Photoalignment of Liquid Crystalline Materials: Physics and Applications

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To our families and wives Larisa, Galina and Ying for their love and constant support

Contents

About the Authors

Vladimir G. Chigrinov obtained his PhD degree in solid-state physics from the Shubnikov Institute of Crystallography, USSR Academy of Sciences, in 1978. In 1988, he defended his doctoral degree and became a professor at the Shubnikov Institute of Crystallography, where he was a leading researcher from 1996. He joined HKUST in 1999 and is currently an associate professor. Since 1974 Professor Chigrinov has published 2 books, 15 reviews and book chapters, about 150 journal papers, more than 300 conference presentations, and holds more than 50 patents and patent applications in the field of liquid crystals. He is a Senior SID Member, SID Fellow and an Associate Editor of the *Journal of the Society for Information Display*.

Vladimir M. Kozenkov graduated from the Moscow Energetic Institute as a scientist in applied physical optics (laser department). For 30 years he worked at the Organic Intermediates and Dyes Institute (NIOPIK) in Moscow. He pioneered research and development of various organic photosensitive materials for holography, waveguide, integral and polarization optics, stereolithography, optical memory, imaging processing, and security applications. He was the first to discover the phenomenon of photoinduced birefringence in polyvinyl-cinnamate films in 1977. He has published more than 100 refereed papers and holds more than 50 patents.

Hoi-Sing Kwok obtained his PhD degree in applied physics from Harvard University in 1978. He joined the State University of New York at Buffalo in 1980 and became a full professor in 1985. He joined HKUST in 1992 and is currently Director of the Center for Display Research (*www.cdr.ust.hk*). Professor Kwok has written over 500 refereed publications and holds 40 patents in laser optics and LCD technologies. He is a Fellow of the OSA, the IEEE, and the SID.

Series Editor's Foreword

Manufacture of liquid crystal displays uses some of the most complex and advanced manufacturing techniques. In active matrix displays, TFT circuits are uniformly manufactured at resolution limits of a micron or less on substrates several square metres in area. In most types of liquid crystal displays, liquid crystal molecules are aligned with high precision in directions parallel and perpendicular to the display substrate. This is usually done by a method which has been in use since the discovery of substrate-aligned layers – rubbing.

Rubbing techniques have developed over many decades. Modern rubbing machines are unrecognisable in comparison to the simple methods used in the 1960s around the time of the birth of liquid crystal displays, but they remain as a somewhat anachronistic method when compared to the advances in technique that have been made in most other aspects of liquid crystal display manufacture. Of course, if traditional rubbing methods (and here I mean physical abrasion) worked perfectly, there would be little reason to change them, but as liquid crystal display technology has advanced, an increasing number of performance and yield-related issues have become attributable to rubbing as an alignment technique. Tribologically induced electrostatic discharge damage of the active matrix circuitry has ever been a problem, although it can be reduced by careful selection and control of the rubbing and alignment layer materials. What have become more difficult or even impossible to control are problems related to high pixel density, or to the requirement for multiple alignment domains on each pixel, or to the use of spacers which are deposited on to the display substrate in the gaps between pixels at a point prior in the process to the alignment step. Rubbing, however well controlled, produces some defects and these become more of a problem as pixel size decreases. With multi-domain alignment, the need to carry out multiple rubbing operations and to mask those areas of the surface not being rubbed is costly and reduces yield. The use of rubbing of substrates with deposited spacers produces a region downstream of the spacer where alignment either is absent or is different from that in the surrounding area. This produces disclination defects, which reduce the contrast ratio of the display.

So what other methods are available to the display manufacturer? Much research and development effort has gone into developing liquid crystal technologies that do not require a rubbed alignment layer. The most obvious exemplar of this is the family of multi-domain vertically aligned nematic liquid crystal displays. However, many other liquid crystal technologies require precise directional alignment of the liquid crystal molecules at one or both of the display substrates. Two non-contact methods have been proposed. One uses ion beams, the other light. Both produce alignment which can be superior to that produced by mechanical rubbing. However, ion beam methods are costly because they operate under vacuum. Because they do not require a vacuum, photoalignment methods are lower cost. They are the subject of this latest book in the Wiley-SID series.

The earliest photoalignment methods involved the selective decomposition of surface adsorbed dye molecules by polarised light to produce a residual anisotropic alignment layer. Such methods can produce stable layers which meet the standards required for manufacture, but there remains an element of uncertainty about the very long term stability of such layers, particularly under high illuminance. The authors of this book have developed techniques to achieve photoalignment by thermodynamic reorientation of alignment layers rather than by decomposition.

But photo-techniques are applicable to more than alignment processes. Retardation films are becoming increasingly important as wider viewing angles and higher contrast ratios are demanded, across the entire visible spectrum, in liquid crystal display products. Photopolymerisable liquid crystals offer the opportunity to match with unprecedented precision and compensate switchable liquid crystal layers. Increasing demand for displays with optimised transmissive and reflective properties requires that retardation films and sometimes polarisers need to be patterned at the pixel or subpixel level and photo-techniques provide capabilities that are transferable from development to manufacturing with relative ease.

The authors are all internationally known in their field. They write with clarity and authority. With good reason, they provide a very detailed review of their own work, but they achieve balance by offering a comprehensive review, replete with references, of all work in the field. Theory, experiment and the application of alignment techniques to working devices are all covered in depth. Indeed, the discussion extends beyond displays to photonic devices, where their intricate geometry often makes them unsuitable for use of mechanical alignment methods. Uniquely, a detailed review of granted patents, listed by subject area and assignee, is also provided.

This book will be an invaluable resource to anyone already undertaking or about to undertake research in this field and also to those in industry who wish to develop and apply photoalignment in manufacture.

Anthony Lowe
Series Editor
Braishfield, UK

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Introduction

Among all the flat panel display technologies, liquid crystal display (LCD) is the most dominant. The manufacture of LCDs is now very mature and done with huge glass substrates measuring over 5 m^2. The availability of such inexpensive high-resolution displays has accelerated the transformation of our society into a display-centric one. However, despite its dominance, LCD is still in need of further improvement. Among other things, light utilization efficiency, cost, and optical performance such as response times of LCD are still not optimal. It is no wonder that much research is still being performed and new LCD modes are still being invented with better properties such as response time or viewing angles.

In this book, we concentrate on one aspect of LCD manufacture, namely that of the alignment surface. In particular, we shall present a comprehensive review of photoalignment technologies. Photoalignment has been proposed and studied for a long time [1–12]. In fact, the subject of light–molecule interactions has been a fascinating subject of research for a long time and is still capturing the imagination of many people. Light is responsible for the delivery of energy as well as phase and polarization information to materials systems. In this particular case, the alignment of the molecules takes place due to a partial ordering of the molecular fragments

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after a topochemical reaction of a photoselection (Weigert's effect). While the first photo-patterned optical elements, based on polyvinyl-cinnamate films, appeared in 1977 [1], the technology became an LCD one only at the beginning of the 1990s [2–5]. It was soon shown that these materials could provide high-quality alignment of molecules in an LC cell. Over the last 20 years, many improvements and variations have been made for photoalignment. Commercial photoalignment materials are now readily available. Many new applications, in addition to the alignment of LCD, have been proposed and demonstrated. In particular, the application of photoalignment to active optical elements in optical signal processing and communications is currently a hot topic in photonics research.

Photoalignment possesses obvious advantages in comparison with the usually 'rubbing' treatment of the substrates of LCD cells. Possible benefits for using this technique include:

1. Elimination of electrostatic charges and impurities as well as mechanical damage of the surface.
2. A controllable pretilt angle and anchoring energy of the LC cell, as well as its high thermal and UV stability and ionic purity.
3. The possibility to produce structures with the required LC director alignment within the selected areas of the cell, thus allowing pixel dividing to enable new special LC device configurations for transflective, multidomain, 3D, and other new display types.
4. A potential increase of manufacturing yield, especially in LCDs with active matrix addressing, where the pixels of a high-resolution LCD screen are driven by thin film transistors on a silicon substrate.
5. New advanced applications of LCs in fiber communications, optical data processing, holography, and other fields, where the traditional rubbing LC alignment is not possible due to the sophisticated geometry of the LC cell and/or high spatial resolution of the processing system.
6. The ability for efficient LC alignment on curved and flexible substrates.
7. Manufacturing of new optical elements for LC technology, such as patterned polarizers and phase retarders, tunable optical filters, polarization non-sensitive optical lenses, with voltage-controllable focal distance etc.

With all these new developments in photoalignment technologies, it is now the right time to take an inventory of the progress made over the last 20 years in the form of a monograph. This book presents the status of the research in LCD photoalignment and photo-patterning. To the best of our knowledge, there are no other books devoted to the subject, though a few review articles are available [6–11]. In this book, we shall concentrate on a recent approach of ours, which is rather promising, namely the photoinduced reorientation of azo-dyes [12]. This technique of photoalignment does not involve any photochemical or structural transformations of the molecules. Further, the new photoaligning films are robust and possess rather good aligning properties such as anchoring energies and voltage holding ratios. They can be very useful for the new generation of LC devices as well as in new photovoltaic, optoelectronic, and photonic devices based on highly ordered thin organic layers. Examples of such applications are light-emitting diodes (OLEDs), solar cells, optical data storage, and holographic memory devices. The novel and highly ordered layer structures of organic molecules may exhibit certain physical properties, which are similar to the aligned LC layers.

This book is intended for a wide audience including engineers, scientists, and managers, who wish to understand the physical origins of the photoaligning technique, its basic advantages and limitations, as well as the application for LC devices, including displays, optical waveguides, optical polarizers and retarders, etc. University researchers and students who specialize in condensed matter physics and LC device development should also find some useful information here.

The principal aims of the book are:

1. To describe the physical mechanisms of LC photoalignment with a special emphasis on the most useful photosensitive materials and preparation procedures suitable for the purpose.
2. To summarize LC surface interaction in photoaligned LC cells to produce the required LC pretilt angles, anchoring energy, ionic purity, IR and UV stability, and sensitivity to the activating light exposure.
3. To show how to produce perfect vertical, twisted, rewritable, and other LC photoalignment in nematic, ferroelectric, lyotropic, and discotic materials on glass and plastic substrates and special LC cell configurations (Si waveguide and 3D surfaces, superthin tubes, etc.).
4. To compare various applications of photoalignment technology for in-cell patterned polarizers and phase retarders, transflective and microdisplays, security and other LC devices.

5. To present recent results in applications of photoaligning and photo-patterning technology in LC devices.

The organization of this book is as follows. In Chapter 2, we shall present the various photoalignment mechanisms. Here the photoaligning techniques will be described and compared. In Chapter 3, the alignment properties of the various films will be discussed, with an emphasis on the azo-dyes. Properties such as anchoring energies and voltage holding ratios are important to LCD applications and will be discussed in detail. In Chapter 4, the application of photoalignment to various LCD modes and LC applications will be presented. Photoalignment on unconventional substrates will also be described to illustrate the power of such a technique. In Chapter 5, various applications of photoalignment to the fabrication of optical elements will be explored. The use of photoalignment to improve the design of transflective displays will be presented as well. Some applications of photoaligning technology for the development of new LC displays and photonic devices are then listed in Chapter 6. The working prototypes of new photoaligned LC devices, e.g. optically rewritable electronic paper, look very promising for future applications. One special feature of the book is a compilation of the most important patents, which forms Chapter 7. They are also classified in various ways for easy comprehension of where the technology is heading. We believe such a compilation will be very useful to readers.

The topic of this book is of particular interest to us, as we have undertaken some of the pioneering research in the field. In a sense it is a form of stock taking for us. We hope that the book will stimulate new research and development in the field of LC photoalignment and enable the technology to be used in large-scale LCD production. We are grateful to many colleagues who have worked with us in the past and are still working with us at the Center for Display Research in the Hong Kong University of Science and Technology, including E. P. Pozhidaev, W. C. Yip, Fion Yeung, Jacob Ho, Y. W. Li, A. Muravsky, A. Murauski, O. Yaroshchuk, A. Kiselev, V. Shibaev, S. A. Pikin, A. Verevochnikov, E. Prudnikova, V. Konovalov, S. Pasechnik, Z. H. Ling, D. D. Huang, X. Li, P. Xu, G. Hegde, and H. Y. Mak. They have provided much important information and have contributed greatly to our research program. We also owe much to our friends Drs H. Takatsu, H. Takada, H. Hasebe, and M. Schadt for many stimulating discussions.

References

[1] E. D. Kvasnikov, V. M. Kozenkov, and V. A. Barachevskii, Birefringence in polyvinyl cinnamate films, induced by polarized light. *Dokladi Akademii Nauk SSSR* **237**, 633 (1977) (in Russian).

[2] K. Ichimura, Y. Suzuki, T. Seki, A. Hosoki, and K. Aoki, Reversible change in alignment mode of nematic liquid crystals regulated photochemically by 'command surfaces' modified with an azobenzene monolayer. *Langmuir* **4**, 1214 (1988).

[3] W. M. Gibbons, P. J. Shannon, S. T. Sun, and B. J. Swetlin, Surface mediated alignment of nematic liquid crystals with polarized laser light. *Nature* **351**, 49 (1991).

[4] M. Schadt, K. Schmitt, V. Kozenkov, and V. Chigrinov, Surface-induced parallel alignment of liquid crystals by linearly polymerized photopolymers. *Japanese Journal of Applied Physics* **31**, 2155 (1992).

[5] A. G. Dyadyusha, T. Ya. Marusii, Yu. A. Reznikov, A. I. Khizhnyak, and V. Yu. Reshetnyak, Orientational effect due to a change in the anisotropy of the interaction between a liquid crystal and a bounding surface. *JETP Letters* **56**, 17 (1992).

[6] L. M. Blinov, Photoinduced molecular reorientation in polymers, Langmuir Blodgett films and liquid crystals. *Journal of Nonlinear Optical Physics and Materials* **5**, 165 (1996).

[7] M. O'Neill and S. M. Kelly, Photoinduced surface alignment for liquid crystal displays. *Journal of Physics D: Applied Physics* **33**, R67 (2000).

[8] M. Schadt, Liquid crystal displays and novel optical thin films enabled by photoalignment. *Molecular Crystals and Liquid Crystals* **364**, 151 (2001).

[9] V. G. Chigrinov, V. M. Kozenkov, and H.-S. Kwok, New developments in photoaligning and photo-patterning technologies: physics and applications. In *Optical Applications of Liquid Crystals*, Ed. L. Vicari, Institute of Physics Publishing, Bristol and Philadelphia, 201–244 (2003).

[10] V. P. Shibaev, S. A. Kostromin, and S. A. Ivanov, *Polymers as Electrooptical and Photooptical Active Media*, Springer-Verlag, Berlin, 37–110 (1996).

[11] V. Shibaev, A. Bobrovsky, and N. Boiko, Photoactive liquid crystalline polymer systems with light-controllable structure and optical properties. *Progress in Polymer Science* **28**, 729 (2003).

[12] V. Chigrinov, S. Pikin, A. Verevochnikov, V. Kozenkov, M. Khazimullin, J. Ho, D. Huang, and H.-S. Kwok, Diffusion model of photoaligning in azo-dye layers. *Physical Review E* **69**, 061713 (2004).

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Mechanisms of LC Photoalignment

The effect of LC photoaligning is a direct consequence of the appearance of the photoinduced optical anisotropy and dichroic absorption in thin amorphous films, formed by molecular units with anisotropic absorption properties [1]. The first publication on LC photoalignment appeared in 1988, which discussed the application of the reversible *cis-trans* isomerization of azobenzene molecular layers attached to a solid surface to the switching of the alignment of the adjacent LC layer from homeotropic to the azimuthally random planar orientation [2]. Optical control of LC alignment was achieved by changing the wavelength of the nonpolarized light illumination [2]. Later it was shown that the alignment of an LC medium could be achieved by illuminating a dye-doped polymer alignment layer with polarized light [3]. LC molecules in contact with the illuminated area were homogeneously aligned perpendicular to the direction of the laser polarization and remained aligned in the absence of the laser light. Soon after the LC photoalignment procedure was derived using cinnamoyl side-chain polymers [4, 5] and polyimide aligning agents [6]. The area of LC photoalignment is developing

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