Optical Characterization and Optimization of Display Components:

Some Applications to Liquid-Crystal-Based and Electrochromics-Based Devices

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Abstract

This dissertation is focused on theoretical and experimental studies of optical properties of materials and multilayer structures composing liquid crystal displays (LCDs) and electrochromic (EC) devices.

By applying spectroscopic ellipsometry, we have determined the optical constants of thin films of electrochromic tungsten oxide (WO₃) and nickel oxide (NiO), the films’ thickness and roughness. These films, which were obtained at spattering conditions possess high transmittance that is important for achieving good visibility and high contrast in an EC device.

Another application of the general spectroscopic ellipsometry relates to the study of a photoalignment layer of a mixture of azo-dyes SD-1 and SDA-2. We have found the optical constants of this mixture before and after illuminating it by polarized UV light. The results obtained confirm the diffusion model to explain the formation of the photo-induced order in azo-dye films.

We have developed new techniques for fast characterization of twisted nematic LC cells in transmissive and reflective modes. Our techniques are based on the characteristics functions that we have introduced for determination of parameters of non-uniform birefringent media. These characteristic functions are found by simple procedures and can be utilised for simultaneous determination of retardation, its wavelength dispersion, and twist angle, as well as for solving associated optimization problems.

Cholesteric LCD that possesses some unique properties, such as bistability and good selective scattering, however, has a disadvantage – relatively high driving voltage (tens of volts). The way we propose to reduce the driving voltage consists of applying a stack of thin (∼1µm) LC layers.

We have studied the ability of a layer of a surface stabilized ferroelectic liquid crystal coupled with several retardation plates for birefringent color generation. We have demonstrated that in order to accomplish good color characteristics and high brightness of the display, one or two retardation plates are sufficient.

Keywords: ellipsometry, liquid crystal, LCD, optical anizotropy, electrochromic, inverse problems

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List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


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## Abbreviations

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<th>Description</th>
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<tr>
<td>CRT display</td>
<td>Cathode-ray-tube display</td>
</tr>
<tr>
<td>R&amp;D</td>
<td>Research and development</td>
</tr>
<tr>
<td>EC</td>
<td>Electrochromic</td>
</tr>
<tr>
<td>LCD</td>
<td>Liquid crystal display</td>
</tr>
<tr>
<td>WO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>Tungsten oxide</td>
</tr>
<tr>
<td>NiO&lt;sub&gt;y&lt;/sub&gt;</td>
<td>Nickel oxide</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>CE</td>
<td>Coloration efficiency</td>
</tr>
<tr>
<td>( T_\text{g}(\lambda) )</td>
<td>Transmittance of bleached films</td>
</tr>
<tr>
<td>( T_\text{c}(\lambda) )</td>
<td>Transmittance of colored films</td>
</tr>
<tr>
<td>( Q )</td>
<td>The transport charge per unit area</td>
</tr>
<tr>
<td>W&lt;sup&gt;6+&lt;/sup&gt;</td>
<td>Tungsten ion</td>
</tr>
<tr>
<td>O&lt;sup&gt;2-&lt;/sup&gt;</td>
<td>Oxygen ion</td>
</tr>
<tr>
<td>s, p, d</td>
<td>Orbitals</td>
</tr>
<tr>
<td>( W_mO_{3m-1} ) and ( W_mO_{3m-2} )</td>
<td>Sub-stoichiometric oxides</td>
</tr>
<tr>
<td>( \varepsilon_F )</td>
<td>Fermi level</td>
</tr>
<tr>
<td>( E_g )</td>
<td>Band gap</td>
</tr>
<tr>
<td>( F )</td>
<td>Centers in reduced tungsten trioxide: oxygen vacancies with a trapped electron</td>
</tr>
<tr>
<td>LC</td>
<td>Liquid crystal</td>
</tr>
<tr>
<td>PhA</td>
<td>Photoalignment layer</td>
</tr>
<tr>
<td>( \varepsilon_\cdot )</td>
<td>Complex dielectric function</td>
</tr>
<tr>
<td>( \vec{H} )</td>
<td>Magnetic vector</td>
</tr>
<tr>
<td>( \vec{D} )</td>
<td>Electric displacement</td>
</tr>
<tr>
<td>( t )</td>
<td>Time</td>
</tr>
<tr>
<td>( c )</td>
<td>Velocity of light in the vacuum</td>
</tr>
<tr>
<td>( \vec{J} )</td>
<td>Electric current density</td>
</tr>
<tr>
<td>( \vec{E} )</td>
<td>Electric vector</td>
</tr>
<tr>
<td>( \vec{B} )</td>
<td>Magnetic induction</td>
</tr>
<tr>
<td>( \rho )</td>
<td>Electric charge density</td>
</tr>
<tr>
<td>( \hat{\sigma} )</td>
<td>Tensor of the conductivity</td>
</tr>
<tr>
<td>( \hat{\varepsilon} )</td>
<td>Tensor of the dielectric permittivity</td>
</tr>
<tr>
<td>( \hat{\mu} )</td>
<td>Tensor of the magnetic permeability</td>
</tr>
<tr>
<td>( \vec{N} )</td>
<td>Surface normal</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>Electromagnetic wave energy density</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$\vec{S}$</td>
<td>Poynting vector</td>
</tr>
<tr>
<td>$t$</td>
<td>Amplitude of the transmitted wave for $p$ or $s$ polarization</td>
</tr>
<tr>
<td>$r$</td>
<td>Amplitude of the reflected wave for $p$ or $s$ polarization</td>
</tr>
<tr>
<td>$A_i$</td>
<td>Amplitude of the incident wave for $p$ or $s$ polarization</td>
</tr>
<tr>
<td>$\theta_i$</td>
<td>Angle of incidence</td>
</tr>
<tr>
<td>$\theta_t$</td>
<td>Angle of transmittance</td>
</tr>
<tr>
<td>$\theta_r$</td>
<td>Angle of reflection</td>
</tr>
<tr>
<td>$\vec{k}_i$</td>
<td>Wave vector of refracted/transmitted wave</td>
</tr>
<tr>
<td>$\vec{k}_c$</td>
<td>Wave vector of the incident light</td>
</tr>
<tr>
<td>$\vec{q}$</td>
<td>Or of the normal of the interface of two anisotropic media</td>
</tr>
<tr>
<td>$\vec{p}$</td>
<td>Dipole moment</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Atomic polarizability</td>
</tr>
<tr>
<td>$N_a$</td>
<td>Number of atoms per unit volume</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Electric susceptibility</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Dielectric constant</td>
</tr>
<tr>
<td>$N$</td>
<td>Complex refractive index</td>
</tr>
<tr>
<td>$n$</td>
<td>Refractive index</td>
</tr>
<tr>
<td>$k$</td>
<td>Extinction coefficient</td>
</tr>
<tr>
<td>$A$</td>
<td>Amplitude</td>
</tr>
<tr>
<td>$B$</td>
<td>Half width</td>
</tr>
<tr>
<td>$E_c$</td>
<td>Resonance energy</td>
</tr>
<tr>
<td>$E$</td>
<td>Photon energy</td>
</tr>
<tr>
<td>$\Theta$</td>
<td>Heaviside function</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Angular frequency</td>
</tr>
<tr>
<td>$A_0, B_0, C_0$</td>
<td>Cauchy parameters</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength</td>
</tr>
<tr>
<td>EMA</td>
<td>Effective medium approximation</td>
</tr>
<tr>
<td>$\varepsilon_{\text{eff}}$</td>
<td>Effective dielectric function</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Absolute phase</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Azimuth angle</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>Relative phase shift</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Rotation angle</td>
</tr>
<tr>
<td>$R(\phi)$</td>
<td>Rotation matrix</td>
</tr>
<tr>
<td>$a, b$</td>
<td>Half-lengths of the major and minor axes of the ellipse</td>
</tr>
<tr>
<td>$J$</td>
<td>The Jones vector</td>
</tr>
<tr>
<td>$I$</td>
<td>Intensity</td>
</tr>
<tr>
<td>$T$</td>
<td>Transmittance</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>Angle describing the orientation of</td>
</tr>
</tbody>
</table>
the director of a cholesteric LC

\( g, \vartheta, \nu \)  
Constants

\( p \)  
Pitch

\( n_e, n_o \)  
Principal refractive indices

\( \gamma, \beta \)  
Parameters

TFT  
Thin film transistor

STN  
Super twist nematic

VA  
Vertical alignment

IPS  
In-plane switching

OCB  
Optically compensated band

e  
Ellipticity

UV  
Ultraviolet radiation

IR  
Infrared radiation

\( \Gamma \)  
Phase retardation

\( \theta \)  
Angle between the direction of propagation and the optical axis

d  
Thickness

\( W \)  
The Jones matrix

ChLCD  
Cholesteric liquid crystal display

CMF  
Color matching function

RGB  
Red-green-blue

TN LCD  
Twist nematic liquid crystal display

\( \chi \)  
The state of polarization

XRD  
X-ray diffractometer

SEM  
Scanning electron microscopy

FEGSEM  
Field emission electron microscopy

AFM  
Atomic force microscopy

RBS  
Rutherford backscattering spectroscopy

\( \alpha(E) \)  
Absorption coefficient

WVASE  
Variable-angle spectroscopic ellipsometer from J. A. Wollfiam Co.

RAE  
Rotating analyzer ellipsometer

MePaLC  
Measuring system

BS  
Beam-splitter
1 Introduction

Nowadays, it is impossible to imagine human life without information displays. The display industry has reached a tremendous state of technology development today. The currently produced displays are often breathtaking. Manufacturers are finding ways not only to increase their size, but also increase the resolution, make them thinner and better for the environment. Presentations of video information in 3D displace the traditional 2D. Barely 20 years ago the market was completely dominated by cathode-ray-tube (CRT) displays with sizes rarely exceeding 30 inches. Since then the achievements of R&D in the area of displays have exceeded the expectations of all but the most gifted visionaries. The manufacturing of liquid crystal displays (LCDs) has reached very mature stages and is currently done with huge glass substrates measuring over 5m² in area. The availability of such inexpensive high resolution displays has accelerated transformation of our society into a display-centric one. However, in spite of its dominance, LCDs are still in need of further improvement. Among other things, the efficiency of light utilization, cost, and optical performance characteristics of LCDs, such as the response time can still be improved.

Along with the new types of displays and improvement of existing applications comes an acute need for detailed theoretical and experimental investigations of components composing the displays. This is done in order to be able to find optimal design parameters and to fully understand the nature of physical effects occurring in them. In fact, displays are multilayered structures, so that investigations are reduced often to consideration of the layers that form a display. Optical measuring techniques which are non-destructive and highly informative are indispensable for characterization of multilayered structures. All of them are based on analysing of the optical response from the sample and further interpretation of the processes producing this response.

In general, an electromagnetic wave can change its amplitude, polarization, and direction of propagation after interaction with matter. These changes depend on geometric shapes and on optical constants of the material that, in turn, are governed by both the structure of the material and its physical properties. Extraction of information about the material from its optical response is an example of inverse problem. Solving any inverse problem involves multiple iterations of calculations of the corresponding forward problem with different initial conditions. This in turn requires deep under-
standing of optical phenomena related to the light propagation in the tested sample and fast algorithms for solving the forward problem.

One of the most powerful optical techniques for characterization of different materials, in particular, thin films is ellipsometry. It is based on exploiting polarization transformations that occur when a beam of polarised light is reflected from or transmitted through a sample under investigation. It has been successfully applied for both surface and volume analysis. Two factors make ellipsometry particularly attractive [1, 2]: (1) its essentially non-perturbing character, provided that the wavelength and intensity of the light beam have been properly chosen, and hence its suitability for in-situ measurements; and (2) its remarkable sensitivity to minute interfacial effects, such as formation of a sparsely distributed sub-monolayer of atoms or molecules.

This thesis is focused on optical investigation of the components of LCDs and electrochromic (EC) materials. The firsts are dominant on the market, whereas the seconds are attractive for manufacturing EC displays and other devices, e.g. "smart" windows.

Visual characteristics of LCD and EC displays, such as the contrast ratio, viewing angles, and colors are very sensitive to physical and geometric properties of thin films from which they are composed, chiefly their thickness and optical constants. In the case of an LCD, an essential role belongs to the configuration of the liquid crystal. To obtain a device with perfect characteristics that satisfies consumers’ constantly increasing demands, the developer should know optimal values of the parameters of the thin films composing the device. Usually, finding the optimal parameters is not an easy task. It involves a combination of experimental work, in order to determine the material’s optical constants and their wavelength dispersion, and theoretical computations that give optimal thickness and configuration. Our work follows the same pattern and includes experimental and theoretical components. Our goal was to apply traditional optical techniques for characterization and optimization of multilayered systems used for LCD and EC devices, as well as to develop new approaches. We paid special attention to modern tendencies in developing display applications. In particular, we focused on:

(1) reflective and transflective LCDs due to their low power consumption and light weight;
(2) bistable reflective polarizer-free cholesteric LCDs due to their attractiveness for numerous portable devices;
(3) birefringent color generation by ferroelectric LC devices due to their microseconds switching time and their low price;
(4) developing methods for fast and simultaneous measurements of several design parameters due to the needs of laboratory research and industrial quality control; and
(5) characterization of metal oxides needed for EC devises.
1.1 Aims

This thesis concerns optical characterization of the LCD components and EC materials, as well as solving optimization problems concerning reflective LCDs. In particular, the following strategic objectives were formulated in the beginning of the work:

- To determine the optical constants, their wavelength dispersions, the thickness and morphology of tungsten oxide and nickel oxide thin films used for EC devices, in order to find the band structure of these materials and better understand the phenomenon.
- To determine the optical constants, their wavelength dispersions and thickness of the alignment layer for nematic liquid crystals, for further interpretation of mechanisms of the trans and cis-transformations, as well as for using the data obtained through measurements in the simulation and optimization procedures.
- To develop a simple method for characterization of reflective and transmissive twisted nematic liquid crystal cells.
- To study bistable stacked low voltage cholesteric LCDs.
- To find optimal parameters of dichromatic ferroelectric LCDs with birefringent color generation.

The common feature of all the above-mentioned items is the necessity to solve inverse optical problems that in turn requires choosing appropriate models and numerical methods for computations.
2 Electrochromic displays

2.1 Principles

**Electrochromism** is the phenomenon displayed by some materials of reversibly changing optical properties under application of an electrical field [3]. Usually, the absorption and emission spectra of such materials are change. As a result, the materials’ colors that associate with the spectra are changed too. The color change is commonly between a transparent (“bleached”) state and a colored state, or between two colored states. It is natural that this phenomenon is attracted serious attention in the field of information displays. Electrochromic display that is based on principles of electrochromism has various merits such as multicolor, high contrast, optical memory, and no visual dependence on viewing angle.

2.2 Materials

Materials that color upon insertion are called cathodic; materials that color upon extraction are called anodic. Tungsten oxide (WO\(_x\)) is cathodic and turns blue when ions are inserted while nickel oxide (NiO\(_x\)) is anodic and turns brown when ions are extracted. The materials bleached if the processes are reversible. The EC properties of these thin films have been studied in the context of high-contrast nonemissive displays [4-6]. Today they have great interest for other applications, such as for anti-dazzling rear view mirrors, energy saving and comfort enhancing “smart windows” for energy efficient buildings [7].

2.2.1 Properties of WO\(_x\)

At room temperature stoichiometric WO\(_3\) exhibits a monoclinic crystalline structure with a density of 7.16 g/cm\(^3\). Corner-sharing WO\(_6\) octaedra is a base of the crystalline material structure [3]. In the amorphous structure one may assume that the basic building blocks are similar, although bond lengths and bond angles exhibit considerable disorder. The bonds are mainly of ionic character, and stoichiometric WO\(_3\) can be picted as being composed of W\(^{6+}\) and O\(^{2-}\) ions. However, the bonding is not completely ionic, and there is also a significant covalent part [8, 9]. The valence band is largely composed of O
2p orbitals, while the condition band derives mainly from W 5d orbitals. The Fermi level is positioned in the middle of the gap, as shown in Fig. 1.1.1.

![Diagram of electron distribution in WO3](image)

Figure. 2.2.1.1 Schematic band structure of WO3. Tungsten and oxygen orbitals are indicated, using standard notation, as well as the location of the Fermi level ($E_F$). The indicated numbers of electrons (e-) can be accommodated in the bands. Filled states are shaded

The stoichiometric tungsten oxide (WO$_3$) is transparent. In addition to it there exist a number of substoichiometric so-called Magneli phases of the forms W$_m$O$_{3m-1}$ and W$_m$O$_{3m-2}$ (m=1, 2, …) all the way down to WO$_2$. The sub-stoichiometric phases exhibit different colors, ranging from blue in the case of slight substoichiometry to brownish for WO$_2$. The ideal amorphous structure is a continuous random network where all bonds are satisfied [10]. In practice, various defects are presented, i.e., vacancies, dangling bonds and interstitials. Such defects are associated with non-stoichiometry. For sputter deposited tungsten oxide, most studies have reported band gap ($E_g$) from 3.0 eV to 3.4 eV [3], with a tendency that at higher pressure of the sputter gas and at higher O$_2$ admixture in reactive sputtering a $E_g$ is lower. Films prepared by sputtering have a columnar structure [3].

Several models of EC coloration of WO$_3$ have been proposed. Deb [11] was first one to suggest the information of F centers in reduced tungsten trioxide: oxygen vacancies with a trapped electron. Faughman et al. [12] have proposed the model of intervalance charge transfer supposed that the injected
electron is trapped at a $W^{6+}$ site adjusted to a proton thus forming a $W^{5+}$ color center. Light absorption occurs due to charge transfer between two neighbouring tungsten sites $W^{5+} \rightarrow W^{6+}$. Injected protons compensate for the negative charge of injected electrons. Schilmer at al. [13] have suggested that injected electrons are localized on $W^{6+}$ sites perturbing the surrounding lattice and forming small polarones. Dautremont-Smith et al. [14] have explained the light absorption by conduction electron interband transition and by transitions between the caution band and the $WO_3$ conduction band. The models of intervalence charge transfer and small polarone are the most widely accepted.

2.2.2 Properties of NiO$_y$

Nickel monoxide, NiO, exhibit a cubic NaCl structure with a density of 6.67 g/cm$^3$ [15]. It is not possible to make stoichimetric NiO crystals, since they always exhibit an excess of oxygen. The extra oxygen cannot be placed inside the NaCl structure; instead vacancies related to Ni$^{2+}$ are created, thus giving a p-type conduction character [16]. In addition to the formation of vacancies, defects, such as impurities, are usually present in NiO samples [17].

A schematic band diagram is depicted in Fig. 2.2.2.1.

![Schematic band structure of NiO](image)

Figure. 2.2.2.1 Schematic band structure of NiO. Nickel and oxygen orbitals as well as majority and minority spin states are indicated using standard notation, together with the Fermi level ($\varepsilon_F$). The indicated number of electrons (e-) can be accommodated in the bands. Filled states are shaded.

The upper part of the valence band consists of Ni 3d states. In reality, these states overlap with a wide O 2p band at ~4 to 8 eV from the Fermi level [18]; the Ni 3d and O 2p states are almost completely hybridized [19]. The
Fermi level is approximately 2 eV higher than the valence band. The optical band gap is approximately 4 eV [20]. The conduction band consists of unoccupied nickel 3d, 4s and 4p states [21].

Structures of deposited by sputtering films are columnar with a fine-grained crystallinity [3]. The intercolumnar regions allow easy mass transport across the film, which is of obvious importance for ion intercalation/deintercalation.

Charge insertion/extraction causes pronounced charges in the transmittance and only minor charges in the reflectance [22]. The pertinent coloration mechanism remains poorly known and understood up to date. There is a controversy in the literature about the type of ionic transferred upon coloration, with evidence being presented for both proton [23-27] and OH- transport [28, 29].

2.3 Device designs

Various configurations exist for electrochromic devices, depending on properties requirements. The basic elements are very similar to those of an electrochemical cell or battery. Electrochromic systems consist, in general, of two electrodes, an electrolyte, and a minimum of one electrochromic active layer. At least one of the two electrodes must be transparent in order to make visible the optical effect of the electrochromic materials situated between the two electrodes. The special interest is for coatings produced by sputter deposition. This technology is notable for its up-scaling capability, and hence stands out as being industrially viable even for large areas.

Figure 2.3.1 shows the cross section of a typical EC device and its layer components. The device consists of two substrates coated with a transparent electrode (ITO), an electrochromic film, and an ion-conducting electrolyte between the electrodes.
An important parameter used to discriminate between electrochromic materials and films is the coloration efficiency (CE) which can be simply determined by the following equation [3]:

$$CE(\lambda) = \frac{\log(T_0(\lambda)/T_c(\lambda))}{Q},$$  \hspace{1cm} (2.3.1)

where $T_0(\lambda)$ and $T_c(\lambda)$ are the transmittance of bleached and colored films, respectively, and $Q$ is the transport charge per unit area.

In order to increase coloration efficiency, improve durability and to obtain faster reaction kinetics, the research aimed recently to develop new composite materials containing mixed oxides [30-36]. A mixture of cathodic material (such as WO$_x$) and anodic material (such as NiO$_y$) offers the opportunity for enhanced behaviour compared to using oxides of either WO$_x$ or NiO$_y$ films.

**Paper I** deals with the ellipsometric study of thin films of tungsten oxide and nickel oxide, which were obtained at spattering conditions that are optimal for EC displays.
3 Liquid crystal displays

3.1 Principles

A liquid crystal display (LCD) is based on the property of LCs to change their orientation under external electric field. Being birefringent, an LC affects the polarization of the light passing through it. A change in the LC molecular orientation, its director, causes a change in the light polarization. In other words, by applying a voltage, it is possible to control the intensity of the light beam that passes through a layer of LC placed between a pair of polarizers. This is the basic principle of nematic LCD and ferroelectric LCD. Beside the LC and the polarizers, the simplest LCD element includes at least one layer of transparent electrode (usually ITO) and two alignment layers needed for setting the initial orientations of LC molecules near the surfaces (Fig.3.1.1).

![Diagram of LC cell](image)

Figure 3.1.1. Schematic presentation of LC cell (PhA – photoalignment layer).

In order to increase the contact ratio (ratio between light intensities in bright and dark states) or to improve the viewing characteristics, one or two retardation films can be added.

Cholesteric LCDs (ChLCDs) and smectic A LCD are based on scattering of the light. By applying electrical field, it is possible to change the LC molecular configuration and, as a result, scattering properties of the LC. Uniqueness of these LCDs is the bistability, i.e. the voltage is needed only for changing the LC configuration.
3.2 Materials

3.2.1 Liquid crystals

Liquid crystal is an intermediate state between a crystalline solid and isotropic liquid. Its mechanical properties are the same as mechanical properties of liquids, e.g. high fluidity, inability to support shear, formation, and coalescence of droplets. At the same time, it is similar to a crystal in that it exhibits anisotropy in its optical, electrical and magnetic properties. Based on their structural properties, LCs are divided into three main classes: nematics, cholesterics and smectics [37, 38]. Figure 3.2.1.1 shows typical orientations of molecules in LCs in these classes.

![Figure 3.2.1.1. Molecule orientations in a) nematic LC; b) cholesteric LC; c) smectic A LC and d) smectic C LC.](image)

Optical and electro-optical properties of LC that play a key role for LCD are determined by such macroscopic material parameters as principal optical refractive indexes ($n_0$, $n_\infty$), dielectric constants ($\varepsilon_{||}$, $\varepsilon_\perp$), elastic constants ($K_{11}$, $K_{22}$, $K_{33}$) and rotational viscosity ($\gamma$).
3.2.2 Photo-alignment layer

The alignment layer is used for setting desired boundary conditions for LC molecules determining the molecular orientation near the surface and the anchoring strength. These two parameters affect the surface and volume molecular orientations. This fact plays an important role in achieving the required visibility, contrast and switching times of LC devices. Traditionally, the alignment layer is a material (usually polyimide) treated with mechanical rubbing [38]. The rubbing direction and other particulars of the mechanical treatment assign the desired boundaries conditions. An attractive alternative to such an alignment layer is obtained through photo-aligning. The effect of LC photo-aligning is a direct consequence of the appearance of the photo-induced anisotropy and dichroic absorption in thin amorphous films formed by molecular units with anisotropic absorption properties. Since photo-aligning is a contactless and non-destructive technique, it enables one to produce multiple aligning patterns on the same substrate with submicron resolution without mechanical damages, avoiding electrostatic charges and dust contamination. These advantages are essential and explain the reason why a lot of efforts have been focused on the study of photo-aligning and synthesis of new materials [38]. However, an adequate explanation of photo-alignment phenomena is still lacking.

Several different approaches to realization of photo-alignment have been presented so far. What is common to all methods is that anisotropy in the alignment layer is induced by exposing linearly polarized UV light to photosensitive materials [39, 40]. The layer of the photosensitive material being an organic thin film, it must have an ability to set the required alignment, have good adhesion to glass or plastic substrates, be transparent in the visible region, be uniform over the surface, possess high resolution and high tolerance to UV and IR radiation.

Several photo-alignment mechanisms have been proposed: cross linking in poly (vinyl) cinnamate derivatives, photo-degradation in polyimides, cis-trans photoisomerization process in azobenzene side-chain polymers [39] and pure reorientation of molecules under the action of polarized light [41]. Photo-alignment due to purely reorientation of molecules under the action of polarized light [41] is especially attractive because of precise control over the pretilt angle and the strong anchoring energy of LC molecules [42]. In this case, UV light can induce an asymmetric potential field under which the stable configuration is characterized by absorption oscillator of molecules perpendicular to the activating UV light polarization. This mechanism of alignment is described by a diffusion model [41]. Under the action of polarized UV light, azo-dye molecules tend to reorient in the direction perpendicular to the plane of polarization. The probability of absorption is proportional to \( \cos^2 \theta \), where \( \theta \) is the angle between the absorption oscillator of azo-dye molecules and the polarization direction of the light (Fig.3.2.2.1).
As a result, the molecules try to orient themselves perpendicular to the plane of the light polarization and the photo-induced anisotropy appears. We have investigated and described this type of alignment material in paper II.

3.3 Types of LCDs

Three types of LCDs have been developed: (1) transmissive, (2) reflective, and (3) transflective. A transmissive LCD uses a backlight for illuminating the LCD panel, which results in high brightness and high contrast ratio. A reflective LCD is based on outside illumination, and a transflective LCD is a combination of the two previous types. Also, depending on the LC used, LCDs can be divided into nematic, cholesteric and smectic (smectic A or ferroelectric) classes.

3.3.1 Nematic liquid crystal displays

Most of the LCDs produced today consist of a nematic LC, whose molecules are easily controlled by an external electrical field. The majority of LCDs on the market are active matrix displays that use thin-film transistors (TFTs) as electrical switches to control the transmission state of LC pixels. Many TFT displays, as well as a lot of passive matrix LCDs, use twisted nematic (TN) mode. The twisted angle is 90°. The thickness of the LC layer is chosen in such a manner that the LC in the field off state acts as an optical rotator. In this case, the normal waves of the LC are linearly polarized and the following condition holds:

$$\Delta nd \gg \frac{\varphi \lambda}{\pi},$$  \hspace{1cm} (3.3.1.1)
where $\varphi$ is the total twist angle, $d$ is the LC thickness and $\lambda$ is the wavelength of light. The Eq. (3.3.1.1) is known as the Mauguin condition [37].

A TN LC cell placed between crossed polarizers is transparent in the field off state and is non-transparent in the field on state.

Among the other modes of nematic LCDs, it is necessary to mention super twist nematic (STN), vertical alignment (VA), in-plane switching (IPS), and optically compensated band (OCB).

Simulation of optical behavior of an LCD consists of two steps: firstly, the orientational distribution of the LC molecules (the optical axis) throughout the layer is established and secondly, the effect on the light propagation through this distribution is determined [37].

3.3.2 Cholesteric liquid crystal displays (ChLCDs)

Chiral nematic or cholesteric LCs are composed either of intrinsically chiral nematic materials or of non-chiral nematics with the addition of chiral dopants. Because of the periodic variation of the dielectric tensor in the helical structure (Fig. 3.2.1.1), the planar texture possesses selective reflection. Another remarkable property of ChLCDs is their bistability. This feature permits the use of the LCD display as a passive matrix with reduced display cost and to display a static image without applying voltage.

When light propagates along the helical axis, the Bragg reflection occurs for the following wavelength range:

$$n_o P < \lambda < n_e P$$

where $n_o$, $n_e$ are the principal refractive indices of the LC medium, and $P$ is its pitch [37, 38, 43-46]. The pitch, $P$, is defined as the distance for the director to rotate the full $360^\circ$ angle. If the incident wave propagates along the helical axis, the Bragg reflected light is circularly polarized with the same sense of polarization as the sense of the helix. The transmitted light has the opposite handedness of circular polarization. The wavelength of the peak selective reflection satisfies the Bragg law:

$$\lambda_o = \bar{n}P = \frac{1}{2}(n_o + n_e)P.$$ (3.3.2.2)

The spectral width of the reflection peak is given by the formula:

$$\Delta \lambda = \Delta nP,$$ (3.3.2.3)

where $\Delta n$ is the cholesteric LC birefringence. The wavelength of reflected light is equal to $\lambda_o$. 
In the focal conical texture in Fig. 3.3.2.1, most of the light can pass through the cell; it is absorbed at the bottom if there is an absorption layer.

Figure 3.3.2.1. Switching between three cholesteric textures.

A small portion of the light is scattered forward. The fingerprint texture of chiral nematic display is an intermediate state. The chiral nematic cell in Figure 3.3.2.1 is used as a reflective display [43-48].

A disadvantage of ChLCDs is these relatively high (tens volts) driving voltage. In Paper V, we proposed a way for reducing the driving voltage down to several volts. The idea is to use a display consisted of a stack of thin layers of cholesteric LC. Our paper is devoted to study optical properties of such a display.

3.3.3 Ferroelectric liquid crystal displays

FLC display offers substantially improved switching times and bistability. In the smectic-C phase the liquid crystal director twists from layer to layer (Fig. 3.2.1.1 d). Clark and Lagerwall invented the surface-stabilized ferroelectric liquid crystal device [49]: the LC is sandwiched between two parallel substrates with the cell gap \( d \) that is thinner than the helical pitch \( P \) of the LC, as shown in Fig 3.3.3.1.
Figure 3.3.3.1 Schematic diagram of the bookshelf cell structure of the surface-stabilized ferroelectric liquid crystal display. (a) The director is along the direction $A_1$ when the applied field is up. (b) The director is along the direction $A_2$ when the applied field is down. (c) Directions of the polarizers and LC.

Our Vi\textsuperscript{th} paper deals with birefringent color generation by ferroelectric LCDs.

3.4 Device designs

A typical LCD involves a LC layer sandwiched between alignment layers and transparent electrodes (Fig.3.1.1). Nematic LCDs include a pair of polarizers. In the field off state, the twist angle of the LC is usually 90 degrees, the pre-tilt angle is around 2-5 degrees, and the thickness of the LC layer varies between 4 $\mu$m - 8 $\mu$m. Image quality and switching characteristics of an LCD depend critically on the cell gap, twist angle and orientations of the polarizers with respect to orientations of the director near the surfaces. That is why it is very important to find optimal values of these parameters during an LCD development and to measure them for LCD manufacturing.

Another essential parameter of any LC cell and an LCD is its anchor energy, i.e. the energy between the molecules of the LC and the surface [38, 50]. This parameter affects the alignment of the molecules near the surface,
their volume orientation, and defines statics and dynamics of electrooptical effects.

In **III and IV papers**, we focus on development of simple and fast methods for characterization twisted nematic LC cells.
4 Colors in display applications

Human color vision is one of the most powerful human senses. It allows perception and recognition of objects at a distance, without any physical contact. The ability to produce a color picture is one of the main characteristics of a display.

Despite the seemingly infinite variety of colors that are available to us, the color of single light source can be reduced to just three variables. This property of human color vision, which is referred to as trichromacy, can be readily demonstrated in a color matching experiment.

Imagine two lights lying side by side: one is illuminated with light consisting of a mixture of three primary colors, red, green and blue, while the other can be of any arbitrary color and intensity. A person with normal color vision is able to make the two lights appear identical to himself, simply by adjusting the relative intensities of the red, green and blue lights.

The color matching functions (CMFs) are obtained from a series of such matches in which the subject sets the intensities of the three colors required to match a series of monochromatic lights of equal energy that traverse the visible spectrum. Sometimes, the value of one of the $r(\lambda)$, $g(\lambda)$, and $b(\lambda)$ CMFs is negative, which indicates that that particular primary light had to be removed from the mixture and added to the monochromatic light in order to complete the match.

Several techniques for color generation in LCDs have been proposed [38, 44]. In our research, we have focused on birefringent colors that can be produced by bistable ferroelectric LCs [38]. The principle of birefringent color generation is based on producing a certain light spectrum that corresponds to the desired color by a stack of anisotropic plates placed between a pair of polarisers [38, 44]. Since such LCDs do not contain color filters, they are cheaper and have increased luminance. From the mathematical point of view, finding optimal parameters of an LCD based on birefringent color generation is a multi-parametric optimization problem, where it is necessary to obtain parameters of the plates in the stack in order to produce the required spectrum. Solving this optimization problem in the most general case involves quite a complicate procedure. The techniques developed for the synthesis of static optical filters require plates having the retardation that is an integer multiple of a certain value, e.g. $d\Delta n$, or is based on some symmetrical orientations of the plates [38, 44]. Consequently, solutions obtained in this way involve a relatively large number of the retardation plates that can
be very far from the optimal number. Moreover, these techniques were developed for static filters and cannot be adapted directly for an LCD with birefringent color generation, because at least two working states, e.g. dark and colored bright, have to be realised. The LCDs based on birefringent color generation reported in the literature, as well as tunable optical filters, have relatively complicated structure that include either several LC layers or many birefringent plates [38]. In the present work, we have made an attempt to overcome this inefficiency by solving the multi-parametric inverse problem: finding the optimal parameters of a system consisting of an LC layer and several retardation films, when the system depending on the state of the LC produces the desired color. To build the composition function for this inverse problem, we have used the color coordinates of RGB space [44]:

$$\begin{bmatrix} R \\ G \\ B \end{bmatrix} = \int \begin{bmatrix} r(\lambda) \\ g(\lambda) \\ b(\lambda) \end{bmatrix} L(\lambda)T(\lambda)d\lambda,$$

where $r(\lambda)$, $g(\lambda)$, $b(\lambda)$ are the spectral tristimulus values [47], $L(\lambda)$ is the spectrum distribution of the illuminating light, $T(\lambda)$ is the transmittance or reflectance of the system. Relative values of the RGB coordinates characterize a color, whereas their absolute values are proportional to the brightness. Evidently, the color gamma and brightness of such a device is defined by the function $T(\lambda)$ that depends on the orientation of the polarizers, orientations and retardations of the LC layer and retardation plates.

In paper VI, we study birefringent color generation by ferroelectric LCD. Dealing with ChLCDs in paper V, we focus on the structures that reflect green color.
5 Light propagation in media

Since our investigation is based on optical measurements and simulations, it is important to have a deep understanding of phenomena related to light interaction with materials under study. Theory of electromagnetic fields is encapsulated in Maxwell’s equations. In combination with Lorentz’s equation for the electromagnetic force, they describe all the phenomena arising from interactions between electromagnetic fields and matter, as long as quantum effects may be neglected. Maxwell’s equations can be written in the form [51, 52]:

\[
\nabla \times \vec{H} - \frac{\partial \vec{D}}{\partial t} = \vec{j}
\]

\[
\nabla \times \vec{E} + \frac{\partial \vec{B}}{\partial t} = 0
\]

\[
\nabla \cdot \vec{D} = \rho
\]

\[
\nabla \cdot \vec{B} = 0.
\]

These equations are supplemented by material equations which describe the behaviour of substances under the influence of the field:

\[
\vec{j} = \sigma \vec{E}
\]

\[
\vec{D} = \varepsilon \vec{E}
\]

\[
\vec{B} = \mu \vec{H}.
\]

Here, \( \vec{H} \) denotes the magnetic vector, \( \vec{D} \) the electric displacement, \( t \) time, \( c \) the velocity of light in vacuum, \( \vec{j} \) the electric current density, \( \vec{E} \) the electric vector, \( \vec{B} \) the magnetic induction, \( \rho \) the electric charge density, and \( \sigma, \varepsilon, \mu \) are, respectively, the tensors of the conductivity, the dielectric permittivity, and the magnetic permeability.

Throughout this dissertation we consider materials that are nonmagnetic (\( \mu = 1 \)) and non-conducting (\( \sigma = 0 \)) in the optical range and assume the absence of electrical charge (\( \rho = 0 \)).
From the equations (5.1-5.7), one can obtain equations for boundary conditions at a surface of discontinuity. The continuity equations for the tangential components of $\vec{E}$ and $\vec{H}$ read:

$$\vec{N} \times (\vec{E}_1 - \vec{E}_2) = 0$$  \hspace{1cm} (5.8)

$$\vec{N} \times (\vec{H}_1 - \vec{H}_2) = 0$$  \hspace{1cm} (5.9)

and the continuity equations for the normal components of $\vec{D}$ and $\vec{B}$ read:

$$\vec{N} \cdot (\vec{D}_1 - \vec{D}_2) = 0$$  \hspace{1cm} (5.10)

$$\vec{N} \cdot (\vec{B}_1 - \vec{B}_2) = 0.$$  \hspace{1cm} (5.11)

Here $\vec{N}$ is the surface normal and indices 1 and 2 refer to two media at the interface.

The energy density of an electromagnetic wave is written as

$$\sigma = \frac{1}{2\mu_0}(\vec{E} \cdot \vec{D} + \vec{H} \cdot \vec{B}).$$  \hspace{1cm} (5.13)

The direction of light propagation is collinear with the Poynting vector:

$$\vec{S} = \frac{c}{\mu_0} (\vec{E} \times \vec{B}).$$  \hspace{1cm} (5.14)

The Poynting vector describes the energy transfer, i.e. the flow of energy per unit area and per unit time. It satisfies the equation of the conservation of energy:

$$\nabla \cdot \vec{S} + \frac{\partial \sigma}{\partial t} = 0.$$  \hspace{1cm} (5.15)
6 Reflection and refraction at interfaces

The phenomena of reflection and refraction, which may occur when an arbitrary, not necessarily electromagnetic, wave hits the interface between two different media, can be quite complicated, in particular for non-isotropic media.

When a plane wave falls onto the boundary between two isotropic media with different optical properties, it splits into a transmitted wave proceeding into the second medium and a reflected wave propagating back into the first medium. This follows from the boundary conditions (Eqs. (5.8-5.11)). Relations between the amplitudes of these three waves are known as Fresnel’s formulae [51]:

\[
t_p = \frac{2 \sin \theta \cos \theta}{\sin(\theta_1 + \theta)} A_p \\
t_s = \frac{2 \sin \theta \cos \theta}{\sin(\theta_1 + \theta)} A_s \\
r_p = \frac{\tan(\theta_1 - \theta)}{\tan(\theta_1 + \theta)} A_p \\
r_s = -\frac{\sin(\theta_1 - \theta)}{\sin(\theta_1 + \theta)} A_s.
\]

Here \( t, r, \) and \( A \) denote amplitudes of the transmitted, reflected, and incident waves, respectively, the indexes \( s \) and \( p \) refer to the corresponding components of the polarization, \( \theta_p, \theta_t, \theta_r \) are the angles of incidence, transmittance, and reflection, respectively. The graphs of reflectivity for \( p \) and \( s \) polarization along the flat interface between air and a transparent medium versus the refractive index of the medium and the angle of incidence are shown in Fig.6.1.
Measuring reflectivity for $p$ polarization versus angle of incidence or the Brewster angle enables one to determine the refractive index. More sensitive and, therefore, more accurate results are obtained from ellipsometric measurements in which the polarization of reflected light is determined. The polarization state of the light in ellipsometry is described by two parameters, $\psi$ and $\Delta$, introduced in the equation [58].

$$\tan(\psi)e^{i\Delta} = \frac{R_p}{R_s}$$

(6.5)

where $R_p$ and $R_s$ are the Fresnel reflection coefficients for $p$ and $s$ components. Figure 6.2 shows the graph of the angle $\psi$ and the phase difference $\Delta$ versus refractive index and the angle of incidence.
Analytic expressions for amplitudes of reflected and transmitted waves in anisotropic medium are much more complicated than in the isotropic case. That is why the majority of the papers that studied the boundary conditions between two media, at least one of which is anisotropic, considered only special cases, e.g. normal incidence, light propagation along the optical axis or parallel to it.

In the coordinate free-approach [53, 54], the wave vectors of refracted and transmitted waves can be expressed through the wave vector \( \vec{k}_i \) of the incident light and the unit normal of the interface of two anisotropic media in the following manner (Fig.6.3):

\[
\vec{k}'_j = [\vec{q}, [\vec{k}, \vec{q}]] + \eta'_i \vec{q} = \vec{b} + \eta'_i \vec{q},
\]

(6.6)

where the index \( j \) corresponds to ordinary (\( o \)) or extraordinary (\( e \)) waves and the index \( i \) corresponds to transmitted (\( t \)) waves.

![Figure 6.3. Orientations of the wave vectors of the reflected and transmitted waves with respect to the normal of the interface of two anisotropic media and their optical axes.](image)

The values of the parameters \( \eta'_i \) are found as solutions of Eq. (6.6) and the equation for the wave normal for the given media 1 and 2 with dielectric tensors \( \hat{\varepsilon}_1 \) and \( \hat{\varepsilon}_2 \) and orientations of the optical axes \( \hat{c}_1 \) and \( \hat{c}_2 \). In other words, the end of the vector of refraction is found as a point of intersection of with the surface of the normals [53-55]. The amplitude relations are found from the boundary conditions, Eqs. (5.8-5.11).
7 Modeling of optical properties

7.1 Introduction to the physics of dielectric function $\varepsilon(\omega)$

Under the influence of electric field, the positive and negative charges inside each atom are displaced from their equilibrium positions [56, 57]. In most dielectrics, this charge separation is directly proportional to and in the same direction as the electric field. The induced dipole moment is

$$\vec{p} = \alpha \vec{E},$$  \hspace{1cm} (7.1.1)

where the constant $\alpha$ is the atomic polarizability. The dielectric constant of a medium depends on the manner in which the atoms are assembled. Let $N_a$ be the number of atoms per unit volume. Then the polarization can be written approximately as

$$\vec{P} = N_a \vec{p} = N_a \alpha \vec{E} = \varepsilon_0 \chi \vec{E},$$ \hspace{1cm} (7.1.2)

where $\chi$ is electric susceptibility, $\varepsilon_0$ is a dielectric constant. The dielectric function $\varepsilon$ of the medium is thus given by

$$\varepsilon = \varepsilon_0 (1 + \chi) = \varepsilon_0 (1 + \frac{N_a \alpha}{\varepsilon_0}).$$ \hspace{1cm} (7.1.3)

The last expression is only valid when the dipole density is very low and the correction for the local field should be done. One common expression for the local field that can be obtained experimentally or theoretically is:

$$\vec{E}_{loc} = \vec{E} + \vec{P} / 3 \varepsilon_0,$$ \hspace{1cm} (7.1.4)

which leads to the Clausius-Mossoti relation:

$$\varepsilon = 1 + \frac{1}{\varepsilon_0 V} \int \alpha dV$$ \hspace{1cm} (7.1.5)

The exact form of Eq. (7.1.5) depends on the structure of the material studied.

Dipoles can be characterized as either permanent or induced. Permanent dipoles cannot follow the rapid oscillation of the electric field at optical frequencies and will not contribute to the dielectric function. Induced dipoles
can be either electronic or ionic. Electronic dipoles arise from the displacement of electrons relative to the nucleus whereas ionic dipoles arise from displacement of a charged ion relative to other ions. The ionic contribution above approximately 1 eV is small due to the inertia of the dipole and therefore the dielectric function for energies above 1 eV is almost completely dependent on the electronic polarization [58]. Excitation of dipoles can explain both the dispersion and absorption. The real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of dielectric function $\varepsilon$ are strongly correlated via the Kramers-Kroning relations [1, 2, 58]. If $\varepsilon_1$ is known for all frequencies $\varepsilon_2$ can be calculated and vice versa. Since many transitions are very local in energy, it is sometimes possible to make approximations that enable to perform a calculation even if one part is not known for all frequencies. The optical properties of the material under study can be obtained in terms of the complex dielectric function $\varepsilon = N^2 = \varepsilon_1 + i\varepsilon_2$, or, alternatively, in terms of the complex refractive index, $N = n + ik$.

7.2 Models of $\varepsilon(\omega)$

7.2.1 Lorentz oscillator

The Lorentz model depicts the oscillating charge as a spring oscillator driven by an external force, where the driving force is the electromagnetic wave. In this case assumes that the particles are bound with an elastic force and that the particles experience “friction” when they oscillate. It describes the dielectric response of bound charges like localized electrons or ions. The complex dielectric function for the Lorentz oscillator is given as [58]:

$$\varepsilon_{\text{Lorentz}}(E) = \varepsilon_1 + i\varepsilon_2 = \varepsilon_- + \frac{A}{E_c^2 - E^2 - iBE}, \quad (7.2.1.1)$$

where $\varepsilon_-$ is a dielectric function at high energy contribution, $A$ and $B$ are the amplitude and the half width of the $\varepsilon_2$ peak, respectively, and $E_c$ is the resonance energy.

7.2.2 Tauc-Lorentz oscillator

This empirical parametrization is based on the Tauc expression for the imaginary part of the dielectric function near the band edge [59], and the Lorentz oscillator model. If only a single transition is considered, then the imaginary part of the dielectric function of the TL model is given by [60]:

$$\varepsilon_2(E) = \frac{AE_cB(E - E_g)^2}{(E^2 - E_c^2)^2 + E^2B^2} \frac{\Theta(E - E_g)}{E}, \quad (7.2.2.1)$$
where $E$ is the photon energy, $A$ and $B$ represent the amplitude and broadening of the $\varepsilon_2$ peak, respectively, $E_r$ is the resonance energy for the Lorentz oscillator, $E_g$ is the Tauc gap and $\Theta(E-E_g)$ is the Heaviside function [$\Theta(E) = 1$ for $E \geq 0$ and $\Theta(E) = 0$ for $E < 0$].

The expression for $\varepsilon_1$ is obtained by a Kramers-Kronig integration of $\varepsilon_2$ [58, 60]:

$$\varepsilon_1(E) = \varepsilon_{\infty} + \frac{2}{\pi} P \int_{E_g}^{\infty} \frac{\xi \varepsilon_2(\xi)}{\xi^2 - E^2} d\xi. \quad (7.2.2.2)$$

where $\varepsilon_{\infty}$ is the high frequency contribution to $\varepsilon$.

### 7.2.3 Cauchy dispersion model

The Cauchy dispersion model [58] corresponds to a region where $\varepsilon_2 \approx 0$ in the Lorentz model and this model can be derived by assuming $B \to 0$ at $\omega \ll \omega_0$. The Cauchy model is given by

$$n = A_0 + \frac{B_0}{\lambda^2} + \frac{C_0}{\lambda^4} + \ldots; \quad k=0 \quad (7.2.3.1)$$

### 7.3 Inhomogeneous materials

#### 7.3.1 Effective medium approximation

Very few interfaces are perfectly flat or consist of only one material. Often non-ideal interfacial effects such as roughness or compositional intermixing have to be included. Transmittance and reflectance of electromagnetic radiation travelling through composite films can be modeled using various theories. When determining the optical constants, effective medium approximation (EMA) is used. Several different approximations exist such as the Bruggeman approximation and Maxwell-Garnett approximation [58]. They all have in common that the effective dielectric function is a function that depends on the volume fractions of the constituents as well as the constituents’ dielectric functions. The Bruggeman EMA, which probably is the most widely used effective medium theory, is based on the Mie theory of scattering. The model assumes the particles to be spherical in shape, much smaller than the wavelength of the incoming light and randomly intermixed. Usually a particle radius of 10 nm or smaller is sufficient. The Bruggeman EMA is defined by

$$\sum_{i=1}^{m} f_i \frac{\varepsilon_i - \varepsilon_{\text{eff}}}{\varepsilon_i + 2\varepsilon_{\text{eff}}} = 0, \quad \sum_{i=1}^{m} f_i = 1 \quad (7.3.1.1)$$
where $\varepsilon_{\text{eff}}$ is the effective optical properties of layers composed of several materials, $m$ is the number of constituents, and $f_i$ and $\varepsilon_i$ are the volume fraction and the complex dielectric function of constituent $i$, respectively. EMA does not take into account any anisotropy and is only valid when the optical anisotropy of the constituents is low.

### 7.3.2 Index-graded model

Index-grading of a film along the direction of the film normal (from top to bottom through the film) is usually described by modeling the film with several thin sublayers (Fig. 7.3.2.1), each of which is uniform, but with the properties of each layer slightly different from the layers above and below.

![Figure 7.3.2.1](image)

Figure 7.3.2.1. Schematic representation of the film by index-graded layer $N_i$, is the complex refractive index of the $i$-th layer.

The properties of the individual layers are calculated from the specified grading profile which in simple cases may be linear but generally can be of arbitrary complexity.

### 7.3.3 Model of uniform twisted media

From the optical point of view, chiral LC (twisted nematics and cholesterics) are nonuniform anisotropic media. The majority of them have a linear helical axis that is perpendicular to the director orientations. This means that optical characteristics of such an LC change only in one direction (see Fig. 7.3.3.1) [37, 38, 61-64].
Figure 7.3.3.1. Schematic illustration of the distribution of the local dielectrical tensor for chiral LC.

Therefore, chiral LC may be treated as a layered structure, where each layer is a thin uniform anisotropic medium whose optical axis is coincident with the director of the LC (Fig. 7.3.3.2.).

![Diagram of chiral LC]

Figure 7.3.3.2. Model presentation of chiral LC as a layered structure.

The angle describing the orientation of the director (or the optical axis) of a cholesteric LC changes along the Z axis according to the formula:

$$\varphi = g z = \frac{2\pi}{P} z,$$  \hspace{1cm} (7.3.3.1)

where $g$ is a proportionality constant, $P$ is the pitch. Such a structure is shown in Fig. 7.3.3.3.
Figure 7.3.3.3. Schematic illustration of the structure of a cholesteric LC. The dielectric tensor in the local system of coordinates has the diagonal form:

$$\hat{\varepsilon}_i = \begin{pmatrix} \varepsilon_1 & 0 & 0 \\ 0 & \varepsilon_2 & 0 \\ 0 & 0 & \varepsilon_3 \end{pmatrix}, \quad (7.3.3.2)$$

where $\varepsilon_1, \varepsilon_2, \varepsilon_3$ are the principal values of the dielectric tensor, and $\varepsilon_1 = \varepsilon_0 n^2_z, \varepsilon_2 = \varepsilon_0 n^2_x, \varepsilon_3 = \varepsilon_0 n^2_y$, $n_x, n_y, n_z$ are the principal refractive indices, and $\varepsilon_0$ is the dielectric constant.

The dielectric tensor of cholesteric LC in the laboratory system of coordinates is:

$$\hat{\varepsilon}(z) = \hat{R}(-\varphi) \hat{\varepsilon}_i \hat{R}(\varphi), \quad (7.3.3.3)$$

where $\hat{R}(\varphi)$ is the coordinate rotation matrix.

Performing the matrix multiplication, we find:

$$\hat{\varepsilon}(z) = \begin{pmatrix} \bar{\varepsilon} + \frac{1}{2} \Delta \varepsilon \cos 2gz & \frac{1}{2} \Delta \varepsilon \sin 2gz & 0 \\ \frac{1}{2} \Delta \varepsilon \sin 2gz & \bar{\varepsilon} - \frac{1}{2} \Delta \varepsilon \cos 2gz & 0 \\ 0 & 0 & \varepsilon_3 \end{pmatrix}, \quad (7.3.3.4)$$

where $\bar{\varepsilon} = 1/2(\varepsilon_1 + \varepsilon_2); \quad \Delta \varepsilon = \varepsilon_1 - \varepsilon_2 = \varepsilon_0(n^2_z - n^2_x)$.

Since molecules of termotropic LC are non-polar [50], the dielectric tensor is a periodic function of the $Z$-coordinate with period $\frac{P}{2}$. Introducing parameters $\gamma = 1/2(n^2_z - n^2_x)$ and $\beta = 1/2(n^2_y + n^2_z)$, Eq. (7.3.3.4) becomes:

$$\hat{\varepsilon}(z) = \varepsilon_0 \begin{pmatrix} \beta + \gamma \cos 2gz & \gamma \sin 2gz & 0 \\ \gamma \sin 2gz & \beta - \gamma \cos 2gz & 0 \\ 0 & 0 & n^2_o \end{pmatrix}. \quad (7.3.3.5)$$
Our investigation is based on ellipsometric methods for characterization of materials and interfaces between them. Ellipsometry, in contrast to the other optical techniques such as reflectometry or spectroscopy, operates with the state of light polarization. That is a reason to go into details of theory of the light polarization.

The propagation of light can be explained by using the description of light as a transverse electromagnetic field. The light wave in a medium is linked to the induced motion of the electric charges of electrons and atomic nuclei, constituting macroscopic electric currents. On the other hand, it is mostly safe to neglect the induced magnetization, since the motion of magnetic moments of electrons and nuclei is too slow to follow the rapid optical oscillations. Thus, the most important quantity describing the light wave is the vector of its electric field amplitude, $\vec{E}$. The existence of preferential directions of the action that the electric field in the wave exerts on electric charges in matter is the reason for the importance of its polarization that is a property of all types of vector waves. In general, once the polarization of $\vec{E}$ has been determined, the polarization of the remaining field vectors $\vec{D}$, $\vec{H}$, and $\vec{B}$ can be found as interrelated by Maxwell’s field equations (5.1-5.4).

The spatial and temporal dependence of the electric field $\left(\frac{\partial}{\partial t}\vec{E}, \frac{\partial^2}{\partial t^2}\vec{E}\right)$ in a uniform, isotropic medium of the complex permittivity $\varepsilon$ is described by the wave equation [1, 2, 51-58, 62]:

$$\nabla^2 \vec{E} - \frac{\varepsilon(\omega)}{c^2} \frac{\partial^2}{\partial t^2} \vec{E}(\vec{r}, t) = 0, \quad (8.1)$$

where $\omega$ is the angular frequency of the light wave, and $c$ is the light velocity in vacuum. A solution of the wave equation is the monochromatic plan wave propagation along the z-axis of an orthogonal coordinate system,

$$\tilde{E}(z, t) = \text{Re} \left\{ \begin{bmatrix} E_x \\ E_y \end{bmatrix} e^{i(z\omega - ct)} \right\}, \quad (8.2)$$

here $E_x$ and $E_y$ are the complex amplitudes of $\tilde{E}$ along the x- and y-axes; they can be arranged conveniently in the 2 x 1 column vector.

The components $E_x$ and $E_y$, to be more precise, their ratio describe the state of polarization. If the ratio is a real number, i.e. both components have
the same phase, the light polarization is linear, otherwise elliptical or circular. Any polarization of light can be decomposed into two mutual orthogonal components. Figure 8.1. shows the example of the decomposition of elliptically polarised light into two mutually perpendicular plane polarised waves.

Figure 8.1. (a) Elliptically polarised light; (b) decomposition of elliptically polarised light into two mutually perpendicular plane polarized waves with a phase difference $\Delta$.

The convenient representation of polarised light uses a set of four parameters, introduced by Sir George Stokes in 1852. The advantage of this representation that is called the Stokes formalism is the use of a description of light polarization that is linked to a measurement scheme. Four values have to be measured to identify the state of polarization that is described by the Stokes vector:

$$\vec{S} = \begin{pmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \end{pmatrix} = \begin{pmatrix} I_x + I_y \\ I_x - I_y \\ I_{\pi/4} - I_{-\pi/4} \\ I_R - I_L \end{pmatrix}, \quad (8.3)$$

where $I_x$, $I_y$, $I_{\pi/4}$, and $I_{-\pi/4}$ are the intensities passed through an ideal linear polarizer aligned at the angles of 0, $\pi/2$, $\pi/4$ and $-\pi/4$, respectively, $I_R$ and $I_L$ are the intensities transmitted by ideal right- and left-circular polarizers, respectively.

The four elements of $\vec{S}$ are directly obtained from intensity measurements and are related by the expression:

$$S_0^2 = S_1^2 + S_2^2 + S_3^2. \quad (8.4)$$

According to Eq. (8.3), $S_0$ is the intensity of the beam, $S_1$, $S_2$, and $S_3$ can have any real value between $-S_0$ and $S_0$. Equation (8.4) allows a representation of the polarization states on the surface of a sphere, which is called a Poincare spherè as shown in Figure 8.2.
Figure 8.2. Poincaré sphere.

The polarization state of the light in ellipsometry is described by two parameters, $\Delta$ and $\psi$ (Eq. 6.5).
9 The Jones vector representation

The Jones vector, introduced in 1941 by R.C. Jones [65], efficiently describes the polarization state of a plane wave. In this representation, the plane wave is expressed in terms of its complex amplitudes \( E_x = |E_x|e^{i\delta_x} = A_x e^{i\delta_x} \), \( E_y = |E_y|e^{i\delta_y} = A_y e^{i\delta_y} \), as a column vector

\[
J = \begin{pmatrix}
A_x e^{i\delta_x} \\
A_y e^{i\delta_y}
\end{pmatrix}
\]  
(9.1).

The Jones vector contains complete information about the amplitudes and the phases of the electric field vector components and specifies the wave uniquely. Figure 9.1 shows examples of some polarization states and the corresponded Jones vectors.

a) Linear x polarized
\[
|E_x| \neq 0 \quad |E_y| = 0
\]

b) Linear -45° polarized
\[
|E_x| = |E_y| \quad \delta_y - \delta_x = \pi
\]

c) Right-hand circular polarized
\[
|E_x| = |E_y| \quad \delta_y - \delta_x = \frac{\pi}{2}
\]

Figure 9.1. Examples of the polarization states and the corresponded Jones vectors.
In a lossless medium, it is convenient to use the normalized Jones vector, which satisfies the following condition:

\[ J^* \cdot J = 1, \quad (9.2) \]

where the asterisk (*) denotes complex conjugation.

The absolute phase of the vibrations is irrelevant; both components of the Jones vectors can be multiplied simultaneously by a complex number of unit modulus, leaving observable quantities of polarized vibrations unchanged.

The Jones vector representation can be used to calculate the transmitted intensity of the light passing through an optical system. The Jones vector of the incident light can be written as

\[ \vec{E} = \begin{pmatrix} E_x \\ E_y \end{pmatrix} \quad (9.3) \]

where \( E_x \) and \( E_y \) are the components in the \( xy \)-coordinate system. The intensity is calculated as follows:

\[ I \approx |E_x|^2 + |E_y|^2 \quad (9.4) \]

Let the emerging beam be represented by

\[ \vec{E}' = \begin{pmatrix} E'_x \\ E'_y \end{pmatrix} \quad (9.5) \]

The transmittance can then be calculated as follows [65-69]:

\[ T = \frac{|E'_x|^2 + |E'_y|^2}{|E_x|^2 + |E_y|^2} \quad (9.6) \]

Note that if the incident light is normalized, the denominator is equal to 1.

9.1 The Jones matrix for twisted nematic liquid crystals

To calculate parameters of the light passed through a twisted nematic liquid crystal (TN-LC) cell at normal incidence, the Jones matrix method described earlier can still be used if the medium is divided into a large number \( N \) of thin plates of equal thickness. Each thin plate is then treated as a homogenous retardation plate with an azimuth angle, \( \psi \). The twist of the liquid crystal medium is assumed to be linear. The phase retardation of each thin plate is \( \Gamma / N \) where [65-69]
\[ \Gamma = \frac{2\pi}{\lambda} (n_e - n_o) d \]  

(9.1.1)

and where \( n_o \) and \( n_e \) are the ordinary and the extraordinary refractive indices of the liquid crystal medium, respectively. For the liquid crystals with positive birefringence \( \Delta n > 0 \) the \( e \)-axis is the “slow” axis and the \( o \)-axis is the “fast” axis. If the optical axis is not parallel to the surfaces, the extraordinary refractive index has to be replaced by

\[ \frac{1}{n_e^2} = \frac{\cos^2 \theta}{n_o^2} + \frac{\sin^2 \theta}{n_e^2} \]  

(9.1.2)

where \( \theta \) is the angle between the direction of propagation and the optical axis. In most nematic liquid crystal cells there is a small pretilt angle (1-3°) relative to the surface. The plates are oriented at azimuth angles \( \rho, 2\rho, 3\rho, \ldots, (N-1)\rho, N\rho \) where \( \rho = \phi / N \) and \( \phi \) is the total twist angle of the liquid crystal. The overall Jones matrix for the \( N \) plates is given by [51, 52, 70-73]

\[ M = W_N W_{N-1} \cdots W_1 W_2 W = \prod_{m=1}^{N} W_m = \prod_{m=1}^{N} R(-m\rho) W_0 R(m\rho) \]  

(9.1.3)

where \( R \) is the rotation matrix, \( W_m \) is the Jones matrix for the \( m \)th plate and \( W_0 \) can be written

\[ W_0 = \begin{pmatrix} e^{-\pi/2N} & 0 \\ 0 & e^{\pi/2N} \end{pmatrix} \]  

(9.1.4)

Using \( \rho = \phi / N \) and \( R(\psi_i)R(\psi_i) = R(\psi_i + \psi_i) \) Eq. (9.1.3) can be written

\[ M = R(-\phi) \left( W_0 R \left( \frac{\phi}{N} \right) \right)^N = R(-\phi) \begin{pmatrix} \cos \frac{\phi}{N} e^{-\pi/2N} + \sin \frac{\phi}{N} e^{\pi/2N} \\ -\sin \frac{\phi}{N} e^{-\pi/2N} + \cos \frac{\phi}{N} e^{\pi/2N} \end{pmatrix}^N \]  

(9.1.5)

where \( \phi \) is the total twist angle. After some algebra and at \( N \to \infty \) the result is given by [57, 74]

\[ M = \begin{pmatrix} \cos \phi & -\sin \phi \\ \sin \phi & \cos \phi \end{pmatrix} \begin{pmatrix} \cos X - i \frac{\Gamma \sin X}{2X} & \phi \frac{\sin X}{X} \\ -\phi \frac{\sin X}{X} & \cos X + i \frac{\Gamma \sin X}{2X} \end{pmatrix} \]  

(9.1.6)
where

\[ X = \sqrt{\phi^2 + \left( \frac{\Gamma}{2} \right)^2} \]  

(9.1.7)

This is the exact expression for the Jones matrix for a linearly twisted nematic liquid crystal medium. If \( V \) is the polarization state of the incident light, the polarization state of the emerging beam is given by

\[ V' = MV \]  

(9.1.8)

where \( M \) is given by Eq. (9.1.6). It is often useful to examine the polarization state in the local principal coordinate system (\( eo \)) where the \( e \) component is parallel to the director and the \( o \) component is perpendicular to the director. In this case the result can be written

\[
\begin{pmatrix}
V'_e \\
V'_o
\end{pmatrix} =
\begin{pmatrix}
\cos X - i \frac{\Gamma \sin X}{2X} & \frac{\phi \sin X}{X} \\
-\phi \frac{\sin X}{X} & \cos X + i \frac{\Gamma \sin X}{2X}
\end{pmatrix}
\begin{pmatrix}
V_e \\
V_o
\end{pmatrix}
\]  

(9.1.9)

We have used the Jones matrix calculations in **papers III, IV, and VI**.
Matrix techniques for handling two variables have been used extensively since their introduction in optics by Jones [65-69, 75] and Abeles [64]. In eliminating the other two electromagnetic field components, Maxwell's first order differential equations are combined to give second order equations.

When a medium has low symmetry, the methods of Jones and Abeles may become impractical. Teitler and Henvis introduced the 4x4-matrix technique [76], retaining two electric and two magnetic field variables throughout the computation for solving such complicated problems. Later Berreman developed an essentially equivalent technique [77-81] in order to solve the problem of reflection and transmission of obliquely incident light by planar layers of a cholesteric LC.

Berreman wrote Maxwell’s equations for light propagated in a layer of uniform anisotropic medium in the matrix form:

\[ \frac{d\tilde{\Psi}}{dz} = i \frac{\omega}{c} \hat{M}(z)\tilde{\Psi}, \tag{10.1} \]

where \( \hat{M}(z) \) is the matrix that obtained as a result of a transformation of Maxwell’s equations Eqs. (5.1)-(5.7). Solving Eq.(10.1) gives:

\[ \tilde{\Psi}(z + dz) = \hat{P}(z, h)\tilde{\Psi}(z) = \exp(i\omega h\hat{M}(z)/c)\tilde{\Psi}(z) = [1 + i\omega h\hat{M}(z)/c - (\omega h\hat{M}(z)/c)^2/2! + ...]\tilde{\Psi}(z) \]

The matrix \( \hat{P}(z, h) \) can also be expressed as:

\[ \hat{P}(z, h) = \tilde{\Psi}(z)\hat{K}(h)\tilde{\Psi}^{-1}(z), \tag{10.2} \]

where \( \hat{K}(h) \) is a diagonal matrix with elements \( K_j = \exp(\imath q_j h) \), \( q_j \) are eigenvalues of the matrix \( \hat{M}(z) \).

The vector \( \tilde{\Psi}(z) \) can be expressed through \( \tilde{\Psi}(0) \) in the following manner:
\[ \Psi(z) = \hat{P}(z-h,h)\hat{P}(z-2h,h)\ldots\hat{P}(0,h)\Psi(0) = \hat{F}(z,0)\Psi(0). \quad (10.3) \]

In contrast to the Jones matrix method, the Bereman method enables one to consider strongly twisted structures, where multireflections play an essential role. We have applied this method in Paper V for calculation of the light selective reflection of ChLCDs. Also, software that was used for modelling the ellipsometric measurements in Papers I and II are based on the Bereman matrix method.
11 Analysis techniques

In addition the optical methods for characterization of thin films, we have used several standard techniques such as atomic forth microscopy (AFM), X-ray diffractometry, scanning electron microscopy, and Rutherford backscattering spectroscopy (RBS). The results obtained were applied for structure modeling of the films under study. This in turn has enabled us to understand optical properties which depend on the structure of metal oxides.

11.1 Structure, morphology and thickness

The structure and grain size of the films for electrochromic displays on silicon were determined by X-ray diffractometer (XRD) using a Siemens D5000 diffractometer [82] operating with CuK$_\alpha$ radiation at a wavelength of 1.54 Å.

Roughnesses of the WO$_x$ and NiO$_y$ on borosilicate glass and Si were measured by AFM VEECO dimension 3100 [83] in tapping mode.

Morphology of the film surfaces and structure of cross sections were investigated by scanning electron microscopy with a field emission gun (FEGSEM) LEO Ultra 55 (ZEISS) [84] at an accelerated voltage of 2 and 5 kV.

A profilometer Dektak 3ST was used for measurements of the thicknesses of the films of SD-1/SDA-2 mixture.

11.2 Composition

We have determined the composition and mass density by RBS [85] using facilities of the Uppsala Tandem Laboratory with 2 MeV He ions backscattered at the angle of 167 degrees. The RBS data were fitted by the use of the program SIMNRA [86].
11.3 Optical tools

11.3.1 Spectrophotometer

Reflectance (R) and transmittance (T) were measured in the wavelength interval 300-2500 nm using a Perkin-Elmer Lambda 900 spectrophotometer, with an integrating sphere coated with highly diffusely reflecting barium sulphate (BaSO₄) paint. In order to analyse the complex dielectric function $\varepsilon$, the absorption coefficient $\alpha(E)$ multiplied by the thickness of the film $d$, as a function of energy $E$ in the range 0.5 to 4 eV, was first calculated from the approximate expression [3]:

$$\alpha(E)d = \ln \frac{1 - R(E)}{T(E)}.$$  \hspace{1cm} (11.3.1.1)

11.3.2 Ellipsometer

We used a variable-angle spectroscopic ellipsometer (WVASE) of the rotating analyzer type (J.A. Woollam Co., Inc., USA) equipped with an autotarder [60].

The experimental setup for rotating analyser ellipsometer (RAE) and its photograph are shown in Fig. 11.3.2.1 and Fig. 11.3.2.2.

![Experimental setup for rotating analyzer ellipsometer](image)

Figure 11.3.2.1. Experimental setup for rotating analyzer ellipsometer.
A light source produces an unpolarized beam with wide spectral distribution. The light beam passes through a monochromator to select the desired wavelength or photon energy. The quasi-monochromatic beam becomes linearly polarized by the polarizer and is reflected at the surface of the sample. After reflection from the sample, the light beam becomes elliptically polarized. Detection of the polarization ellipse by measuring the intensity of the reflected light is accomplished after the light beam has passed through the rotating analyser (see Fig. 11.3.2.1).

The measurements were carried out in the spectral range 250 - 1700 nm with angles of incidence in the range 50° to 80°. For in-plane anisotropic samples the measurements were performed at different sample orientations. The non-effective spectral range of the fiber between monochromator and entrance polarizer was 1350-1450 nm and it was excluded from the measuring procedure. For ellipsometric measurements, the backs of the glass substrates were roughened to eliminate incoherent reflection from these surfaces.

11.3.3 MePaLC measuring system

The optical arrangement of the system MePaLC which was developed by us for characterization of LCD components is shown in Fig. 11.3.3.1.
It is adapted for measuring reflective and transmissive LC cells and consists of a wide band light source (L), a polarizer (P), an analyser (A), a beam-splitter (BS), a reflector (R), and an LC cell to be tested, which may be either reflective (R LC C) or transmissive (T LC C). Mutual orientation of the polarisers for measurements of transparent liquid crystal cells can be arbitrary, whereas reflective cells are measured in crossed polarisers.

MePaLC uses a real-time spectrometer controlled by a computer. The spectrum of light reflected from or passed through an LC cell divided by the lamp spectrum is processed by the specially developed software.

An advantage of MePaLC is a possibility to test LC cells in a production line in real time during a non-stop process. The relatively short measuring time (around several hundred milliseconds) allows investigating distribution of the cell gap.
12 Summary of the papers and author’s contribution

Paper I.
Thin films of amorphous tungsten oxide (WO$_x$) and polycrystalline nickel oxide (NiO$_y$) used for electrochromic devices have been studied with spectroscopic ellipsometry. The oxides were deposited by reactive dc magnetron sputtering. The WO$_x$ was modelled by a homogeneous isotropic layer whereas the NiO$_y$ was modelled by an anisotropic layer with the optical axis perpendicular to the surface. Using parametric models for the layers the complex-valued refractive index of the oxides, film thicknesses and surface roughness have been determined. The dispersions of the refractive indices are presented in the 250 – 1700 nm range. Band gap value of 3.15 eV for WO$_x$ was determined from Tauc-Lorentz parametric model. Assuming direct optical transitions band gaps for NiO$_y$ along the optical axes, perpendicular to it and for isotropic intermediate layer in the bottom of the film, were estimated from extracted absorption coefficients and are equal to 3.95 eV, 3.97 eV, and 3.63 eV, respectively.

The author was responsible for the measurements, simulation and writing the paper.

Paper II.
The SD-1/SDA-2 films on silicon substrates before and after the action of the linearly polarized UV light have been investigated with general reflective ellipsometry. The Lorentz oscillator model was applied to isotropic and photo-induced anisotropic layers. The obtained results confirm diffusion model of pure reorientation of azo-dye molecules under the action of the linearly polarized UV light that was proposed earlier.

The difference between the refractive index of the isotropic mixture and the average refractive index of the anisotropic mixture can point to the change of the conformation of the SDA-2 molecules under the action of linear polarized UV light.

The obtained results can be used for simulation of the optical properties of the LC devices.
The entire studies in the paper were carried mostly by the author.
Paper III.

In this paper, we have presented a method for simultaneous measurements of such essential parameters of reflective LC cells as the cell gap, twist angle, orientation of the input director, and dispersion of the birefringence. Both theoretical analysis and experimental procedures are presented. The method is based on spectral measurements of reflectance of the LC cell in the polarized light. There are two measurements for two LC cell orientations. The angle between these orientations is 45°, and one of the orientations can be chosen to be arbitrary. The polarizer and analyzer are crossed, which allows us to avoid influences of Fresnel reflections from the top substrate of the LC cell. The method suited for reflective LC cells with small and large cell gaps is easy to implement. It may find applications in the development and manufacturing of LCoS as well as of the other reflective LC cells. The author was responsible for the measurements and simulations.

Paper IV.

We have derived characteristic functions for determination of parameters of reflective as well as transmissive twisted nematic LC cells in the field off state. Being invariant with respect to LC cell orientation, these functions enable simultaneous determination of optical retardation and twist angle. Measurement methods based on the characteristic functions have been demonstrated. The methods can be applied for characterization of LC cells with low and large cell gap. The experimental setup is quite simple and can be easily carried out in a polarized microscope.

In addition to measuring purposes, the characteristic functions can be applied for determination of optimal parameters of liquid crystals in LC devices. We have demonstrated how to evaluate in a simple way optical retardation and twist angle of LC used in microdisplays. The techniques presented in the article can be applied for studies of optical properties of other materials that are characterized as twisted birefringent media.

The author was responsible for the measurements, simulation and writing the paper.

Paper V.

We have simulated optical properties of thin layered ChLCD, when reflectivity of each layer is not saturated. Our investigations have shown that the total reflection of the multi-layered structure, the layers of which separated by isotropic plates, is always lower than the reflection of a monodomain one. In addition, the total reflection from the multi-layered display separated by
birefringent plates is higher comparing with the same one where the isotropic separators are used. Thin thickness of the layers (~1μm) allows us appreciably to reduce driving voltage. Moreover, at Δn≥0.15 only 2 - 5 layers are enough to obtain the good selective reflection. This has a huge impact when applying multi-layered ChLCDs in many mobile devices, such as smart cards.

The presented results can be applied to optimize the driving voltage and the reflective properties of ChLCDs.

The author made simulations and was responsible for the presentation of the paper.

Paper VI.

We studied the possibility of birefringent color generation in a layer of a surface stabilized ferroelectric liquid crystal coupled with several retardation plates. Double and single polarizer reflective bistable dichromatic ferroelectric liquid crystal displays were considered. We demonstrated that one or two retardation plates are sufficient for a display having good color characteristics and high brightness. Optimal parameters for green/red and blue/yellow ferroelectric liquid crystal displays were found. The author developed theory and carried out the simulations.
13 Summary

This work describes research in optical characterization and optimization of multilayered structures used in LCD and EC devices. The thesis is structured as follows. The outline formulates basic principles of the display science and familiarizes a reader with problems of optical computation and characterization of the materials under study.

Our first paper introduces ellipsometric characterization of EC thin films of amorphous tungsten oxide and polycrystalline nickel oxide which are used in EC devices. Using parametric models for the layers, we determine complex-valued refractive index of the oxides, wavelength dispersions of the refractive indices in the 250 – 1700 nm range, film thicknesses and surface roughness. The band gaps of the oxides are likewise estimated.

Our second paper describes ellipsometric study of photo-alignment layer used in LCD. We investigate a mixture of materials possessing photo-induced birefringence SD-1/SDA-2. The wavelength dispersions of principal optical constants of the mixture before and after its polymerization by UV light are measured. To model electromagnetic wave interaction with the material, its dielectric function is described as an ensemble of Lorentz oscillators. Our results confirm the diffusion model proposed recently to explain formation of photo-induced order in azo-dye films under polarized light.

The third and fourth papers present a new approach to fast characterization of LC cells. The third paper studies transmissive LC cells, whereas the fourth considers reflective LC cells. We introduce two characteristic functions based on acquired light spectra that are invariant with respect to a LC cell orientation. Extremums of these characteristic functions report on the LC cell parameters: optical retardation and twist angle. We demonstrate how to extract values of these parameters and use them to derive pretilt angle and wavelength dispersion of the LC birefringence.

The fifth paper studies low voltage bistable ChLCD. To decrease driving voltage down to several volts, we propose to use multiple thin (∼1μm) LC layers. In order to achieve good selective reflection, such display should contain a stack of these LC layers. Our next goal is to find optimal number of layers and their optimal thickness. We demonstrate that reflection of a ChLCD containing from 3 to 4 1μm-1,3 μm-thick layers and separators with λ/2-retardation is more than 50% that of the traditional one-layer ChLCDs.

In the sixth paper, we research birefringent color generation by ferroelectric LCD. Using custom-developed software for solving inverse problems,
we find optimal performance of ferroelectric LCDs. We demonstrate that in order to accomplish good color characteristics and high display brightness, one or two retardation plates are sufficient. Optimal parameters for green/red and blue/yellow ferroelectric liquid crystal displays are also described.

The results of our research can be applied to solve analogous problems in other fields of applied optics, e.g. photoelasticity, structural analysis, and other thin film studies.
14 Suggestions for future work

This work describes the first application of spectroscopic ellipsometry for systematic investigation of the EC materials made by sputtering at optimal deposition conditions. This powerful technique has not yet been established for wider use to date. There have been several previous reports on investigation of the tungsten and nickel oxides by ellipsometry, but scarcely any paper has studied sputtered deposited films possessing the best electrochromic efficiency. In future, to increase EC efficiency, evolution of refractive indices should be studied for mixtures of cathodic tungsten oxide and anodic nickel oxide in the whole concentration range. Applying voltage between the ITO layers shuttles the ions between the electrochromic oxides. To balance the charge, electrons are inserted/extracted from the ITO which alters optical properties of NiO and WO. Optical modulation is reflected in intervalency transitions, however the relevant details are poorly understood. The dielectric function that is obtained with spectroscopic ellipsometry for the “live” devices, as well as its theoretical interpretation based on a model of photon-polaron interactions [4], will provide essential information on physics underlying colouring/bleaching processes. Future research should also include dynamics where application of the time resolved ellipsometry is recommended. When ions and electrons are inserted/extracted, the understanding of their motion is still lacking.

Application of ultraviolet (UV) and infrared (IR) ellipsometry to photoalignment materials will provide additional information about photo-aligning and will deepen our understanding of physics underlying this process. Another useful application of ellipsometry for the LCD technology is the study of interaction between photo-aligned molecules and LC. Due to high sensitivity of ellipsometric method, it can measure encore energy more accurately compared to alternative methods [35]. Furthermore, future studies should include photosensitive materials deposited by different methods, at different concentration, and illumination time. Ultimately, the results of such investigations will be useful for developing new LCDs with improved characteristics.
Vår undersökning handlar om optisk karaktärisering och optimering av mångskiktade strukturer som används i Flyande kristall displayer (LCD) och Elektrokroma (EC) anordningar. Strukturen i avhandlingen är följande. I sammanfattningen har vi formulerat de grundläggande principerna inom displayteknik och introducerat läsaren för den problematik som kan uppstå vid optiska beräkningar och karaktärisering av material.

**Artikel I** ägnas åt ellipsometrisk karaktärisering av elektrokroma tunna filmer av antingen amorft volframoxid eller polykristallint nickeloxid, vilka kan användas i elektrokroma enheter. Med hjälp av parametriska lagermodeller har vi bestämt film tjocklek, ytjämnhet, komplext värderade brytningsindex för metalloxiderna, samt spridningen av våglängdsberoendet för brytningsindex i området 250 - 1700 nm. Även metalloxidernas bandgap har beräknats.

**Artikel II** behandlas en ellipsometrisk studie av anpassningslager som används i LCD. Vi har studerat materialet SD-1/SDA-2 som har fotoframkallande dubbelbrytning. Spridningen i våglängd för de optiska konstanterna måttas före och efter det att materialet polymeriserats med hjälp av UV-ljus. För att kunna göra en modell av interaktionen mellan den elektromagnetiska vågen och materialet, har dess dielektriska funktion betraktas som en samlng av Lorentz oscillatorer. Våra resultat bekräftar diffusionsmodellen beskrivet i [42] vilken förklarar bildandet av foto-inducerad ordning i azo-dye filmer under påverkan av polarisert ljus.

**Artikel III och IV** presenterar en ny metod för snabb karakterisering av LC celler. Artikel III behandlar reflekterande LC celler, medan artikel IV behandlar genomskinliga LC celler. Vi har infört två karakteristiska funktioner som bygger på registrerade ljusspektra och är invarianta med avseende på en LC cell orientering. De extrema karaktäristiska funktionerna innehåller information om LC cellernas optiska retardation och vridvinkel. Vi har visat hur man kan extrahera dessa parametrar för att erhålla lutnings vinkel och våglängdspridning av dubbelbrytning i LC.

**Artikel V** ägnas åt applicering av låg spännings överen bistabil kolesterolisk LCD. Vi har föreslagit att man kan använda tunna (∼1μm) skikt av LC för att
kunna minska den drivande spänningen ner till några volt. För att uppnå god selektiv reflektion, för till exempel en bildskärm, bör denna bestå av en trave av dessa LC lager. Vår målsättning har varit att ta reda på det optimala antalet lager och tjocklek. Vi har visat att reflektionen är mer än 50 % större för en ChLCD bestående av 3-4 skikt med tjockleken 1μm-1.3 μm och separatörer med ett fasskift på λ/2, än för traditionella ChLCDs bestående av endast ett skikt.

I artikel VI har vi studerat färggeneration genom dubbelbrytande plattor i en ferroelektrisk LCD. Vi har hittat en optimal prestanda genom att använda programvara utvecklad för att lösa inversa problem, Vi har visat att en eller två retarderingsplattor är tillräckliga för att åstadkomma bra färgegenskaper och hög ljusstyrka på displayen. Optimala parametrar för grön / röda och blå / gula ferroelektriska flytande kristaller har hittats. Resultaten från vår forskning kan användas till att lösa liknande problem inom andra områden av tillämpad optik, t.ex. photoelasticitet, strukturell analys och studier av tunna filmer.
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