Smectic C liquid crystal growth through surface orientation by Zn$_x$Cd$_{1-x}$Se thin films

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Abstract. A smectic C liquid crystal (LC) texture, consisting of distinct local single crystals (DLSCs) was grown using predefined orientation of ternary nanocrystalline thin films of Zn$_x$Cd$_{1-x}$Se. The surface morphology and orientation features of the Zn$_x$Cd$_{1-x}$Se films were investigated by AFM measurements and micro-texture polarization analysis. The Zn$_x$Cd$_{1-x}$Se surface causes a substantial enlargement of the smectic C DLSCs and induction of a surface bi-stable state. The specific character of the morphology of this coating leads to the decrease of the corresponding anchoring energy. Two new chiral states, not typical for this LC were indicated. The physical mechanism providing these new effects is presented.

1. Introduction

The liquid crystals (LCs) are highly anisotropic liquids. Their molecules tend to orient parallel to each other along one direction characterized by the director $\mathbf{n}$ ($n^2=1$) [1]. This direction is arbitrary in space and imposed by the anisotropic interactions between liquid crystal molecules and a boundary wall. Uniform and homogeneous orientation of the liquid crystal, in particular nematic (N) LC, was obtained by using various surface treatments including mechanical striations or rubbing of thin polymeric layers [2]. The same orientation, using the same treatments, was reached also for the more complex layered smectic LC and specially for smectic C (S$_C$) LC, where the director $\mathbf{n}$ is tilted on an angle $\omega$ (tilt angle) with respect to the layer’s normal $\mathbf{N}$. Deposition of SiO layer by evaporation at oblique incidence has been long ago known to provide nematic liquid crystal alignment. For an angle of evaporation incidence $45^\circ<\alpha<80^\circ$, from the normal ($z$ direction) of the LC cell substrate (xy plane), the N LC orientation is planar. For grazing incidence $80^\circ<\alpha<90^\circ$, the N LC orientation is oblique in the incidence plane with a tilt angle toward the evaporation direction [3]. The orientation properties of LC molecules on the surface were explained by elastic models: the LC bulk is deformed to minimize its elastic energy in response to the anisotropic structure of the surface treatment, which could be SiO obliquely evaporated rough surface, providing well controlled films, or polyimide unidirectional rubbed surfaces [2]. Very often the rough orienting surfaces like that of SiO obliquely evaporated cause a continuous transition between the planar and the oblique orientations [3]. Such complicated state of the director, caused by the anisotropic interactions between LC molecules and a boundary wall, could be understand by the correlation between a complicated topography and the LC molecules orientation. This requirement is still more necessary when the LC molecules are those of S$_C$ LC, where the director $\mathbf{n}$ is restricted to rotate (or reorient) simultaneously around two cones: one with apex angle $2\omega$ within each layer and another one on the surface, coaxial with the...
substrate’s surface normal \( z \). Being put under these two constrains the director \( n \) near the surface thus predetermines the orientation of the grown \( S_C \) texture. Unlike the NLC, and due to these constrains the alignment of the smectic C characterizes with polycrystal textures, known as distinct local single crystals (DLSCs) [4]. Obtaining of large and well oriented DLSCs, that are convenient for experimentation, as well as for the needs of the contemporary display techniques, practically is a tough problem, since one must control independently the molecular and the layer orientation and to avoid fragmentation of the \( S_C \) texture. Due to its strong elasticity, however, \( S_C \) ensures comparatively fast electro-optical response (decay times of only few ms) [5], and is of practical interest for the fast LC displays. This motivates the study of the surface forces driving the DLSCs growth and efforts to grow comparatively large single crystals. Since the details of LC surface alignment are not well understood, the search for more easily quantifiable alignment materials continues, seeking to achieve adequate control of the surface orientation forces. Such new materials must be well acquainted, on a nano-scale dimension, in order to deduce the physico-chemical mechanism controlling the surface orientation of the \( S_C \) LC system. Till now it is not known whether that the strong or the weak surface anchoring could provoke growth of large and well oriented DLSCs. Furthermore, a bistable surface state, which could be induced at rough surfaces, is especially important for the display and other LC device techniques. Since the \( S_C \) is rather faster system than the nematic one the surface bistability in \( S_C \) must be a desired effect. This determines the goal of the present work: to obtain large, oriented and able to ensure fast bistable switching smectic \( C \) DLSCs. We expect that using as orienting surface film nanocrystalline layers of \( \text{Zn}_{0.59}\text{Cd}_{0.41}\text{Se} \) with thickness of 400 nm, we will be able to find an electrically controllable bi-stable texture. The understanding of the physical mechanism of this texture will be an important fundamental goal of the present work. We also observed two new states, not typical for the here investigated heptyloxybenzoic acid (7OBA) substance: chiral smectic \( C \) (\( S_C^* \)) and biaxial fluid low-temperature chiral smectic phase (\( C_{\text{G}} \)). These states due to the externally forced symmetry decrease. The orientation, light polarization characteristics as well as the size of the grown DLSC will be verified using predefined orientation of \( \text{Zn}_{0.59}\text{Cd}_{0.41}\text{Se} \) treated glass surface. The anchoring strength will be estimated and compared with those at \( \text{SiO}_x \)- and \( \text{ITO} \)- treated surfaces.

2. Experimental results and discussion

The experiments have been carried out with 4, n-heptyloxybenzoic acid (7OBA) which has following phase transitions:

\[
Cr \leftarrow \underbrace{365.2K}_{371.2K} \rightarrow S_C \leftarrow \underbrace{2.371K}_{2.365} \rightarrow N \leftarrow \underbrace{2.419K}_{2.414} \rightarrow I
\]

The LC material in its isotropic phase was filled in the cell using the capillary force action. The gap between the glass plates, defining a cell thickness, was maintained with Mylar spacers. The temperature of the sample was varied with a rate of 0.2 K min\(^{-1}\) by a hot stage temperature controller Linkam TMS 90, and the chosen experimental temperature was stabilized with an accuracy of \( \pm 0.1 \)K.

Thermal evaporation of \( \text{ZnSe} \) and \( \text{CdSe} \) powders (Merk, Suprapure) from two independent, simultaneously heated tantalum crucibles was applied for the preparation of \( \text{Zn}_{x}\text{Cd}_{1-x}\text{Se} \) layers with \( x=0.59 \) and thickness of 400 nm. The crucibles were disposed in the bottom of two cylindrical screens (not intentionally heated) whose top is close to the substrates. Thus, the deposition of each material was carried out in a quasi-closed volume.

The layers of \( \text{Zn}_{x}\text{Cd}_{1-x}\text{Se} \) were deposited on crystalline Corning 7059 glass substrates maintained at room temperature. During the film deposition the substrates were rotated at a rate \( V_r=20 \) turns/min and during each turn pass they spent over each crucible 1/12 of the turn time. The time \( \Delta t \) between the consecutive deposition of \( \text{CdSe} \) and \( \text{ZnSe} \) is 5/12 of the turn time. The substrate rotation was started after fixing the desired deposition rates for both \( \text{CdSe} \) and \( \text{ZnSe} \). The rates were controlled by two independent preliminary calibrated quartz microbalance systems MIKI FFV. The layer composition was varied by changing the ratio of the deposition rates of both materials; a ratio 1.5/1.5 (\( V_d^{\text{CdSe}} \) (nm/s))/\( V_d^{\text{ZnSe}} \) (nm/s)) was used. Thus, \( \text{Zn}_{x}\text{Cd}_{1-x}\text{Se} \) single layers were prepared by alloying of the
consecutively deposited small portions of CdSe and ZnSe with equivalent layer thicknesses $d = 0.37 \text{nm}$ (at 15 nm/s) [6,7].

The surface morphology of the thin films was investigated by AFM measurements that were carried out using a Multimode V (Veeco, Santa Barbara, CA). Imaging was performed in tapping mode and height, amplitude, and phase images were recorded. The scan rate was in the range 1-2 Hz, the image resolution was 512 lines per scan direction. At least three different points on the sample surface were explored. Silicon cantilevers for soft tapping mode (TAP150-Al-G, BudgetSensors Innovative Solutions Bulgaria Ltd., 1113 Sofia, Bulgaria), with a nominal resonance frequency of 150 kHz and a typical force constant of 5 N/m were used. The tip radius for these probes is less than 10 nm. Image processing was performed by means of the Nanoscope 7.30 programme. All the images were flattened and no further processing was carried out.

Monitoring of the optical textures, in the LC cell $xy$ plane, prepared using Zn$_x$Cd$_{1-x}$Se coated substrates, was carried out using a video camera Hitachi on a microscope Zeiss NU2.

In figure 1 the bi-stable texture of grown DLSCs in LC cell prepared by two different plates with respect to the coating (hybrid LC cell): one coated with Zn$_x$Cd$_{1-x}$Se (upper plate) and the other one coated with rubbed ITO (lower plate). By rotation (on right) of the cell in crossed polarizers on an angle of $\approx 45^\circ$, one notes the change of the black into white DLSCs and conversely the change of white into black at left rotation. This is interesting for the fast display techniques due to the fast response of the smectic C to external electric field, as well as for the observed good contrast. The AFM morphology of upper, covered with fresh Zn$_x$Cd$_{1-x}$Se, plate is indicated in figure 2 in its planar and 3D images. We do not found any difference in the orienting properties of the fresh and old (e.g. 4 years old) Zn$_x$Cd$_{1-x}$Se coatings, although nanosized grains of the last coating seem ordered in one direction.

Figure 1. Bi-stable smectic C texture for planarly oriented hybrid LC cell. $T=368.3 K$. Crossed polarizers.
Using two equal Zn$_x$Cd$_{1-x}$Se coated plates as upper and lower for LC cell preparation we found transformation of achiral smectic C, typical for 7OBA, in chiral smectic C$^*$. One notes that such texture is only S$_C^*$ fluctuation and exists with great difficulty 2 degrees. At further cooling this chiral state transforms in a chiral biaxial, fluid in the layer planes, smectic C$_G$ phase. These chiral states are seen in figure 3. We confirmed the biaxiality and fluidity, as well as the double tilting character of this state, by suitable microtexture polarization analysis. The S$_C^*$ phase does not change the character of the achiral nematic phase above it.

Considering the N phase (figure 4), in such prepared non hybrid LC cell, after cooling from the isotropic phase, we found well underlined Neel walls allowing the calculation of the surface anchoring energy. Hence we can use the formula [8] $W_s = \pi^2 K d / 2 l^2$, where $d$ and $l$ are the cell and wall thicknesses and $K$ is the elastic constant (10$^{-11}$ J m$^{-1}$) considered in the one-constant approximation [1]. We measured the wall width at temperature 408.2K in the N phase for two cell thicknesses d=8 and 12μm.
to be \( l = 14 \) and \( 15\mu m \) respectively. The wall thickness \( l \) was derived from a study of interference fringes for normally incident monochromatic light. Using the measured \( l \) values and the Rapini-Papoular formula [9] \( W_s = K(n.n_o)^2 L^{-1} \), we determine the extrapolation length \( L \) which is a measure for the anchoring strength. We estimated the anchoring energy for the basic surface treatments and found the extrapolation lengths for the two thicknesses to be \( 5 \) and \( 3.85\mu m \) respectively, corresponding to anchoring energies \( 0.2 \times 10^{-5} \) J m\(^{-2}\) and \( 0.26 \times 10^{-5} \) J m\(^{-2}\) respectively. These values indicate that the anchoring strength at Zn\(_x\)Cd\(_{1-x}\)Se coating is about one order weaker than those of the anchoring induced by SiO or ITO orientations (see for comparison [10])

\[ \begin{align*}
W_s &= K(n.n_o)^2 L^{-1} \\
L &= K^{-1/2} W_s^{-1/2}
\end{align*} \]

Figure 4. The Neel walls in the nematic phase in non hybrid LC cell at \( T = 408.2K \) in crossed polarizers.

The weak anchoring at the interface Zn\(_x\)Cd\(_{1-x}\)Se coating – LC allows modeling of the physical mechanism responsible for the observed bistability and the chiral phases induction.

Varying the coating layer thickness, one can observe a column to needle nanostructure transition, with increasing surface roughness. The Zn\(_x\)Cd\(_{1-x}\)Se surface roughness is expected to induce a nematic surface order decrease (surface melting).

Therefore, we indicate the effect of the surface topography and roughness created by the Zn\(_x\)Cd\(_{1-x}\)Se surface on the N LC molecules orientation. The results could be quantitatively explained by an “order electric” model. In this model, the Zn\(_x\)Cd\(_{1-x}\)Se roughness destroys the LC order at the surface, inducing a gradient of this order towards the ordered bulk [11]. An order electric polarization proportional to this gradient rises to an electrostatic term in the LC orienting surface free energy. The surface roughness induces decrease of the surface order parameter to zero i.e. the LC phase near the surface would melt (goes to the isotropic state). This order parameter variation creates an order – electricity polarization \( P \) near the surface which tends to orient the molecules on the surface toward the magic angle \( \theta_m \). The competition between the van der Walls interaction with the surface and the order-electric effect may give the zenithal molecular orientation. We can present this effect using the scalar form of the order parameter \( S = (3\cos^2 \theta - 1)/2 \). When, due to the gradient of \( S \) along the normal to the substrate, the \( S \) value goes to zero, then the \( \theta = \theta_m \approx 54^\circ \) is magic angle defined by \( \cos^2 \theta = 1/3 \). The pre surface molecules are tilted on this angle and only the horizontal component of the polarisation keeps \( P = 3 \times 2Vs\sin \theta \cos \theta \). \( 2Vs \) is the ratio of the reduction in the order parameters \( S \) between the surface and the bulk. The surface horizontal order electric polarization \( P \) could provoke twist rotation of the surface director \( n_o \). On the Zn\(_x\)Cd\(_{1-x}\)Se grains \( P \) produces electric charges, which create a depolarizing electric field \( E_D \) parallel to the plate surfaces (xy plane). This electric field must disappear on the
conductive surface as that of ITO but is active on that low-conductive Zn_{x}Cd_{1-x}Se surface and is able to create director rotation, dominating on the conventional van der Walls interaction with the surface.

This horizontal polarization action on the upper Zn_{x}Cd_{1-x}Se plates and corresponding rotation creates the observed bi-stability seen in figure 1. The P surface action on the two plates for LC cell constructed by two Zn_{x}Cd_{1-x}Se plates could create a deformation of the dimmer ring of 7OBA leading to decrease of the symmetry and induction of both chiral phases: Sc^{*} and C_{G}. The effect of decrease of symmetry and in turn induction of a low-symmetric phase (transformation of achiral smectic C into Sc^{*} and C_{G} phases) is unique and due to the possibility of the dimmer molecules to vary (at external action) between open dimmer state and monomers. The study of this new effect as well as the electrical control of the detected in this work bistability will be our important future task.

3. Conclusion

The surface morphology and orientation features of the Zn_{x}Cd_{1-x}Se films were investigated by AFM measurements and micro-texture polarization analysis. The Zn_{x}Cd_{1-x}Se surface causes a substantial enlargement of the smectic C liquid crystals monodomains in the 7OBA. Using of a hybrid LC cell, built by two different substrate plates, treated by Zn_{x}Cd_{1-x}Se and rubbed ITO, we detected grown of a surface bi-stable smectic C texture. Two new chiral states, namely ferroelectric smectic C^{*} and the unique chiral, biaxial and fluid in the layer’s plane smectic C_{G} phases, (not typical for 7OBA) were indicated when the two liquid crystal cell’s substrates were treated only with Zn_{x}Cd_{1-x}Se. A model explaining the observed bi-stability on the base of the surface induced ordo-electric polarisation was presented. The specific character of the morphology of this coating leads to the decrease of the corresponding anchoring energy. The physical mechanism providing these new effects is presented.

Acknowledgments

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