applied triangular waveform to our test cells to observe electro-optical response. Typical waveform is shown in Figure 5.4. The solid line on the figures below corresponds to the increasing voltage, and dashed line corresponds to the decreasing voltage. Considering a display device that would be able to operate in a DC balanced mode, we acquired the optical response of our devices for the case of crossed polarizers aligned parallel and perpendicular to the smectic layer normal.

5.3.1 Materials

In our experiments, I used ferroelectric liquid crystal material Displaytech MX10498, which has large spontaneous polarization ($P_s \sim 200 \text{ nC/cm}^2$) and tilt angle $\sim 45^\circ$.

I have used various alignment layers: conventional PI 2555 that induces low-pretilt alignment of liquid crystals ($\sim 20 \text{ nm thickness}, \text{ zenithal anchoring energy } W_z \sim 10^{-3} \text{ J/m}^2, \text{ azimuthal anchoring energy } W_a \sim 10^{-5} \text{ J/m}^2$ [81]), SiO\textsubscript{x} deposited at the angle of $5^\circ$ (high pretilt alignment, $\sim 20 \text{ nm thick}, W_z \sim 10^{-5} \text{ J/m}^2, W_a \sim 10^{-6} \text{ J/m}^2$ [81]), SiO\textsubscript{x} deposited at the angle of $30^\circ$ (low pretilt alignment, $\sim 20 \text{ nm thick}, W_z \sim 10^{-5} \text{ J/m}^2, W_a \sim 10^{-6} \text{ J/m}^2$ [81]), Glymo (3-Glycidoxypropyl trimethoxysilane, $\sim 20 \text{ nm thick}, W_a < 10^{-6} \text{ J/m}^2$ [82]), PI Nissan 7511 and its analog PI Nissan 1211 (homeotropic alignment, $\sim 20 \text{ nm thick}, W_z \sim 10^{-4} \text{ J/m}^2$.
W_{a} \sim 10^{-5} \text{ J/m}^2 [84], \text{ and bare ITO. Anchoring energies measurements reported in references were made for nematic liquid crystals and for the low pretilt.}

5.3.2 Experimental set-up and data acquisition

Aligned FLC cell was placed on the stage of a polarizing microscope between crossed polarizers. Typical thickness cell was ~ 4 µm. Waveform was applied to the cell using Stanford System Research function generator DS345. We registered optical response of the FLC cell by measuring light intensity at the output of the polarizing microscope. For that, we used either photodiode or video camera mounted on the top of the polarizing microscope, depending on the waveform frequency. For frequencies higher than 1 Hz, we used photodiode connected to the oscilloscope Tektronix TDS 420A. For lower frequencies we used video camera connected to the computer in order to observe FLC texture behavior during switching.

Using photodiode with oscilloscope, we directly obtained electro-optical response, but with video camera we initially recorded movies of the FLC texture during switching. To convert these movies to electro-optical characteristics, we have written computer program that analyzes movies recorded by the video camera. By decomposing a movie to the single frames and analyzing statistics of pixels’ color in every frame, program builds dependence of light transmission on time and normalizes it relatively to the light transmission level of crossed and parallel polarizers.
Figure 5.4. Triangular waveform applied to the FLC cells
5.3.3 Results: electro-optical response for different alignment layers

Obtained electro-optical response graphs for different aligning layers along with screenshots of movies depicting switching are presented in Figures 5.5-Figure 5.10.

We did two sets of experiments. Results shown in Figures 5.5-Figure 5.10 were included in the first set. In the second set, we repeated experiment with PI 7511 and were able to achieve better alignment quality (Figure 5.10).

Video screenshots were taken from the initial phase of triangular waveform (increasing voltage). Dots marked with letters on the plots relate to the corresponding screenshots in the adjacent picture. Light transmission on the plots is in the relative units. 0% and 100% correspond to the transmission of light in our system through crossed and parallel polarizers correspondingly.
Figure 5.5. Electro-optical response (*top*) and screenshots of switching video (*bottom*) of the polyimide 2555 FLC cell. Waveform frequency is 0.2 Hz.
Figure 5.6. Electro-optical response (top) and screenshots of switching video (bottom) of the $5^\circ$ SiO$_x$ FLC cell. Waveform frequency is 0.2 Hz.
Figure 5.7. Electro-optical response (*top*) and screenshots of switching video (*bottom*) of the polyimide $30^\circ$ SiO$_x$ FLC cell. Waveform frequency is 0.2 Hz.
Figure 5.8. Electro-optical response (top) and screenshots of switching video (bottom) of the Glymo FLC cell. Waveform frequency is 0.1 Hz.
Figure 5.9. Electro-optical response (top) and screenshots of switching video (bottom) of the Nissan 7511 FLC cell (set #1). Waveform frequency is 0.2 Hz
Figure 5.10. Electro-optical response (top) and screenshots of switching video (bottom) of the Nissan 7511 FLC cell (set #2). Waveform frequency is 0.2 Hz
Except uniformity of director rotation, hysteresis-free and threshold-less electro-optical characteristic is important for the work of analog grayscale device. It has been shown that for voltage drive of the device, V-shaped form of the electro-optical response is only observed in the very narrow frequency range and for all other frequencies V-shaped switching is accompanied by the hysteresis, which direction can change from normal to abnormal one (in this case, FLC dipoles lag behind electric field) depending on drive frequency. At the frequency where this transition occurs (inversion frequency), one can observe threshold-less and hysteresis-free switching. The value of inversion frequency typically is pretty low (<10 Hz) and depends on electric properties of the cell, such as FLC conductivity and capacitance of alignment layers.

We have measured frequency dependence of the electro-optical response for two cells (30° SiO₂ and PI 1211) with capacitance connected in series to demonstrate inversion of hysteresis direction (Figure 5.12, Figure 5.13). For the given thickness of alignment layers and capacitors connected in series, inversion frequency for PI 1211 cell was 0.2Hz, for 30° SiO₂ cell it is close to 0.3Hz.
Figure 5.11. Angular dependence of electro-optical response for PI 7511 FLC cell: 0°, 20°, 45° with respect to polarizer axis
Value of inverse frequency of threshold-less switching can be adjusted by connecting capacitance in series and resistor parallel to the FLC cell. Choosing right parameters, it is possible to tune the FLC cell to operate at needed frequency. In Figure 5.14 we demonstrate threshold-less V-shaped switching at standard display working frequency, 60Hz for PI 1211 and 30° SiOx FLC cells. For these cells, external capacitor of 10 nF is connected in series, and resistors of 300 kOhms and 150 kOhms are connected in parallel.

Additionally, we have measured optical response of the FLC cell without alignment layer and any external electrical elements, just bare ITO. As capacitive alignment layers are necessary condition for V-shaped switching, we expected to obtain response with a hysteresis. Characteristic response in presented in Figure 5.15. We present this result to demonstrate switching of the aligned FLC cell without alignment layers, which was made possible by the aligning method described above.
Figure 5.12. Frequency dependence of electro-optical response for $30^\circ \text{SiO}_x$ cell with 10 nF capacitor connected in series for frequencies (a) 0.1 Hz, (b) 0.2 Hz, (c) 0.5 Hz.
Figure 5.13. Frequency dependence of V-shaped electro-optical response for 1211 cell with 100 nF capacitor connected in series for frequencies (a) 0.2 Hz, (b) 0.5 Hz.
Figure 5.14. V-shaped switching of PI 1211 and 30° SiOx FLC cells at 60Hz with the connected capacitor and resistor.
Figure 5.15. Electro-optical response of ITO FLC cell (waveform frequency $f=20$ Hz)
5.4 Computer simulation

In order to explain observed effect of the surface alignment layer, we need to better understand the behavior of the director on the aligning surface during switching. In previous works surface boundary conditions were defined by the fixed surface easy axis and the anchoring energy of the director associated with it. Anchoring energy is typically written in the form of Rapini-Papoular potential which includes both azimuthal (in-plane) and zenithal (out-of-plane) anchoring energies. It was considered that smectic ordering does not change in the proximity of the surface. While this approximation may work on very smooth surfaces, it was shown that in many cases effective surface melting of the smectic phase occurs\textsuperscript{44,45,46}. Theoretical\textsuperscript{42} and experimental\textsuperscript{43} work on smectic phase in confined geometries allows us to suggest that a likely scenario for the smectic phase in the close vicinity of the rough surface is elimination of the smectic order parameter and serious decrease of nematic order parameter. For this model, we assume that a thin nematic layer exists between aligning surface and the smectic bulk of the cell.

Another effect often discussed in the relation to the surface dynamic effects is gliding of the surface easy axis\textsuperscript{85}, which is usually observed for nematic liquid crystals as slow drift of the easy axis under the action of the external torque applied to the bulk of the liquid crystal. Surface gliding has not been considered to our knowledge as the effect that can play a role in a switching behavior of the V-shaped FLC device.

Finally, observation of characteristic undulations of the smectic layers for some cells during switching may suggest change in layer spacing that occurs during rotation of
the director. Variation of the smectic layer thickness requires additional work, amount of which is proportional to the compressibility module $K_4$ (or $B$, as it more frequently denoted). In smectic materials this elastic module is typically quite large, $\sim 10^6$-$10^7$ J/m$^3$, therefore considerable smectic layer thickness change does not occur in the conventional smectic devices. Very strong zenithal surface anchoring may overcome condition for the constant smectic layer thickness which would lead to layer thickness change and appearance of undulations of the smectic phase. Here we try to simulate this scenario and see if it can occur given the reasonable values of the $K_4$ and $W_z$ (zenithal anchoring energy).

Taking this into account, we can visualize four following scenarios for the switching of the smectic director at the surface.

a) **Standard approach**: smectic ordering and layer spacing is preserved in the bulk down to the very surface. Surface provides fixed easy axis, which, along with elastic and electrostatic forces, define position of the surface director.

b) **Surface melting**: we assume thin nematic layer (~100 nm) next to the aligning surfaces.

c) **Deformation of smectic layer spacing**: surface anchoring competes with smectic bulk elasticity and director may slide along the surface instead of moving on the cone during switching.
d) **Easy axis gliding:** due to finite surface viscosity, easy axis follows director on the surface.

To consider these possible scenarios, we have done computer simulation using technique described in Chapter 2. We did one modification to this method. In order to correctly demonstrate effect of abnormal hysteresis in the V-shaped SSFLC cell, one no longer can ignore conductivity of the FLC. Resulting system of equations that describe current and voltage in the equivalent circuit (shown in Figure 5.16) is

\[
\begin{cases}
C \frac{dU_C}{dt} = A \frac{dD_z}{dt} + \frac{U_{LC}}{R_{LC}} \\
U_{LC} = U - U_C
\end{cases}
\]

Here \( A \) is the electrode overlapping area, \( C \) is capacitance of alignment layers, \( U_C \) and \( U_{1,LC} \) are voltages across the aligning layers and FLC; \( D_z \) is the \( z \)-component of electric displacement in a FLC with constant ohmic resistance \( R_{LC} \).

We have used parameters of the cell and the FLC material that were used in experiment: cell thickness \( d=4 \) µm, FLC spontaneous polarization \( P_s=200 \) nC/cm\(^2\), elastic constant of the FLC \( K_{11}=K_{12}=K_{33}=5\) pN, FLC viscosity \( \gamma=0.5 \) Pa·s, cone angle of the material \( \Psi=45^\circ \), dielectric constants of the FLC \( \varepsilon_{\parallel}=\varepsilon_{\perp}=3 \), electrode area \( A = 0.3 \) cm\(^2\), electric resistance of electrodes \( R_0=0 \), orientation of the smectic layer normal \((k_\perp,k_\parallel,k_z)=(1,0,0)\).
Figure 5.16. Simplified equivalent electric circuit of the FLC cell
Other parameters, such as waveform frequency, compressibility module $K_4$, surface zenithal and azimuthal anchoring energies $W_z$ and $W_a$, capacitance of alignment layers $C$ and electric resistance of the FLC $R_{LC}$ were varied according to conditions of experiment and simulation. In the case if we did not have the exact value for the parameters, we estimated it using literature data (according to the references specified in the experimental section of this chapter). Waveform frequency that we used for these simulations was 2 Hz (unless specified otherwise), which is higher than typical frequency of 0.2 Hz used in the experiment. The reason for this we address in discussion section of this chapter.

A. **Standard approach.** To investigate effect of surface anchoring energy and pretilt on the switching characteristics of the V-shaped device, we simulate electro-optical response of three cells with different alignment layers that we measured experimentally: PI 2555, 30° SiO$_x$ and PI 7511/1211. These surfaces provide different anchoring energies (both azimuthal and zenithal) and pretilt. Results of the simulation are shown in Figure 5.17.

B. **Surface melting.** Here we repeat simulations shown for the case A, but include thin (100nm) nematic layer at the surfaces. This is realized by eliminating compressibility module $K_4$ (which is responsible for maintaining of the smectic ordering) for the layers next to the surfaces. Obtained results do not significantly change from the case A for 30° SiO$_x$ and PI 7511, but a noticeable effect on the shape of V is observed for the case of PI 2555 (Figure 5.18).
Figure 5.17. Simulated electro-optical response of FLC cell with different surface alignment layers: (a) PI 2555: $W_z=1 \text{ mJ/m}^2$, $W_a=0.01 \text{ mJ/m}^2$, pretilt angle $\theta=1^\circ$, $K_4=10^6 \text{ J/m}^3$, $R_{\text{LC}}=50 \text{ MOhm}$, $C=20 \text{ nF}$; (b) 30° SiO$_x$: $W_z=0.01 \text{ mJ/m}^2$, $W_a=0.001 \text{ mJ/m}^2$, pretilt angle $\theta=0.1^\circ$; $K_4=10^6 \text{ J/m}^3$, $R_{\text{LC}}=100 \text{ MOhm}$, $C=13 \text{ nF}$ (c) PI 7511: $W_z=0.1 \text{ mJ/m}^2$, $W_a=0.01 \text{ mJ/m}^2$, pretilt angle $\theta=89.9^\circ$, $K_4=10^6 \text{ J/m}^3$, $R_{\text{LC}}=50 \text{ MOhm}$, $C=13 \text{ nF}$.
C. **Effect of layer expansion.** We start by setting reasonably high zenithal anchoring energy \((W_z=1 \text{ mJ/cm}^2)\) and watch the motion of the director. Figure 5.19 shows angle of the director with respect to the vertical axis \(\hat{z}\) (director tilt from the plane of the cell) during switching cycle depending on the value of \(K_4\). It is clear that behavior of the director has threshold character is sensitive to the value of \(K_4\). Critical value of compressibility module for the set of used parameters which makes director slide on the surface instead of moving on the cone is \(\sim 2\times10^3 \text{ J/m}^3\), which is at least three orders of magnitude smaller than typically observed values.

D. **Easy axis gliding.** In this case we take into account gliding of the surface’s azimuthal easy axis. It has been shown in numerous works for the nematic phase that easy axis can ‘glide’ along the surface following bulk director due to effective ‘surface viscosity’ \(\gamma_s\) of the easy axis. Different mechanisms of the surface viscosity has been reported; most frequently easy gliding is related to the anisotropic adsorption/desorption of the liquid crystal molecules on the surface. Characteristic times of this gliding are usually very high - from minutes to days. Leaving out study of the nature of the surface viscosity, we incorporate simple model of the easy axis gliding.
Figure 5.18. Simulated electro-optical response of PI 2555 cell with 100 nm nematic layer at the surfaces. Parameters of the surface are the same as in the simulation presented in Figure 5.17.
Figure 5.19. Simulated motion of the director in the FLC cell dependence on compressibility module $K_4$: (1) $K_4=1 \times 10^3$ J/m$^3$, (2) $K_4=2.5 \times 10^3$ J/m$^3$, (3) $K_4=5 \times 10^3$ J/m$^3$. Other used parameters: $C=13$ nF, $W_\ell=1$ mJ/m$^2$, $W_a=0.01$ mJ/m$^2$, pretilt angle $\theta=0.1^\circ$, frequency $f=20$ Hz.
We assume that the easy axis will move to lower the surface energy $W = W_0 \sin^2 \Delta \varphi$

Here $\Delta \varphi$ is the difference between the azimuthal director at the surface and the azimuthal easy axis (defined by $\varphi_a$). We may say that the torque on the easy axis due to the anchoring energy ($2W_a \sin \Delta \varphi \cos \Delta \varphi$) is balanced by a viscous torque $\gamma_s \frac{d \varphi}{dt}$:

$$2W_a \sin \Delta \varphi \cos \Delta \varphi = \gamma_s \frac{d \varphi}{dt}$$

Change of the easy axis position $d \varphi$ is calculated from this torque balance, and the speed of the gliding is related to the value of surface viscosity $\gamma_s$. Simulation of the effect of $\gamma_s$ on V-shaped switching is presented in Figure 5.20.

E. Frequency dependence. We also simulated effect of the FLC conductivity (or, equivalently, effect of the resistance connected parallel to the FLC) with constant waveform frequency on the form of electro-optical response (Figure 5.21) for comparison with obtained experimental data.
Figure 5.20. Simulated electro-optical response of the FLC cell with easy axis gliding depending on the value of surface viscosity $\gamma_s$: (1) $\gamma_s=\infty$ (no gliding), (2) $\gamma_s=1\times10^{-4}$ Js/m$^2$, (3) $\gamma_s=1\times10^{-5}$ Js/m$^2$. Other used parameters: $W_z=1$ mJ/m$^2$, $W_a=0.1$ mJ/m$^2$, pretilt angle $\theta=0.1^\circ$, $C=13$ nF, $K_4=10^6$ J/m$^3$. 
5.5 Discussion

Comparing experimental results for all aligning materials that I have studied, one can see that when triangular waveform is applied to the cell with polyimide 2555 as alignment layer, director of FLC is not uniform in the plane of the cell during switching; there are numerous domains which are not switching simultaneously and uniformly. Such behavior leads to low contrast ratio and a bistable character of the switching. In order to separate effect of domains, we attempted to analyze the response of a single domain. The limit of applying of this method in our case lies in the resolution of the camera relative to the domain size. In most of the cases, domain size was too small for this purpose, but we were able to analyze optical response for a small domain on the middle of the viewing area, as shown in Figure 5.22. One can see that minimal transmission went down to ~25% compared to 40% in the case of looking at the full viewing area (Figure 5.5). This result shows the effect of domain switching. The fact that the V-shaped response does not go to zero for the single domain could be explained by insufficient resolution of our measurement, or possibly due to twisting of the director field in a single domain.

Using Glymo (3-Glycidoxypropyl trimethoxysilan) as an alignment layer leads to inhomogeneous texture, probably non-uniform director field and very high value of the minimal light transmission. I suggest that it is related to much lower anchoring energy of the Glymo compared to PI 2555.
Figure 5.21. Simulated electro-optical response of the FLC cell depending on the resistance of the FLC: (a) $R_{LC}=1$ MOhm, (b) $R_{LC}=2.5$ MOhm, (c) $R_{LC}=50$ MOhm.

Other used parameters: waveform frequency $f=10$Hz, $W_c=0.01$ mJ/m$^2$, $W_a=0.001$ mJ/m$^2$, pretilt angle $\theta=1^\circ$, $C=13$ nF, $K_a=10^6$ J/m$^3$. 
Figure 5.22. Small domain of the PI2555 FLC cell; (a) FLC texture; (b) Electro-optical response of the PI2555 FLC
5°SiO₃ provides more uniformity of the director during switching, and smoother, more analog-like switching and higher contrast ratio. Device with 30°SiO₃ which is distinguished from the latter case by inducing low pretilt alignment has somewhat higher minimum value of light transmission, caused by striped texture which resembles the textures observed in the case of change of the smectic layer spacing, which was considered in the previous section. The homeotropic alignment layers (PI 7511/1211) provide the most uniform director configuration and allow smooth, analog switching.

These results show that for the different cells values of minimum transmission vary from very high to fairly low. The smallest value of minimum transmission was observed for homeotropic PI 7511/1211. This result cannot be explained in the frame of 1-D switching model described above, because if director is switching perfectly uniformly in the plane of the cell, the minimum transmission will go to zero when director is parallel to the polarizer axis. As I observed in the experiment, high values of minimum transmission are related to the domain switching (it is easiest to see for the PI 2555 cell).

In Table 2, I summarize properties of some of the alignment surfaces along with the tendencies of domain switching. \( W_z \) is the zenithal anchoring energy for the case of in-plane director configuration, \( \theta \) is the pretilt angle (measured for the nematic LC).
Table 2 Properties of alignment layers and domain switching

<table>
<thead>
<tr>
<th>Aligning surface</th>
<th>$W_z$, mJ/m²</th>
<th>Pretilt $\theta$</th>
<th>Domain switching tendency</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI 2555</td>
<td>1</td>
<td>$\sim 1^\circ$</td>
<td>Strong</td>
</tr>
<tr>
<td>$30^\circ$ SiO$_x$</td>
<td>$10^{-2}$</td>
<td>$0^\circ$</td>
<td>Weak</td>
</tr>
<tr>
<td>PI 7511/1211</td>
<td>$10^{-1}$</td>
<td>$\sim 90^\circ$</td>
<td>Very weak</td>
</tr>
</tbody>
</table>

Domain switching is a 2-D (or 3-D) effect, so it cannot be described by our 1-D model. Qualitatively, it is easy to understand tendency for domain switching for stronger surface anchoring. Under the action of electric field, dipoles rotate to minimize electric field in the cell and the electrostatic bulk energy of the FLC. At the same time, the surface anchoring energy can be reduced when domains of ‘UP’ and ‘DOWN’ configurations are formed in the cell in order to minimize electric field inside the cell. Depending on relation between zenithal surface anchoring energy and energy associated with the walls between domains, either domain or uniform structure may appear energetically favorable. The value of pretilt angle promoted by the surface plays an important role, as in that case director prefers to rise above the surface, this effectively making anchoring weaker. This can explain tendency of the domain switching in the PI 2555 cell that is characterized by strong zenithal surface anchoring. Weaker anchoring, such as in the case of PI 7511/1211 and $30^\circ$ SiO$_x$ promotes more uniform switching. Undulation defects that occur during switching of $30^\circ$ SiO$_x$ could be related to the layer expansion at the surface, which we discuss below.
Bedsides domain effects, the results of our simulation has helped to explain other effects of the surface alignment layers related to the shape of electro-optical response. I have shown that strong and anisotropic anchoring energy (as in the case of simulated PI 2555 cell, Figure 5.17a) leads to more narrow shape of ‘V’, which results in highly non-linear electro-optical response. These results are in good correspondence with the experimental observations of electro-optical response of PI 2555 cell (Figure 5.5).

Weaker anisotropic anchoring (as in the case of simulated 30° SiO_x cell, (Figure 5.17b) leads to wider ‘V’ and smoother response, which also corresponds with our measurements (Figure 5.7).

Both previous aligning surfaces provided low pretilt for the FLC director. For the case of homeotropic anchoring (simulated PI 7511/1211 cell, Figure 5.17c), I used the following values of anchoring energy : \( W_z = 0.1 \text{ mJ/m}^2 \), \( W_a = 0.01 \text{ mJ/m}^2 \). Simulations have shown that such anchoring conditions lead to the widest ‘V” and smooth, analog switching. Experimentally cell with homeotropic aligning surface PI 7511/1211 has shown the best analog switching among all tested surfaces (Figure 5.9).

Now I shall discuss other possible scenarios for switching of the surface proposed above. Strong deformations of the smectic director field suggest substantial lowering of smectic ordering in the close vicinity of the surface, effectively leading to appearance of the nematic layer, thickness of which, according to different estimates, can vary from few nanometers to hundreds of nanometers. It is easy to visualize that rough surfaces should melt smectic ordering stronger than smooth surfaces, which can better accommodate
undistorted smectic layers. Results of the simulations may suggest that having melted layer next to the surface affects switching of the cells with strong surface anchoring by ‘softening’ this anchoring and effectively lowering the surface energy. For lower anchoring energies, this effect is weaker: simulated ‘PI 7511’ and ‘30° SiO,’ cells virtually did not react to the 100 nm nematic layer next to its surfaces.

Considering case of smectic layer expansion (presumably leading to appearance of the surface undulations), the simulation has shown that values of compressibility module $K_4$ that may allow surface anchoring to compete with smectic elasticity are at least three orders of magnitude lower than typical measured values. It may mean that this scenario is unlikely to take place, unless we assume very strong decrease of $K_4$ constant due to reduced smectic ordering near the surface.

Considering case of easy axis gliding, I have found that values of surface viscosity that considerably affect switching start at $10^{-4}$ Js/m$^3$, which is at least three orders of magnitude lower than reported values for nematic liquid crystals$^{86}$. However, one may speculate that in the case of smectic distortion of the director field near the surface is very high and the torque transferred from the bulk to the surface layer is much stronger than in nematic, which may explain higher easy axis gliding rates for smectic liquid crystals. I believe that effect of surface gliding in V-shaped switching should not be ignored and will be subject of the future work.

Finally I address the question of effect of waveform frequency on V-shaped response. Blinov et al has shown$^{75}$ that real V-shaped switching without hysteresis and
threshold voltage can occur only at one characteristic frequency $f_i$ (which can be quite low, <1 Hz) and is accompanied by change of the hysteresis direction from the normal to the abnormal one. This ‘inversion frequency’ depends on the electrical properties of the cell, such as capacitance of alignment layers and conductivity of the liquid crystal (and connected external elements, if any), which strongly affects form of the response (‘V’, normal ‘W’ or inverse ‘W’), as shown by the simulation (Figure 5.21) and experiment (Figure 5.12, Figure 5.13). Conductivity of FLC is strongly temperature dependent and also is affected by the mobility and concentration of the ions in the cell. Consideration of these factors was done in details in the work of Blinov et al.

In my simulations I attempted to reproduce experimental results at low frequencies of 0.2 Hz with measured parameters of the cell. However, we only could see the simulated response similar to the experimental results only for higher frequencies closer to 2 Hz. We believe that discrepancy between inversion frequency in the experiment ($f_i <$0.2 Hz) and simulations (1 Hz < $f_i$ <2 Hz) is related to the effects mentioned above: conductivity of the FLC is hard to determine accurately and the actual value of it may be way off the estimated value.

In conclusion, in this chapter I present results of the study of influence of the alignment layer on characteristics of director rotation and analog switching of ferroelectric liquid crystal that exhibit IAC phase sequence and reduced layer shrinkage. These materials allowed for the first time to test surfaces that could not be used with conventional INAC materials. I found that a homeotropic alignment layers shows the best
analog switching with most uniform director configuration and good contrast ratio, while conventional alignment layers that provide low pretilt alignment and stronger anchoring, lead to domain-like switching. I have shown that aside from considerations of 1-D model, to achieve V-shaped switching with low minimum light transmission, small zenithal anchoring energy is desired. The width of $W$ that is related to the symmetrical response of the FLC cell, allowing to use it in AC-driven devices, can be controlled by adding external capacitors/resistors or by using charge drive.
Chapter 6

Summary and Conclusions

In this dissertation I conducted experimental study on the effect of surface alignment layer on the electro-optical characteristics of surface stabilized ferroelectric liquid crystals.

- For bistable SSFLC device display, I investigated deposition parameters of obliquely evaporated SiO$_x$ on threshold voltage of the device. The lowest values of threshold voltage (~4 volts) were obtained for very thin SiO$_x$ films (~5 nm). Increase of threshold voltage with increase of SiO$_x$ thickness is mostly related to the voltage drop on SiO$_x$ film that acts as a voltage divider and to polar dipole-dipole interactions between surface and FLC molecules, which are thought to increase with thickening of the SiO$_x$ film. However, for thin SiO$_x$ aligning layers, as effects of voltage divider and polar interaction are strongly reduced, I have shown that the factor that is holding threshold voltage is the rotational viscosity of the FLC.

- I have developed experimental technique of liquid crystal alignment that does not rely on surface treatments for aligning liquid crystal materials that have a smectic-A/isotropic phase transition. It uses an air bubble, located by a
photolithographically-defined channel, to create a smooth wall for nucleation of smectic layers and to induce perpendicular molecular orientation for liquid crystal molecules.

- After being able to align ferroelectric liquid crystal that lack nematic phase, I studied the effect of the alignment layer on characteristics of director rotation and analog V-shaped switching of FLC that exhibit I-SmA-SmC phase sequence and reduced layer shrinkage. This allowed for the first time to test surfaces that could not be used with conventional I-N-SmA-SmC materials. Homeotropic alignment layers show the best analog switching with most uniform director configuration and good contrast ratio, while conventional alignment layers that provide low pretilt alignment and stronger anchoring, lead to domain-like switching, and to low contrast.

- I have done study of characteristics of processes of adsorption/desorption of liquid crystal molecules on the glass surface and proposed method which is based on correlation analysis of digital images of Shlieren textures of the studied liquid crystal. This process is also responsible for the gliding of the easy axis and can play a role in electro-optical characteristics of the SSFLC display devices.

Computer simulation work has also been done as part of the dissertation. To better understand effect of the surface alignment layer for both analog V-shaped and bistable SSFLC devices I wrote computer program that is able to simulate switching of both kinds of devices taking into account all important parameters of the FLC and the surface
alignment layer. Results of the simulation have confirmed many experimental results and allowed us to better understand the observed effects.
Appendix A

Surface gliding effect in liquid crystals

A.1 Background and introduction

Surface gliding, also known as drift of the easy axis, may play an important role in many phenomena in liquid crystals. Traditional description of the LC director in assumes a fixed position of the easy orientation axis \( \vec{e} \) on the aligning surfaces of the cell. At the same time, deviation of the director near the surfaces (for example, field-induced) from the direction \( \vec{e} \) due to a finite anchoring may result in a gradual drift of the easy axis out of its initial position. This phenomena was called ‘the gliding effect’. It is usually attributed to:

a) adsorption/desorption of LC molecules on/from the aligning surface;

b) cooperative reorientation of polymer fragments and LC molecules.

The adsorption/desorption mechanism was first proposed by Vetter et al.\textsuperscript{85} for description of the gliding effect on the surface of polyvinyl-alcohol. According to Vetter, drift of the easy axis is caused by rotation of the symmetry axes of the distribution function of the adsorbed LC molecules caused by a reorientation torque. Authors suggested that the adsorbed molecules are oriented preferably along the initial director distribution in the cell. Applied torque reorients the director next to the surface that
results in the adsorption of molecules along the new direction. As a consequence, symmetry axes of the angular distribution function of the adsorbed molecules reorients together with the associated easy axis.

The model of cooperative reorientation of the director and polymer fragments was proposed first by Kurioz et al\textsuperscript{87} for explanation of unexpectedly slow relaxation of the director in the polar plane after application of electric field to the cell with a soft polymer aligning surface. Authors proposed the following mechanism: due to the weak anchoring, the electric field rotates the director on the polymer aligning surface, which, in turn, drags the flexible polymer fragments of this surface. As a result, electric field aligns both LC molecules and flexible fragments which leads to the drift of the easy axis.

The drift of the easy axis in the azimuthal plane over a soft polymer surface was explained by Janossy et al\textsuperscript{88} in a similar way. His interpretation of the azimuthal gliding assumes that the polymer main chains can undergo conformational transitions because of the anisotropic interaction with the liquid crystal. Reorientation of the director at the surface leads to conformational changes in the polymer and, in turn, to the rotation of the easy axis towards the director. The reorientation of the easy axis decreases the anchoring torque which allows director to rotate further towards the minimum energy state (governed by an external field), resulting in the drift of the easy axis. The experiment supports this model due to the fact that easy axis’s drift speeds up when the temperature of glass-like transition in the polymer is approached.
Figure A.1. Typical setup for observing surface gliding as drift of the easy axis.
Typically drift of the easy axis is observed in the experimental set-up shown in Figure A.1. Liquid crystal cell is placed between crossed polarizers and in the external field (typically magnetic) and position of the director at the aligning surfaces is controlled by the testing laser beam.

As I mentioned before, two main mechanisms are thought to be responsible for the surface – adsorption/desorption of the molecules on/from the surface and reorientation of the flexible polymer fragments in the case of the soft aligning surface. In this chapter I consider the first mechanism. It is important to mention that timescales for the drift of the easy axis are typically quite large, of the order of magnitude of minutes or even hours\(^9\).

Another effect for which adsorption/desorption mechanism is responsible is so-called ‘\textit{Memory effect}’\(^9\). It was shown that liquid crystal molecules adsorbed to the surface can define alignment of the liquid crystal in the bulk, so alignment history affects the current state of the alignment in the bulk of the cell.

Recently two works demonstrating effects of anisotropic surface adsorption/desorption of liquid crystal molecules were published\(^91,92\). In one of them\(^92\), particularly beautiful experiment was done. Liquid crystal was filled in the cell and then was ‘sucked’ out and replaced by another liquid crystal that has drastically different pretilt angle with the surface of the cell. After that pretilt of the LC in the cell slowly changes. This effect is also due to the desorption/adsorption of LC molecules from/on the
adsorbed LC film at the substrate; change of the composition of the adsorbed layer leads to the change of the pretilt angle.

Here I discuss temperature dependence of characteristics of adsorption of molecules of the nematic liquid crystal mixture E7 on the surface that induces planar degenerated alignment of the liquid crystal. I use new technique which is based on correlation analysis of digital images of Shlieren textures of the studied liquid crystal. This method allows quantifying the memory effect and changes of its characteristics under effect of temperature and external fields. These changes in turn, allow studying the processes of adsorption and desorption of LC molecules on/from the aligning surface.

**A.2 Investigation of thermal desorption of the surface monolayer**

The proposed method for investigation of memory effect and characteristics of adsorption and desorption of liquid crystal molecules on the surface is the following. Molecules of liquid crystals that are adsorbed on the surface create so-called surface monolayer, which is bound to the surface. There is a competition between surface binding energy and thermal energy of adsorbed molecules. At the moment when thermal energy prevails, a molecule pops off from the surface. My goal was to see and quantify this process of monolayer desorption.

To achieve it, I used correlation analysis of digital images of liquid crystals Shlieren textures. A conventional glass cell was filled with liquid crystal and viewed in the
polarizing microscope between crossed polarizers. As no alignment layer was used, surface of glass induced planar degenerated alignment of the liquid crystal in the bulk of the cell, which leads to appearance of a Shlieren texture. At this point, a monolayer of liquid crystal molecules is formed on the glass surface, as molecules from the bulk adsorb at the surface.

At this moment, I take digital picture of this texture. Then, the sample is heated up to a certain temperature that is usually higher than the clearing point of the liquid crystal. By doing this, surface monolayer molecules are supplied with thermal energy which may overcome surface binding energy. The higher the heating temperature is, the higher the probability of the molecule to pop off the surface. After holding the sample with this temperature for a certain time it is cooled back to the initial temperature and the digital picture of the same cell area is taken.

It is possible to qualitatively make conclusions about adsorption/desorption processes by just looking at two obtained images. If in some area of the sample, surface monolayer did not desorb from the surface during heating, molecules of the bulk will align on this monolayer the same way as they did before, which will lead to the same pattern in the Shlieren texture in this area. In the other case, if thermal energy overcame binding energy of the monolayer and all the molecules desorbed from the surface, resulting Shlieren texture will most probably appear different, due to isotropic alignment properties of the glass surface.

To quantify this effect, I introduce correlation function
Here \( A \) and \( B \) are numeric matrices corresponding to the obtained digital images. Each of its elements represents intensity of an image pixel. This function describes similarity of two images. It returns value of one in the case of identical images and zero if two images are completely uncorrelated. Plotting correlation function versus temperature will show temperature dependence characteristics of adsorption/desorption process.

It was shown that doping of liquid crystal with fluorosurfactant significantly reduces surface memory effect\(^{93}\). It was my intention to confirm this effect using proposed technique.

### A.3 Experimental results and discussion

Liquid crystal cells were assembled from two cleaned glass substrates. The cell gap was 4.7 \( \mu \)m and was controlled by glass fiber spacers. I used two materials in our experiment: pure nematic liquid crystal mixture E7 (Merck Corp.) and the same liquid crystal doped with 2\% of Novec FC-4430 fluorosurfactant by 3M Corp. Hot stage HS-1 by Instec Inc. was used as a heater and temperature controller.
For both our samples, I conducted several thermal cycles by heating them to certain temperature \( T \) and cooling back to room temperature. For each of this cycle, I took digital pictures of the certain area of the cell in the beginning of the cycle (before heating) and in the end (after cooling). These two pictures were analyzed and correlation function was found for every temperature \( T \). The results of measurements and calculations are presented in Figure A.2.

Some of digital images taken during this experiment are shown in Figure A.3 and Figure A.4. They correspond to the points on the correlation function plot (marked with corresponding letters). As one can see, large values of correlation function as with images (a) and (b), are obtained from almost identical images, while small values, as with (c) and (d), are obtained from images that are quite different.
Figure A.2. Correlation function vs temperature for pure E7 and E7 doped with fluorosurfactant.
Figure A.3. Digital images of Shlieren texture for pure E7. (a) and (b) – before and after heating to 58°C; (c) and (d) – before and after heating to 150°C. Pairs of pictures (a), (b) and (c), (d) are taken for two different regions of the sample.
Figure A.4. Digital images of Shlieren texture for E7 doped with fluorosurfactant. (e) and (f) – before and after heating to 58ºC; (g) and (h) – before and after heating to 150ºC.

Pairs of pictures (a), (b) and (c),(d) are taken for two different regions of the sample.
As one can see from the correlation function vs temperature plot, there is some critical temperature, \( T_c \), when correlation function starts to decrease. Thermal desorption energy can be derived from this temperature. This question was raised in the work by A. Nych et al\(^{94}\) and is subject of the future work.

### A.4 Discussion

In this chapter I describe study of characteristics of processes of adsorption/desorption of liquid crystal molecules on the glass surface. I propose method which is based on correlation analysis of digital images of Shlieren textures of the studied liquid crystal.

It has been shown\(^{93}\) that fluorosurfactant dopant reduces surface anchoring energy. For degenerated azimuthal anchoring, azimuthal anchoring energy may be assumed to be zero, but zenithal anchoring energy is positive. Zenithal anchoring energy of E7 on unrubbed polyimide was measured to be 1.6 mJ/m\(^2\) without fluorosurfactant dopant, and 0.13 mJ/m\(^2\) with 2% of FC430 fluorosurfactant. Reduction of anchoring energy is also accompanied by increase of pretilt angle (0° to 21.4°).

It was also argued that 2% of fluorosurfactant can screen out aligning effect of a rubbed polymer surface which aligns liquid crystal via an anisotropic Van der Waals interaction, which leads to the reduction of the order parameter occurring in a surface
layer with a thickness of 3–200 nm (similarly to the similar effect that occurs at the rough surfaces, such as SiO).

Decrease of pinning strength of liquid crystal molecules to the surface and ‘smoothing out’ surface defects leads to large size of brushes in the Shlieren texture of the planar degenerated nematic liquid crystal. Addition of fluorosurfactant changes adsorption/desorption dynamics of the LC molecules on/off the surface which in my experiment affects change of the Shlieren in the heating/cooling cycle. The adsorption/desorption mechanism is also responsible for the speed of the drift of the easy axis. We study, among other factors, the effect of easy axis gliding on the switching of SSFLC cells in the following chapters.
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