

RIPPLE STRUCTURES CREATED BY PHOTOALIGNMENT IN DOPED DYE NEMATIC LIQUID CRYSTALS: THE ROLE OF CELL THICKNESS

Marius Ciprian VĂRUȚ¹, Constanța DASCALU² and Ion PĂLĂRIE³

The need to obtain well defined nanometer structures it's a goal difficult to attain. This is even harder when the patterns are needed to be created inside of glass cell containing dye doped nematic liquid crystals (DDNLC). By irradiating cells filled with DDNLC, with a laser beam (476.5 nm), we obtained optically induced patterns, on the inner surface of the glass cell. The surface characterization of the photo-patterns was performed by using atomic force microscopy (AFM). Following the measurements for the regularity of the photo-patterns, optimal parameters that were required to have ripple structures on large areas, with greater heights and lower abnormalities have been obtain.

Keywords: DDNLC; ripple structures, Atomic Force Microscopy (AFM), nematic liquid crystals, photoalignment.

1. Introduction

The interest in the development of new methods for photoalignment of liquid crystals on different surfaces is increasing. This is because of the demand for a new type of holographic plates with low threshold intensity (as low as 3mW/cm^2) and a response time from few hundred microseconds to 100 ms, demands well fulfilled by DDNLC [1]. Short relaxation times, when switching off the electric applied voltage, were experimentally registered in nematic cells aligned with conducting polymers [2,3]. Some study is made on the behaviour of a ferrocholesteric liquid crystal in magnetic and laser external fields, taking into account the influence of the molecular anchoring to the solid boundaries [4].

For the holographic industry, photoalignment is used to create holographic vector gratings [5]. Creating a new type of holographic displays based on photoaligned structures could seriously improve the time response and the view angle [6]. Another field of research that can benefit by the development of

¹ Assistant, Faculty of Pharmacy, University of Medicine and Pharmacy of Craiova, Romania, e-mail: varutmarius@yahoo.com

² Lecturer, Dept. of Physics, University POLITEHNICA of Bucharest, Romania, e-mail: dascaluc@yahoo.com, correspondent author

³ Lecturer, Dept. of Physics, Faculty of Science, University of Craiova, Romania, e-mail: palarie_i@yahoo.com

photoalignment process is the domain of ultrahigh resolution and ultrahigh wide viewing angle LCD's [7]. Companies that produce LCD panels, already announce that based on the photoalignment process will release 8K ultra high resolution LCD panels [8].

The photoalignment permits the reorientation of the director of a cell already filled with LCs. This non-contact method does not induce a mechanical stress on the polymeric surfaces of the inner cell surfaces. The classical method for aligning the nematic director implies a mechanical rubbing process of the polymer surface that coats the inner surface of the cell plates. So, by using photoalignment, particle free surfaces can be assured, as well the anchoring energy can be varied by changing laser intensity and irradiation time.

If only LC is used to fill the cell, the high intensity regime is needed to rotate the director of the nematic structure formed inside the cell [9]. By adding small concentrations of dyes, the interaction of the LC mixture with the laser beam will highly increase. The light-induced dye adsorption on the control surface (S_c), leads to the accumulation of dye molecules on the substrate. The new created twist nematic structure will be locked in by the process previously described [10].

Previous research had identified the appropriate parameters for creating large surfaces covered with ripple structures based on the adsorption of the methyl-red (MR) dye from the 5CB mixture. This was done in a pump-probe experiment, in high intensity regime, so precious information regarding the moment in time when the nematic director starts to rotate were obtained by Palarie et al. [11]. From AFM measurements, the surface characterization revealed that the ripple structures appear occasionally on the surface of the irradiated zone. For high pump powers, it was found that the center of the irradiated zone exhibit a high rugose area, created by the adsorption of the colorant in a chaotic way [12].

A systematic study regarding the concentration of the dye, performed by Palarie et al. [13], had shown that the MR concentration in MR doped with 5CB need to be greater than a threshold value. For a pump power of 12 mW, the value of MR concentration had to be greater than 0.79 % by wt. If the pump power is increased to 20mW, the threshold stops to exist.

In this work, we present an experimental study based on the influence of the LC cell thickness on the ripple structures induced by 476.5 nm linearly polarized laser beam. Cells were filled with 5CB doped with 2% MR, through capillarity. The structures induced through laser irradiation, are analyzed by AFM in the center of the irradiated zone, but also in the periphery. The roughness of the surfaces was estimated from the registered profiles.

2. Experimental details

The experiments were realized at a temperature of 25°C by using seven standard sandwich glass cells filled with mixtures of 5CB doped with 2% MR. The concentration of the MR dye, was chosen after the results obtain by Palarie et al. [13]. For this concentration and pump powers ranging from 8 to 20mW, the surface covered with ripple structures it was outlined better, compared to the other cells with smaller concentrations. The heights of the ripple structures and the dye conglomerate deposits were also taken into account for choosing the 2% MR in 5CB.

The thickness of the cells chosen for this experiment had the values: 8µm, 19µm, 23 µm and 32 µm. The thickness of the cells was varied by means of a Mylar spacer. The inner surface of the glass plates were previously covered with a thin polymeric film, using a spin-coating method. The polymer, polyvinyl alcohol (PVA), was deposit on the inner surface of the cell just like in the experiment made by Palarie et al. [13].

An easy axis was induced by unidirectional rubbing of both surfaces. These inner rubbed surfaces of the cells impose a planar alignment within the nematic cells. Each cell was placed perpendicular to the exciting beam of an Ar⁺ laser (of type INNOVA 308C) working at wavelength $\lambda = 476.5$ nm.

The pump power, P, was measured with a power-meter Field Max II-Top, from Coherent. The pump powers chosen for this experiment had the values 5, 10, 15, 20, and 25 mW. The irradiation time was also varied in 4 steps: 5, 10, 15 respective 20 minutes.

The diameter of the Ar⁺ laser spot, on the cell, was ~2 mm. The mean intensity of the pump beam, in the irradiated areas, had the rough value 500 mW/cm². This mean value indicates that we are working in high intensity regime despite other researchers that made similar experiments in low intensity regime [14].

The direction of rubbing (easy axis) was perpendicular to the direction of polarization of the Ar⁺ laser beam; a smaller value of the azimuthal anchoring energy is obtained for this configuration. The induced permanent structure in the samples is twisted nematic, as shown in our previous studies [11,12].

To analyze the laser-induced surface morphology, the LC cell was submerged for a few minutes in hexane until 5CB was completely dissolved. A really difficult problem is that some MR+5CB mixture remains impregnated in some polymer areas, because of the dismantling process. This effect can make some irradiation zones to be impossible to examine.

Regarding the method of LC extraction from the cell, better results were obtained by using a paper towel to extract the LC from the cell through capillarity. After this step the cell is washed with hexane and again the mixture inside de cell

is absorbed with a paper towel. These steps are repeated till the colour of the cell disappears, this means that a large part of the MR+5CB mixture was extracted between the plates. In the end, the cells plates can be disassembled and analyzed by AFM.

Like in the other reports, the adsorption of the dye on the polymer layer had been observed only on the plate situated in the front of the Ar^+ laser beam. An image of the cell and cell plates after disassembly can be seen in Fig.1

On the irradiated glass plate, S_c , red zones that coincide with the pumped regions appeared. These red areas are due to the MR molecules adsorbed on this surface during irradiation. The other surface, reference surface (S_C), was transparent, showing that the MR molecules have not been adsorbed on this surface.

The spacing and the depth of the ripple structures, induced by a laser beam, were analyzed by AFM using Park XE-100 equipment (a silicon tip with conical shape). The noncontact mode was used to examine the irradiated zones.

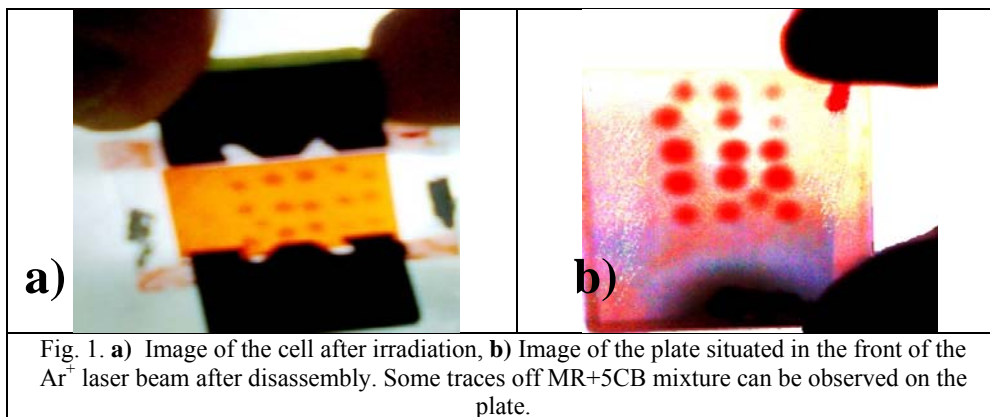


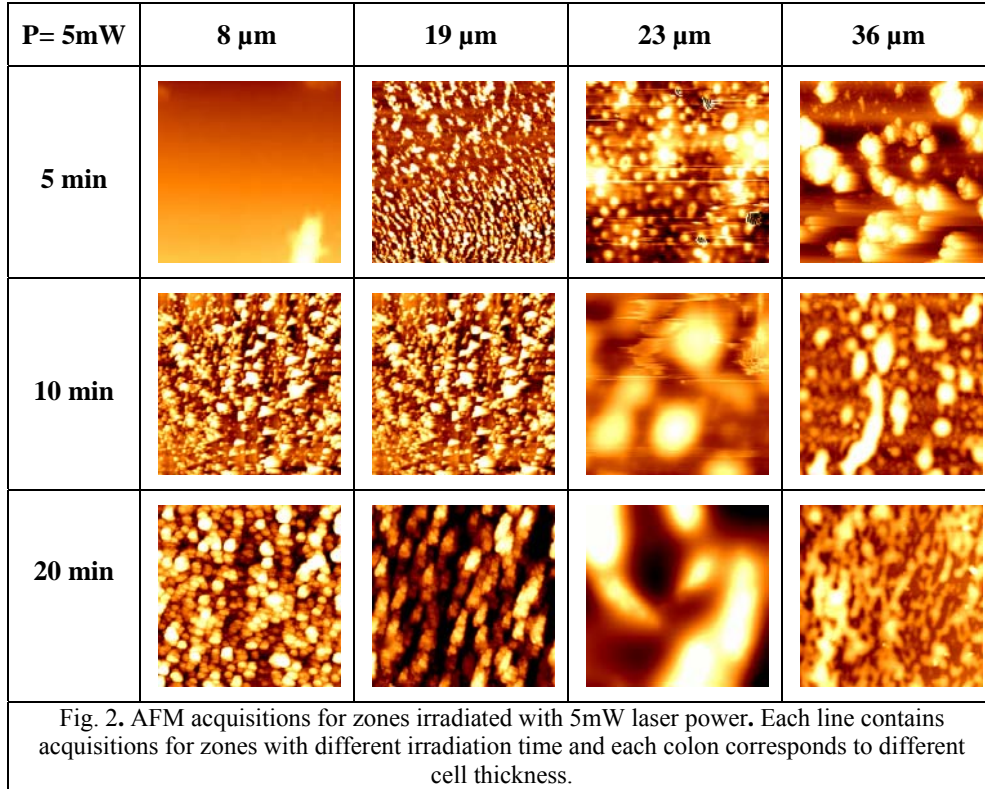
Fig. 1. **a)** Image of the cell after irradiation, **b)** Image of the plate situated in the front of the Ar^+ laser beam after disassembly. Some traces off MR+5CB mixture can be observed on the plate.

3. Results and discussion

In the first place we have to say that all the AFM acquisitions were made in the center of the irradiation zone unless otherwise specified. Because the beam is not a top-hat, but rather a TEM_{00} , intensity of the beam decreases from the center of the beam to its periphery. Usually, from our observations is more likely to find ripple structures in periphery rather than in the center.

A real interest was to see if exist a low power threshold in having ripple structures. As we can see in Fig. 2, for the irradiation at 5 mW for 5 min. long, the acquisition seems clear, being the only one of this kind. We can put that on the fact that: for a given thickness, we need to have certain fluence for having a dye

adsorption. This statement is sustained by the fact that adsorption is taking place for greater irradiation times.



Regarding the presence of the ripple structure at 5mW pump power, we should get large areas without dye conglomerates on top of them. This is because at higher pump powers, large areas of ripples are seen under big blocks of conglomerate but this is not the case, in reality.

The reason for this behaviour is that the formation of ripple structures and the formation of the conglomerates are taking place simultaneous. In the later phases of irradiation the big blocks formed in bulk are adsorbed on top of the already created ripple structures.

The roughness of the conglomerate deposits is increasing with the increase of pump power and also with irradiation time. So, we can say that the roughness induced by conglomerate deposits is proportional with the laser fluence.

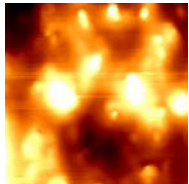
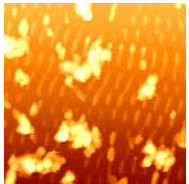
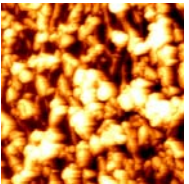
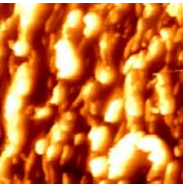
Taking into account the average diameter of the irradiation zone, approx. 1mm, despite the fact that the beam diameter is aprox.2mm, for 5mW of laser

power and 5min irradiation time, the fluence on that area will be of approx. 3.18 mJ/ cm^2 .

We know from Lee et al. [14], that for an intensity of 3mW/ cm^2 (week regime) and an irradiation time of 3 hours, he obtained dye adsorption on S_c . The fluence value for the above parameters is approx. 68.75 mJ/ cm^2 . We have to say that Lee et al. used E7 doped with 1% MR like a dye. E7 is a LC that is a mixture of different LC: 5CB - 51%, 7CB - 25%, 8OCB - 16%, 5CT 8%.

Lee et al. obtained nice ripple structures with small conglomerate deposits, even though the fluence is 20 times greater. This can mean that it is a threshold also for creating the conglomerates from the bulk.

AFM acquisitions of the zones from $23 \mu\text{m}$ cell, irradiated for 10 and 20 min, have a distinct topography that could indicate a contamination of the polymer layer with MR+5CB mixture. This could be happening in the moment when the cell is dismantled.

D= 23 μm	5 min	10 min	15 min	20 min
15 mW				
Fig. 3. AFM acquisitions for zones irradiated with 15mW laser power for different irradiation time. The AFM acquisitions are made in the center of irradiated zone. Cell thickness is $23 \mu\text{m}$.				

Let's consider for the same cell, the irradiation power of 15 mW (fig.3). The AFM acquisition for 5 min. irradiation time was magnified for being able to distinguish the details. We can observe that no ripple structures are present. On the other hand, for 10 min. irradiation time, ripple structures are seen. For a greater irradiation time ripple structures cannot be observed. So, for the $23 \mu\text{m}$ cell thickness, the optimum fluence would be approx. 19 mJ/cm^2 .

In periphery, the things are quite different. The presence of the ripple structures is quite obvious and the conglomerate deposition are less visible. In fig. 4, an AFM image taken at the edge of the irradiated zone is shown. In the right of each acquisitions, we can see the profile of some ripple structures. A colored line on the image will indicate where the profil line corresponds. Also, another graph indicates the periodicity of the structures registered.

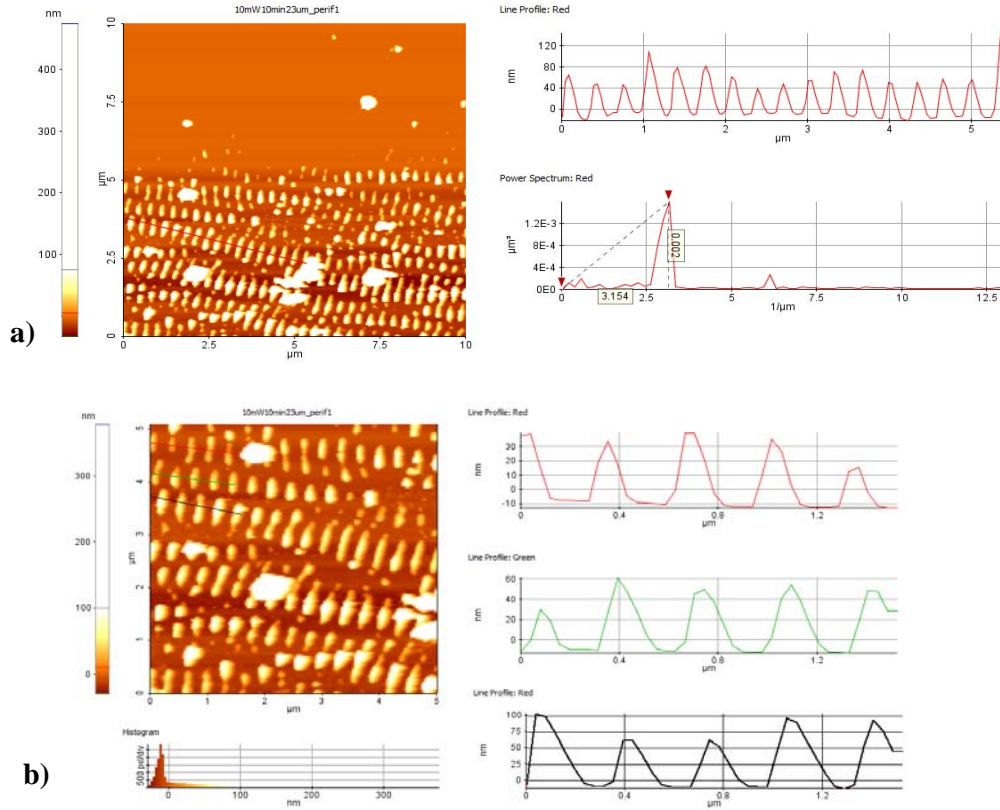


Fig. 4. a) AFM image, $10 \times 10 \mu\text{m}^2$, at the border of irradiation zone for $23 \mu\text{m}$ cell, 2% MR, irradiated with 10mW for 10 min. b) $5 \times 5 \mu\text{m}^2$ AFM image of the same area.

The registered periodicity was found to be approx. 3.15 periods per micrometer, which means approx. 300 nm for each ripple structure period. In fig. 4 b) it is easy to observe that the heights of the ripple structures are getting smaller as they are closer to the border. The spacing of the ripple structures is the same, no matter the distance from the border.

Another interesting aspect regarding the length of the ripples is that we observe a weak periodicity of the ripple structures length. This could be the effect of the interference inside the cell for a tilt angle with the laser beam or the plates are not exactly parallel.

In fig. 5, we can see that for a similar cell, the irradiation at 8 mW for 9 min. give rise to large length ripple structures. Some ripple structures have more or less than $4 \mu\text{m}$ length.

A AFM image, $5 \times 5 \mu\text{m}^2$, for $23 \mu\text{m}$ cell, 2% MR, irradiated at 15 mW for 20 min can be see in fig.6.. The two colored profile lines, from the right part of the image, are represented by two colored lines on the AFM image. Ripple structure seems to be 30 nm in height. The green profile shows that the height of the ripple structure is 4 times lower that the height of the conglomerate structures. The length of the ripple structures are approx. $1 \mu\text{m}$. The same periodicity for the length of the ripple structures could be seen, just like in fig. 3.

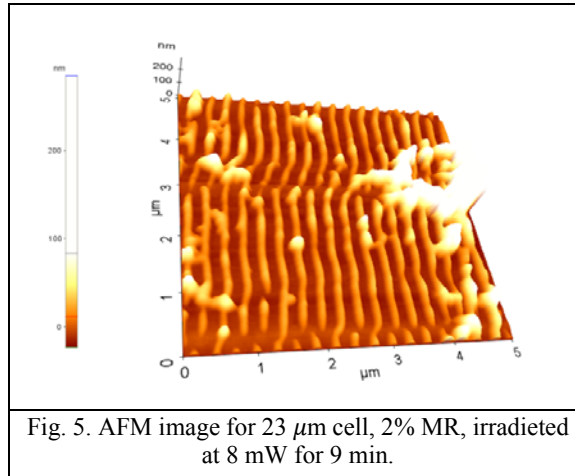


Fig. 5. AFM image for $23 \mu\text{m}$ cell, 2% MR, irradiated at 8 mW for 9 min.

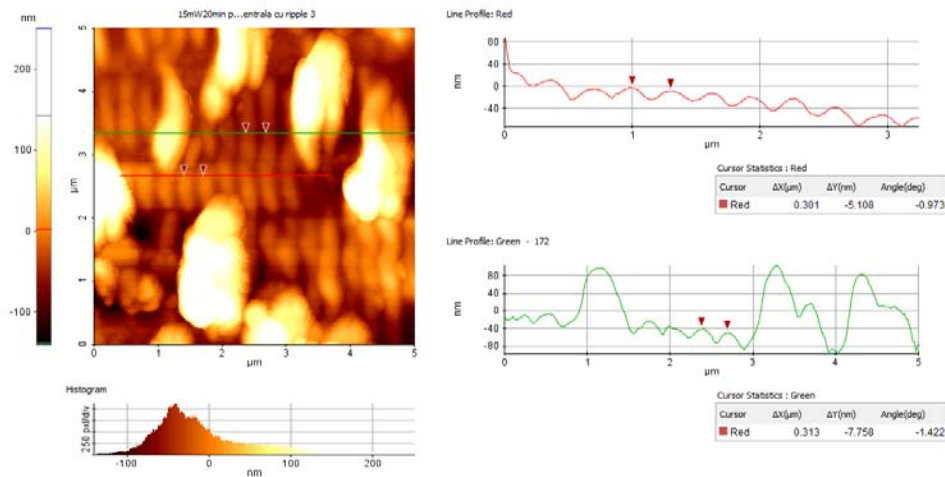


Fig. 6. AFM image, $5 \times 5 \mu\text{m}^2$, for $23 \mu\text{m}$ cell, 2% MR, irradiated at 15 mW for 20 min. At the right, two profile lines of ripple and conglomerate structures are shown.

4. Conclusions

We have shown that an increased thickness of the cell makes the conglomerate deposits to have greater volume. This could mean that the conglomerates are created in bulk.

Also, the increase of irradiation time amplifies this phenomenon. The cells with small thicknesses got to be irradiated with a greater fluence, for having MR molecules adsorbed on the irradiated plate.

The best thickness values, for creating ripple structures, seemed to be equal with 23 μm . For the examined cells, with thickness less than 23 μm , the ripple structures were found neither in center nor in periphery.

In general, the appearance of the ripple structures is less likely to appear in the center of the irradiation zone. The ripple structures tend to appear in the peripheral areas.

The length of the ripple structures seems to be interrupted at periodic values. This can be the effect of laser beam interference inside the cell.

Acknowledgements

C. Dascalu acknowledges this paper to be supported by a grant of Romanian National Authority for Scientific Research, CNCS UEFISCDI, Project No. PN-II-ID-PCE-2011-3-0535.

The authors thank to Assoc.Prof.dr. Gabriela Iacobescu for fruitful discussions regarding AFM protocols.

REFERENCES

- [1] *A. G. Chen, D. J. Brady*, Real-time holography in azo-dye-doped liquid crystals, *Optics Letters* Vol. 17, Iss. 6, pp. 441-443 (1992).
- [2] *R. Atasiei, C. Dascalu, M. Raicopol*, The time dependence of the electric charge in a nematic cell aligned with doped polypyrrole, *UPB Scientific Bulletin, Series A: Applied Mathematics and Physics*, 75 (4), pp. 293-298, (2013)
- [3] *C. Dascalu, R. Atasiei, M. Raicopol*, Evaluation of the debye length for a nematic liquid crystal aligned with conductive polymers, *UPB Scientific Bulletin, Series A: Applied Mathematics and Physics*, 71 (4), pp. 89-94, (2009)
- [4] *C. Cartoaje*, Ferrocholesteric - Ferronematic transition in magnetic and laser field, *UPB Scientific Bulletin, Series A: Applied Mathematics and Physics*, 76 (1), pp. 187-196, (2014)
- [5] *T. Sasaki, T. Shohol, K. Goto*, Appl. Phys. B Photoalignment and resulting holographic vector grating formation in composites of low molecular weight liquid crystals and photoreactive liquid crystalline polymers, *Appl. Phys. B*, Iss. 120, p. 217-222 (2015)
- [6] *Li, C. P. Chen, H. Gao, Z. He, Y. Xiong, H. Li, W. Hu*, Video-rate holographic display using azo-dye-doped liquid crystal, *IEEE/OSA J. Displ. Technol.* 10(6), p. 438-443, (2014)
- [7] *A. Ogiwara, H. Maekawa, M. Watanabe, R. Moriwaki*, Formation of holographic memory for optically reconfigurable gate array by angle-multiplexing recording of multi-circuit information in liquid crystal composites, *Emerging Liquid Crystal Technologies*, IX, (2014).

- [8] *Sharp's "8K full-spec. LCD Display"* receives Minister of Internal Affairs and Communications Award of "CEATEC Award 2014" in Japan, SHARP Press Release, (2014).
- [9] *V.G. Chigrinov, V.H Kozenkov, H.S. Kwok*, Photoalignment of Liquid Crystalline Materials: Physics and Applications; Wiley: New York, 2008.
- [10] *T. Nanba, H. Naito, K. Matsukawa, A.* Weak anchoring of nematic liquid crystals on photo-induced surface relief gratings of organic polysilan, *Thin solid film* (2), p. 767-770, (2009).
- [11] *I. Palarie, C. Dascalu, G.E. Iacobescu*, Study on laser-induced ripple structures in dye-doped liquid crystal films in high-intensity regime, *J. O. Adv. Mater.*, Iss. 12, 1115, (2010).
- [12] *I.Palarie, C. Dascalu, G.E. Iacobescu*, The influence of the easy axis on laser-induced ripple structures in dye-doped liquid crystal films, *Phys. Scr.* 82 (2010).
- [13] *I. Palarie, C. Dascalu, G.E. Iacobescu, M. C. Varut*, Surface morphology of doped nematic liquid crystals: role of dye concentration, *Liquid Crystals*, 39(7) p 833-837, (2012).
- [14] *C.R. Lee, T.L. Fu, K.T. Cheng, T.S. Mo, A.Y.G. Fuh*, Surface-assisted photoalignment in dye-doped liquid-crystal films, *Physical Review*, E 69, 031704 (2004).