# Liquid crystal alignment on the films deposited by sputtering: dependence on target material and gaseous feed

***O. Yaroshchuk[1], R. Kravchuk[1], L. Dolgov[1], E. Telesh[2], A. Khokhlov[3], J. Brill[4], N. Fruehauf[4], M.A Reijme[5],***

[1]Institute of Physics, NASU, prospekt Nauki 46, 03028 Kyiv, Ukraine,
[2]Belarusian State University of Informatics and Radioelectronics, Brovki Str. 6, Minsk, Belarus
[3]Izovac Ltd., Bogdanovicha 155, 220040 Minsk, Belarus;
[4]LfB, University of Stuttgart, Allmandring 3b, 70569 Stuttgart, Germany;
[5]Philips Research, Prof. Holstlaan 4, 5656 AA, Eindhoven, the Netherlands

The alignment of liquid crystals (LC) on the films made by oblique ion beam sputtering deposition is comprehensively studied. The sputtering setup was constructed on the base of anode layer source designed by Izovac Ltd. (Belarus). We used vitreous silica and graphite as target materials and Ar, $CF_4$, $Ar/CH_4$ and $Ar/C_3H_8$ as feed gases. Independently on deposition angle, the tested LC with $\varepsilon<0$ aligns in the incidence plane of particle beam (1st alignment mode), while LCs with $\Delta\varepsilon>0$ in the plane perpendicular to the incidence plane (2nd alignment mode). More specifically, LC with $\Delta\varepsilon<0$ shows high pretilt angles (87°-90°) on silica films (Ar, $CF_4$, $Ar/CH_4$ and $Ar/C_3H_8$ feed gasses). The value of pretilt angle on these films, in case of $Ar/CH_4$ and $Ar/C_3H_8$ gaseous mixtures, can be smoothly varied by varying the hydrocarbon gas concentration. On graphite films (Ar and $CF_4$ feed gasses) the initial alignment of LC with De<0 is similar to that on the silica films. However, the pretilt angle relaxes to zero for about one week. The LCs with $\Delta\varepsilon>0$ on the silica films shows planar alignment in the 2nd mode independently of the type of gas that was fed. In contrast, on graphite films, the alignment of LC with $\Delta\varepsilon>0$ depends on the gas that was fed during deposition. Under Ar gas this LC aligns in the 2nd mode, while when feeding $CF_4$ gas it aligns in the 1st mode. The alignment in the 1st mode deteriorates within several weeks and so only planar LC alignment is stable on the films sputtered from the graphite target.

## 1. INTRODUCTION

The oblique deposition, as a method of liquid crystal (LC) alignment, was proposed by J. Janning three decades ago [1]. In his experiments highly uniform LC alignment was observed on $SiO_x$ films obtained by oblique vapor deposition (VD). These results excited tide of research interest [2-7], because of excellent alignment uniformity, use of inorganic layers, non-contact processing *etc.* It was established that alignment of many LC (mainly LC with $\Delta\varepsilon>0$ and some LC with low $\Delta\varepsilon<0$) on VD layers is very sensitive to the angle of deposition a (in this paper, the angle between the film normal and particle flux). In case of a greater than some critical angle $\alpha_c$, which usually is within 70°-80°, the easy axis of LC lies in the incidence plane of particle flux and tilts towards direction of particle flux incidence (1st mode). In the opposite case, $\alpha<\alpha_c$, planar alignment is induced with the easy axis perpendicular to the particles' incidence plane (2nd mode). By analogy with the particle beam etching procedure [8,9] we define the described alignment types as the 1st and the 2nd alignment mode. They are schematically presented in Fig. 1a and Fig. 1b, respectively. For the LC with $\Delta\varepsilon<0$ developed for VAN LCD the VD technique provides homeotropic or tilted vertical alignment in the 1st alignment mode [5-7].

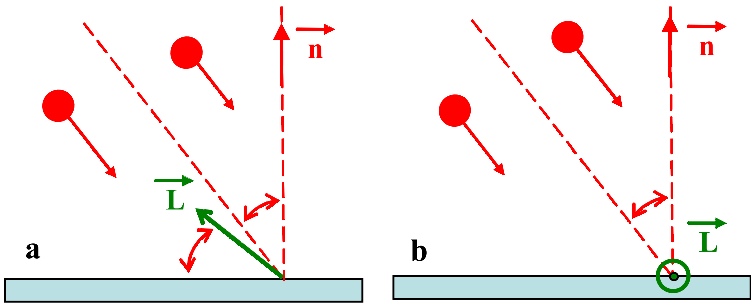



**Fig 1.**

In spite of big promise and great research efforts paid for VD technique it remains to be the technique for laboratory use. This is caused by technological limitations (e.g., it is hard to adapt this technique for the alignment coating on the large area substrates and for the mass line production) and non-suitable alignment parameters (e.g., pretilt angle of LC with $\Delta\varepsilon>0$ is higher than $10^{o}$).

The new impulse to the oblique deposition LC alignment technology gave the ion beam sputtering deposition (SD). In this process the material is only extracted from the top layer of the material (target) due to bombardment with ion beam. It substantially lowers power consumption, as compared with a vapor deposition. Using extended sputtering sources one can produce SD coatings on the large area substrates, including G6 and G7 fabs [10]. It is also important that SD operates with particles of substantial energy (several electonvolts and higher) that may bring alignment properties different from VD.

In spite of big promise, a small attention is only paid to this alignment procedure [11-14]. In fact, mostly LC alignment on $SiO_x$ films is considered. There is lack of data concerning the dependence of LC alignment on the material and processing conditions, corresponding alignment modes and alignment stability.

With the present paper we try to fill partially this important gap. We extend the quantity of alignment materials by the use of two different targets. Besides, varying the beams sputtering target the type of gaseous feed during deposition is also varied. The LC alignment modes and pretilt angle control are investigated. Finally we consider the alignment stability in time.

## 2. EXPERIMENTAL

### 2.1 Setup

For film deposition we utilize sputtering device designed by Izovac Ltd. (Belarus). This device is based on the anode layer accelerator (the other common name is source with closed electron drift) [15] with circular area of glow discharge. The focused beam of ions or, precisely speaking, accelerated plasma (primary beam) bombards target that results in extraction of target's particles (mainly, atoms). The atomic flux formed (secondary beam) reaches substrate producing alignment coating. The substrate is positioned obliquely with regard to atomic flux. The general construction of sputtering device and the position of the aligning substrate under deposition are presented in Fig. 2. The target was a disc of vitreous silica or graphite with diameter of 6 cm. As a gaseous feed we used Ar, $CF_4$, $Ar/CH_4$ and $Ar/C_3H_8$ gases and gaseous mixtures. The following operation parameters were used: residual pressure $2*10^{-5}$ Torr, working pressure $5*10^{-4}$ Torr, anode potential 4 kV, and discharge current 60mA. The deposition angle a was varied between $0^o$ and $85^o$.

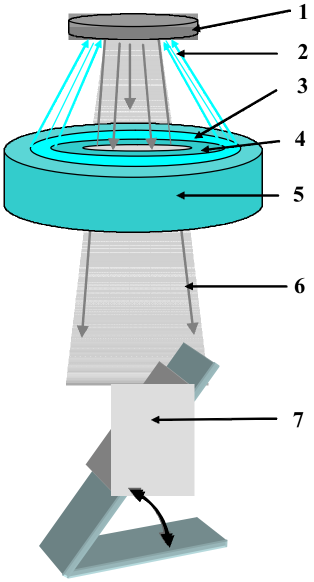



**Fig. 2.**

### 2.2 Samples

The substrates were 2x3 $cm^2$ glass slabs coated by ITO electrode layers with a thickness of 50 nm. The alignment films were coated over ITO layers. Their thickness was about 20 nm. Before deposition the electrode films were pre-cleaned with ion beam from the anode layer source of etching type.

Two types of LC cells have been prepared: (1) tested substrate contains deposited layer, while the reference substrate has a rubbed polyimide layer (asymmetric cells); and (2) both substrates contain tested layers and assembled in an antiparallel fashion (symmetric cells). The asymmetric cells were used to determine easy axis direction on the tested substrate (LC alignment mode). The symmetric cells were used to measure the pretilt angle by crystal rotation method. The cell gap was kept with spacers of 20 mm in diameter. We used TN mixtures E7 and ZLI2293 from Merck as LCs with $\Delta\varepsilon>0$ and VAN mixture MJ961180 from Merck Japan as LC with $\Delta\varepsilon<0$. The in-plane uniformity of LC alignment was tested by observation of samples in viewing box or in polarizing microscope. The out-of-plane uniformity was judged from the measurement of LC pretilt angle.

## 3. RESULTS

### 3.1. Alignment films sputtered from the silica target

For sputtering of silica target we used ion beams obtained from Ar, $CF_4$, $Ar/CH_4$ and $Ar/C_3H_8$ feed gases. The atoms of these gases, together with target's atoms, may be presented in the sputtered films. On account of this the corresponding films are marked as $SiO_x$, $SiO_xC_yF_z$, and $SiO_xC_yH_z$. In case of normal incidence of atomic beam ($\alpha=0^o$) and Ar or $CF_4$ feed we observed homeotropic alignment of LC MJ961180 and non-uniform alignment of LCs ZLI2293 and E7. The increase of deposition angle to $40^o$ does not lead to the substantial change of LC alignment. The subsequent increase of a results in gradual decrease of pretilt angle $\theta$ for LC with $\Delta\varepsilon<0$ and 2nd mode alignment ($\theta=0^o$) for LCs with $\Delta\varepsilon>0$. In case of tilted alignment, LC tilts towards deposition direction of atomic flux. With the increase of deposition angle up to $85^o$ no transition from the 2nd to the 1st alignment is observed. This is in contrast with the vapor deposition (VD) study [2], where transition from the 2nd to the 1st mode at $\alpha_c=(70^o-80^o)$ was detected. No difference in the type of alignment is observed for different feed gases, Table 1.

**Table 1. LC alignment on the films obtained by sputtering *silica target* with plasmas of different gases. $\alpha=55^o-85^o$.**

| Gas / LC | *Ar* | *$CF_4$* | *$CH_4$* | *$C_3H_8$* |
|---|---|---|---|---|
| *ZLI 2293, E7 ( >0)* | 2 mode, = 0 , good time stability | 2 mode, = 0 , good time stability | 2 mode, = 0 , good time stability | 2 mode, = 0 , good time stability |
| *MJ 961180 ( <0)* | 1 mode, = $88^o$-$89.5^o$, good time stability | 1 mode, = $86.5^o$-$87.5^o$, satisfactory time stability | 1 mode, <30 , good time stability | 1 mode, < 30 , good time stability |

In case of Ar and $CF_4$ gases, similarly to VD experiments [7], LC with $\Delta\varepsilon<0$ shows 1st mode alignment with pretilt angle close to 90°. But the use of $CF_4$ gas gives slightly lower pretilt angle comparing with Ar gas (86.5°- 87.5° vs. 88°-89.5°).

In case of $Ar/CH_4$ and $Ar/C_3H_8$ mixtures also the 2nd mode alignment for LCs with $\Delta\varepsilon>0$ and 1st mode alignment for LC with $\Delta\varepsilon<0$ is observed. In the latter case, pretilt angle substantially depends on the relative content of components: it gradually decreases with concentration of $C_nH_{2n+2}$ gas (Fig. 3). At 100% concentration of hydrocarbon gas the pretilt angle is within 40° and 15°. For LC with $\Delta\varepsilon>0$ the 2nd mode alignment is observed independently on the relative content of the components.

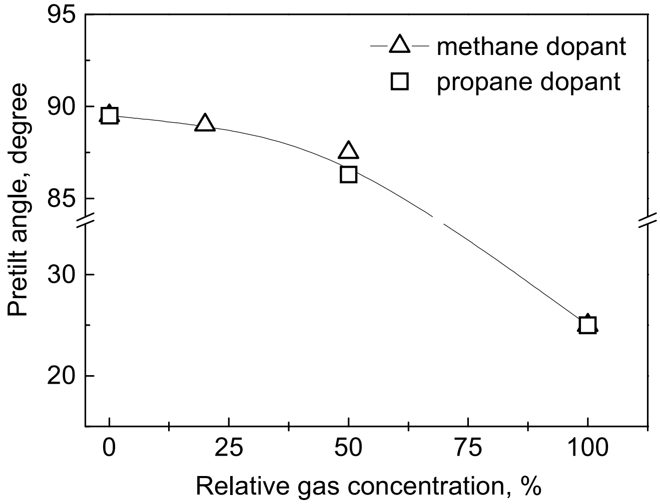



**Fig 3.**

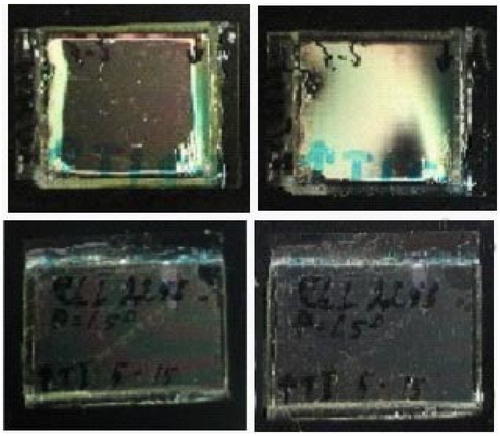
The alignment was rather stable except some samples with silica films made under $CF_4$ gas. The reason of this is unclear yet. Possibly, fluorine is presented in chemically active form so that chemical reactions with LC occur that change boundary conditions.

### 3.2. Alignment films sputtered from the graphite target

In case of graphite target only Ar and $CF_4$ were used as a feed gas. The corresponding films are marked as C and $CF_x$. The LC alignment properties of these films are summarized in Table 2. In case of Ar feed, same as in case of silica target, we observed 2nd mode alignment for LCs with $\Delta\varepsilon>0$ and 1st mode alignment with high pretilt angle ($\theta$=87°-89°) for LC with $\Delta\varepsilon<0$. By contrast with Ar, use of $CF_4$ feed leads to the 1st mode alignment of LCs with $\Delta\varepsilon>0$ (the pretilt angle is about 10°). As far as we know, it is the first observation of the 1st mode alignment of LC with $\Delta\varepsilon>0$ on SD substrates. The LC MJ961180 with $\varepsilon<0$ demonstrates under $CF_4$ feed high tilt alignment in the 1st mode, just as in case of Ar feed, but with lower pretilt angle (within 85°-87°).

The stability of LC alignment on C and $CF_x$ substrates is, unfortunately, poor. First of all, it relates to alignment on $CF_x$ films. Within two weeks the 1st mode alignment of LCs with $\Delta\varepsilon>0$ deteriorates (Fig. 4, (1), (1')), while the high-tilt alignment of LC with $\Delta\varepsilon<0$ relaxes to the low-tilt and, subsequently, to the planar alignment in the 1st mode. The same happens with alignment of LC with $\varepsilon<0$ on C films. Interestingly that the 1st mode planar alignment of LC ($\Delta\varepsilon<0$) on C and $CF_x$ films and the 2nd mode planar alignment of LCs ($\Delta>0$) on C films persisted over half year period of our observation (Fig. 4, (2), (2')). Thus, only planar alignment of the used liquid crystals is stable on C and $CF_x$ substrates.

1 1'



2 2'

**Fig 4.**

## 4. CONCLUSIONS

The results obtained show big variety of LC alignment characteristics on sputter deposition (SD) films, which depend on the deposition geometry, target material and feed gas. The conclusions listed below can be drawn:

1. The conventional configuration (silica target and Ar feed) results in 1st mode high-tilt alignment (tilted vertical alignment) for VAN LC MJ961180 ($\Delta\varepsilon<0$) and 2nd mode alignment for TN LCs ZLI2293 and E7 ($\Delta\varepsilon>0$). The result for LC ($\Delta\varepsilon<0$) is rather similar to previous results described for VD [7]. The difference with VD is a lack of the 1st alignment mode for LCs with $\Delta\varepsilon>0$ in

case of grazing deposition (α>80°). This might be caused by different surface morphologies of $SiO_x$ films in case of VD and SD processes operating with particles of different energy. Namely, in case of thermal deposition, the adatoms have energy of several milli-electronvolts meV, while in case of sputtering deposition the energies are of several electonvolts eV and higher.

2. The feed gas can influence LC alignment. In case of $C_nH_{2n+2}$ gases the pretilt angle of VAN LC with Δε<0 is lower than in a case of Ar feed. This may be used to optimize pretilt angle for some operation modes, for instance for STN VA requiring lower pretilt angle as a common TN VA.

3. The use of fluorine containing feed gases is undesirable, because they usually accelerate alignment aging. Presumably, the fluorine presented in the alignment coating is not combined with other atoms so that it can react with LC in interface changing boundary conditions.

4. In case of graphite target and $CF_4$ feed ($CF_x$ films) 1st alignment mode for LCs with ε>0 is realized. The pretilt angle is about 10°. However, this alignment is unstable and deteriorates within several weeks.

5. Initially, VAN LC with Δε<0 shows tilted VA on the graphite films. However, this alignment is unstable: for about one week the pretilt angle falls to zero. Thus, summarizing (4) and (5), only planar LC alignment is stable on the graphite films (1st mode planar alignment for LC with Δε<0 and 2nd mode planar alignment for LCs with Δε>0).

We believe that majority of these rules are rather general and so applicable to the films obtained by other combinations of targets and feed gases.

**Table 2. LC alignment on the films obtained by sputtering *graphite target* with plasmas of different gases. α=55°-85°.**

| Gas / LC | *Ar* | *$CF_4$* |
|---|---|---|
| *ZLI 2293 (     >0)* | 2 mode,<br>= 0<br>good time stability | 1 mode,<br>~ 10<br>poor time stability: deterioration within 2 weeks |
| *MJ 961180 (     <0)* | 1 mode,<br>= 87°-89<br>poor time stability:      0<br>for 1 week. | 1 mode,<br>= 85°-87<br>poor time stability:      0<br>for 1 week. |

## Acknowledgment

These studies were supported by INTAS foundation (grant 03-51-5448).

## References

1. J. Janning, "Thin film surface orientation for liquid crystal", Appl.Phys.Lett. 21(4), 173-174 (1972).
2. W. Urbach, M. Boix, and E. Guyon, "Alignment of nematics and smectics on evaporated films", Appl.Phys.Lett., 25 (9), 479-481 (1974).
3. E. Reynes, D. Rowell, and I. Shanks, Liquid crystal surface alignment treatment giving controlled low angle tilt", Mol.Cryst.Liq.Cryst., 34, 105-110 (1976).
4. D. Meyerhofer, "New technique of aligning liquid crystals on surfaces", Appl.Phys.Lett., 29 (11), 691-692 (1976).
5. A. Lackner, J. Margerum, L. Miller, and W. Smith, Photostable tilted-perpendicular alignment of liquid crystals for light valves, SID'90 Digest, 98-101.
6. H. Vithana, Y.K. Fung, S.H. Jamal, R. Herke, P.J. Boss, and D.L. Johnson, "A well-controlled tilted-homeotropic alignment method and a vertically aligned four-domain LCD fabricated by this technique", SID'95 Digest, 873-876.
7. M. Lu, K. Yang, T. Nakasogi, and S. Chey, "Homeotropic alignment by single oblique evaporation of $SiO_2$ and its application to high resolution microdisplays", SID'00 Digest, 446-449.
8. O. Yaroshchuk, R. Kravchuk, A. Dobrovolskyy, L. Qiu, O. Lavrentovich, "Planar and tilted uniform alignment of liquid crystals by plasma-treated substrates", Liq.Cryst., 31 (6), 859-869 (2004).
9. O.V. Yaroshchuk, R.M. Kravchuk, A.M. Dobrovolskyy, P.C. Liu, C.D. Lee, Plasma beam alignment for the large area substrates: equipment and process. J.SID, 13 (4), 289-294 (2005).
10. V. Shiripov, A. Khokhlov, S. Maryshev, M. Levchuk, A. Khissamov, K. Krivetski "Display thin-film coatings produced by ion-beam processing", J. SID, 13( 4), 315-320 (2005)
11. T. Motohiro and Y. Taga, "Sputter-deposeted $SiO_2$ films for LC alignment", Thin Solid Films, 185, 137-144 (1990).
12. "Inducing tilted parallel alignment in liquid crystals", US patent 5,529,817 (1996).
13. Y. Kolomsarov, P. Oleksenko, V. Sorokin, P. Tytarenko, and R. Zelinsky, "Orienting properties of $SiO_x$ films for high resolution LCD", Proc. of ADT'04 (Sept. 7-10, 2004, Raubichi, Belarus), 83-88 (2004).
14. A. Murauski, A. Khakhlou, V. Shiripov, and A. Cerasimovich, Ion beam sputter deposition process of inorganic vertical alignment layers, SID'04 Digest, 574-576.
15. V Zhurin, H Kaufman, and R Robinson, "Physics of closed drift thrusters," Plasma Sources Sci Technol 8, R1–R20 (1999).