Plasma-beam alignment of passive liquid crystals *(Invited Paper)*

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Abstract — A plasma-beam process, developed for the alignment of liquid crystals (LC) in electro-optic applications, has been successfully applied to align "non-standard" LC, such as crystalline materials with LC phases at elevated temperatures and reactive mesogenes. In addition to the high alignment quality of the materials, there is no need for an intermediate layer between the substrate and the LC layer. Furthermore, the construction of our source simplifies the alignment procedure of large-area rigid substrates and the roll-to-roll processing of flexible films. This method opens new horizons for optical retarders and polarizers, as well as anisotropic semiconducting films for organic electronics.

Keywords — *Liquid-crystal alignment, ion-beam alignment, reactive mesogene, compensation film, liquid-crystal semiconductors.*

1 Introduction

The proper alignment of liquid-crystal (LC) compounds is a key technological problem of modern LC devices. The planar/tilted alignment of LCs is usually achieved by rubbing a polymer substrate or film.[1] However, the uniformity of the LC alignment layer provided by rubbing is far from ideal, which is especially critical for microdisplays. The rubbing causes electrical charging, dangerous for surface electronics, and surface dusting. It is difficult to apply rubbing to produce some alignment patterns. Finally, this method is not efficient for substrates that are not flat.

The method that shows special promise for planar/low-pretilt alignment is the so-called ion-beam alignment method. It was originally proposed by Little[2] and then further developed by IBM[3,4] and number of other groups.[5–9] In this process, the alignment surface is modified by a beam of accelerated particles obliquely impinging upon substrate. The particles mill or etch the surface of the substrate causing modification of the surface relief[10,11] or break the molecular bonds.[12] For an oblique-incidence particle beam, this results in surface anisotropy and hence in the alignment of the LC. This method provides excellent alignment of the LC commonly used in TN-, STN-, and IPS-LCDs characterized by low pretilt angle. High pretilt alignment for VA LC was also introduced[13] for a limited number of hydrophobic surfaces by using extremely low irradiation doses. Previously, a number of excellent LCD prototypes based on this alignment method has been demonstrated.[4,8,9]

2 Plasma-beam processing approach

In most studies devoted to ion-beam alignment, a Kaufman source was utilized. This is an electrostatic source of rather complicated construction, generating cylindrical beam of ions. The ion energy, determined by the accelerating potential on the corresponding grid, is 50–200 V.

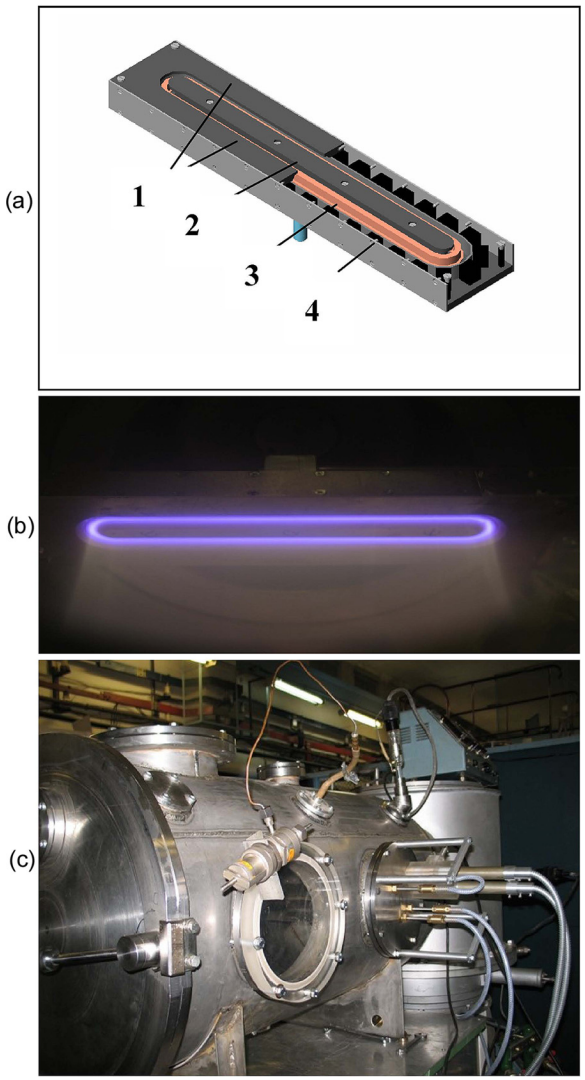

FIGURE 1 — (a) Sketch of ALS, (b) photograph of ALS and generated plasma "sheets," and (c) photograph of plasma-beam setup. ALS structure: 1 – outer cathodes, 2 – inner cathode, 3 – anode, 4 – permanent magnets.

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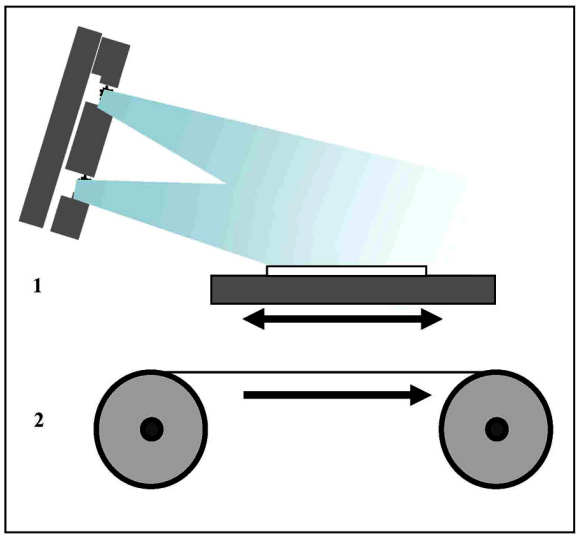


FIGURE 2 — Plasma-beam exposure geometry. 1 – Cycling translation regime (mainly used for rigid substrates); 2 – roll-to-roll translation regime (used for flexible plastic strips).

Instead of using the Kaufman source, we adapted an electrodynamic anode layer source (ALS) from the Hall family.[14] It can work in the beam mode and in the diffusive mode without a specific direction of plasma flux. In the beam mode, ALS provides a collimated flux of accelerated particles from practically any gaseous feed.

The scheme of this source is presented in Fig. 1(a). It consists of cathodes, an anode, and a system of magnets. The inner and outer cathodes and anode form a slot in which glow discharge is initiated. The particle flux is formed in the crossed electric and magnetic fields directly within the discharge channel [Fig. 1(b)]. The generated beam and glow discharge are not spatially separated so that the beam is part of the generated plasma. The ions in this beam are accelerated by a strong anode potential (500–5000 eV), while the involved electrons are rather "cold." Therefore, we refer the generated beam as a beam of accelerated plasma rather than ion beam to emphasize the difference with the beam generated by the Kaufman source.

Thus, compared with a Kaufman source, ALS has an extremely simple construction. It does not contain grids and hot elements (such as filaments and other secondary electron sources). This allows one to substantially increase reliability and simplify the maintenance procedure. The linear design of our source allows one to treat relatively large substrates (40×40 cm^2) by translation of the solid substrates or roll-to-roll rewinding for flexible plastic films across two plasma "sheets" (Fig. 2).

A general view of the exposure setup is presented in Fig. 1(b). The feed gas is argon. The working pressure in our experiments, that determines the current density of plasma ions, j, was $(2–10) \times 10^{-4}$ Torr. The ion energy controlled by the anode potential U_a was within 200–1000 eV.

The exposure geometry preferably used is shown in Fig. 2. By rotation of the source, the incident angle of the plasma beam can be varied. The incident angle typically used was about 70°. The substrates were treated in a cycling (there and back) translation regime or in a roll-to-roll translation manner by mounting a corresponding moving system in the vacuum chamber. The translation speed was about 2 mm/sec. The substrates were treated entirely or partially. In the latter case, masks of different configurations were used.

Based on this approach, earlier we realized excellent alignment of liquid crystals commonly used in electro-optic devices. The alignment modes and ranges of alignment parameters obtained are summarized in our previous papers.[10,13]

3 Passive liquid crystals

In the common case, liquid crystals are designed for electro-optic switching, *i.e.*, the LC director is controlled by an electric field. In this sense, the LC is active. In contrast to the common case, some optical and electronic applications of liquid crystals do not require director activation. Usually, for these purposes solid films of liquid-crystalline materials are used. These materials can be classified according to solidification process. One class is formed by *reactive mesogenes* (RM). The RM molecules contain terminal or lateral groups capable of cross-linking through thermal- or photo-excitation.[15] The aligned and subsequently crosslinked RM form solid and highly birefringent films. They can be used in passive optical elements such as retarders, dichroic polarizers, and color filters,[16–19] and in thin electronic devices such as thin-film transistors, organic light-emitting diodes, *etc.*[20,21] Additionally, solid anisotropic films can be obtained from materials exhibiting LC mesophases at elevated temperatures. Such materials, aligned in the mesophase, may keep their orientational order in the crystalline or glassy state when cooled. Let us call these materials *"frozen" LCs*. The two types of LC materials described above are called "passive" liquid crystals to emphasize their difference with common LC materials that are orientationally activated by an electric field. In the present work, we demonstrate the effectiveness of a plasma-beam alignment technique for passive LC materials.

4 Alignment peculiarities

4.1 Alignment of reactive mesogenes

In these tests, we used planar RM mixtures (p-RM) RMM141 and RMS04-073 and a homeotropic mixture (h-RM) RMS04-007 from Merck. The mixtures RMS04-073 and RMS04-007 were received in solution form, while the mixture RMM141 was dissolved in toluene (30 wt.%). The RM films were obtained by spin-coating RM solution on the appropriate substrates. The substrates we used

(1) polymer layers (polyimide, polymethylmethacrylate, as well as color-filter polymer layers);

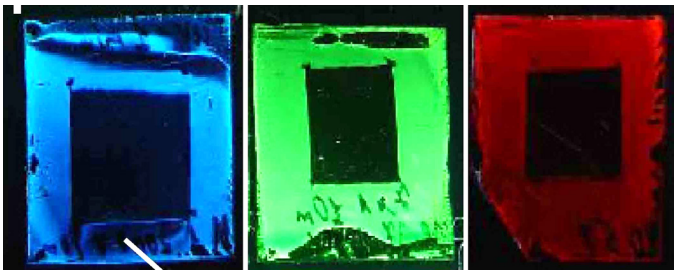


FIGURE 3 — Layers of p-RM RMM141 deposited on color-filter films partially processed by the plasma beam (rectangular area in the middle of sample). Treatment conditions: $\alpha = 75°$, $j = 6–8$ μA/cm^2, $U_a = 600$ V. The substrates are cyclically moved (2 mm/sec, 5 min) during irradiation. Samples are viewed between two crossed polarizers.

(2) bare glass substrates (microscope slides from Fisher Scientific);
(3) bare silicon wafers;
(4) plastic flexible strips (TAC and COP isotropic and anisotropic films).

After treating the substrates with a plasma beam, the RM mixture was spin-coated on the substrate and kept at 60°C for 1 minute to remove residual solvent and improve RM alignment. Then, the film was polymerized by irradiating for 1 min with a broad-spectrum UV light from a high-pressure mercury lamp (light intensity, 50 mW/cm^2).

The quality of the RM alignment was examined by using sample observation in a polarizing light box and a polarizing microscope. The retardation properties were studied by using a null ellipsommetry technique.[13]

First, we investigated the alignment quality, depending on the exposure dose. The optimized processing conditions for RMs were found to be similar to conventional (active) LC mixtures (current density, 6–15 μA/cm^2, exposure time, 1–10 minutes). At these processing conditions, we achieved excellent alignment of RM films on all substrates involved in our tests. Figure 3 shows the alignment of planar RM on the color-filter films. One can clearly see a difference in RM alignment between the plasma-processed part (rectangular area in the middle of the film) and the unprocessed area in the peripheral part of the film. The alignment of the same high quality was also realized on color-filter arrays used in color LCDs (Fig. 4). One can see that the alignment is highly uniform on the microscopic

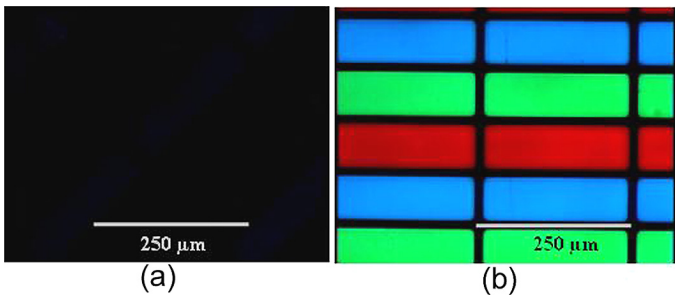


FIGURE 4 — Layer of p-RMM 141 deposited on a color filter array viewed by a polarizing microscope. The polarizers are crossed. The angle between the polarizer and alignment direction is (a) 0° and (b) 45°.

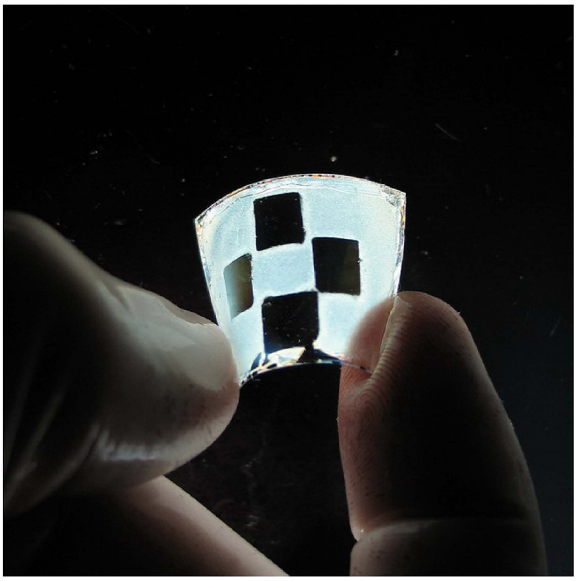


FIGURE 5 — p-RM RMS04-073 film deposited on TAC isotropic substrate obliquely irradiated by a plasma beam through a mask. Treatment conditions: $\alpha = 75°$, $j = 6–8$ μA/cm^2, $U_a = 600$ V. Sample is viewed between two crossed polarizers.

level. This shows that simple stacking of LCD components is possible, which makes RM especially suitable for in-cell purposes.

High-quality alignment of the p-RM mixtures was also obtained on plastic substrates. Figure 5 shows an RM film with alignment patterns disposed on COP film. The corresponding plastic strip was treated with a plasma beam in the course of roll-to-roll translation. No noticeable worsening of RM alignment was observed due to the winding of treated plastic strips before coating the RM films. Moreover, after applying the RM film, the strips can be curved without any damage to the RM films.

The h-RM RMS04-007 aligned well on all substrates involved in our tests. Note that the plasma processing step was not important for some of them from the viewpoint of RM alignment, but it always improved the adhesion of RM films. However, for plastic substrates, plasma treatment was principally important to obtain homeotropic alignment of good uniformity. A positive result was obtained for both oblique and normal irradiation. Moreover, processing with a diffuse plasma (diffusive mode of ALS source) also radically improved the quality of homeotropic alignment. As described below, tilted alignment of h-RM was also realized.

Figure 6 demonstrates the retardation properties of RM films aligned differently. Curve 1 corresponds to angular dependence of phase retardation of RMM141 film deposited on blue-filter film shown in Fig. 3. Optically, this sample is equivalent to a positive A plate which indicates planar alignment of the RM molecules. A qualitatively same result is obtained for other type of p-RM – RMS04-073. The type of alignment for planar RM does not depend on the alignment material or exposure conditions. Curve 2 in Fig. 6 corresponds to h-RM RMS04-007 film on the color-filter layer. This retardation profile is typical for a positive C plate hav-

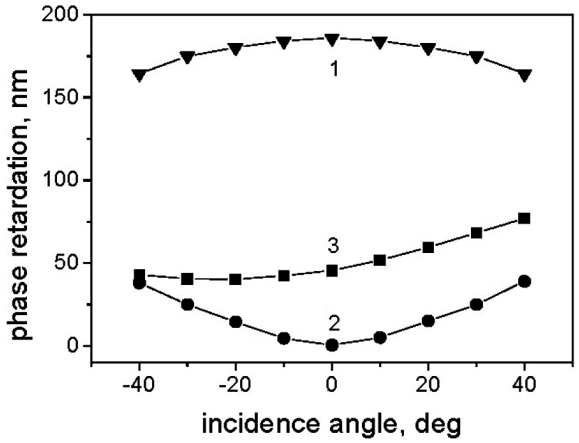
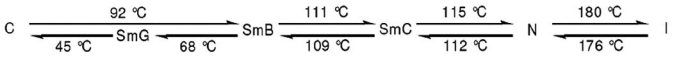


FIGURE 6 — Phase retardation *vs.* sample rotation curves for RMM141 film aligned with color-filter substrate (1), RMS04-007 film aligned with color filter substrate (2), and RMS04-007 film aligned with TAC film (3).

ing an optical axis coinciding with the film normal. This confirms the homeotropic alignment of RM molecules. Finally, in some range of exposure doses, RMS04-007 layers on COP films demonstrate a retardation profile typical for positive O plates (curve 3 in Fig. 6), which implies tilted alignment of RM.

4.2 Alignment of "frozen" LCs

In the experiments in this series, we used organic semiconductor 5,5″-bis(5-hexyl-2-thienylethynyl)-2,2′:5′,2″-terthiophene (HTET). This compound exhibits a sequence of liquid-crystalline phases by heating and cooling as shown below. At room temperature, it exists in crystalline phase.



Earlier, HTET was successfully aligned on rubbed polyimide layers.[22] For this purpose, the HTET films spin-coated on the rubbed PI layer were heated to the nematic phase to easily align and then slowly cooled down to room temperature. By undergoing a transition of one LC phase to another, the compound enhanced molecular order and viscosity finally transitioned to the crystalline phase. As a result, aligned monodomain films were obtained.

As substrates, we used glass and quartz plates and silicon wafers. The wafers were bare as well as coated with interdigitated gold electrodes covered by a 200-nm-thick SiO_2 dielectric layer and n^{++}-Si gate electrode. The substrates were processed by using a plasma beam at the following conditions: $\alpha = 70°$, $j = 8$ μA/cm^2, $E = 600$ eV, $t = 15$ min. Following Ref. 22, HTET films were prepared by spin-coating a 2-wt.% filtered solution of the semiconductor in toluene on plasma-processed substrates. Subsequently, the substrates were heated to 150°C and then cooled down to 30°C at a cooling rate of 5°C/min. As a result, monodomain films with a highly uniform alignment were obtained. The dichroic ratio of the polarized absorption spectra, estimated for quartz-based films, reached 20. Figure 7 shows a bottom-gate transistor with a HTET semiconducting layer aligned by the plasma-beam process. The samples with alignment patterns having different in-plane alignment directions were also easily fabricated.

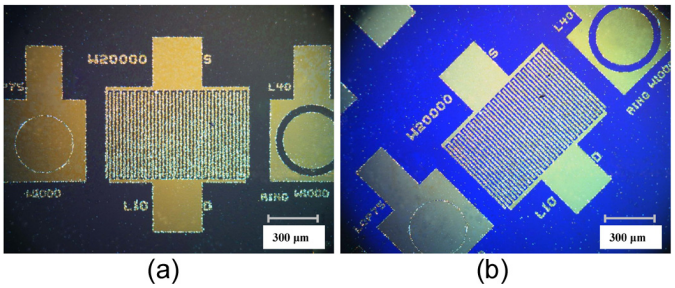


FIGURE 7 — Thin-film transistor–on–silicon wafer containing top HTET semiconducting layer aligned by plasma-beam process ($\alpha = 70°$, $j = 8$ μA/cm^2, $E = 600$ eV, $t = 15$ min). Sample is viewed by a reflective microscope in crossed polarizers. The angle between the polarizer and alignment direction is (a) 0° and (b) 45°.

5 Conclusions

The plasma-beam alignment method is shown to be effective for the alignment of non-standard liquid crystals, used for non-electro-optic applications. These liquid crystals, being in the solid-state phase at ambient temperatures, are used as passive optical films and electronic elements. As examples of these compounds, we used optical reactive mesogenes and semiconducting material showing a liquid-crystal behavior above 40°C. The alignment of these LC on the plasma-processed substrates is characterized by high uniformity on both the macroscopic and microscopic levels. The method easily realizes patterned alignment and provides good adhesion of the LC film to the substrate. Thus, plasma-beam alignment opens new horizons for anisotropic organic films currently used in optics as well as promising significant advances in organic electronics.

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