COVERING OBLIQUELY DEPOSITED SiOx WITH POLYVINYL CARBAZOLE CHANGES THE ORIENTATION PROPERTIES

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Alignment layers of polyvinylcarbazole (PVK) were obtained by withdrawing from different solutions in toluene onto glass plates having SiOx layers obliquely evaporated in vacuum at 82°. The alignment direction of nematic liquid crystal molecules with cyan-end group imposed by bare SiOx layers is changed when these layers are coated with PVK; the same happens with over layers of polyvinylimidazole or of polyvinylcinnamate. The effect is inhibited by doping PVK with fullerene C60 (0.1%), when the liquid crystal orientation specific for bare SiOx obliquely evaporated substrates is obtained. Other nematic (with methoxy-end group) does not show change of the orientation properties by covering the SiOx obliquely deposited layers with the mentioned polymer over layers.

Key words: SiOx obliquely deposited, polyvinyl carbazole, optical microscopy.

1. INTRODUCTION

Since the discovery of the liquid crystal alignment by Mauguin, a large variety of alignment techniques were developed to valorize the crucial role that liquid crystals (LCs) play in production of displaying devices (e.g. [1]). An equal motivation was the need to understand the alignment mechanisms since there is not yet a satisfactory knowledge of the whole field of these phenomena. Non-stoichiometric SiOx films deposited on glass plates by evaporation in vacuum at large incident angles [2, 3] align the liquid crystal molecules in the evaporation plane tilted against glass surface. There is a very rich literature describing this alignment behavior, either experimental works ([4–7]) or theoretic ones ([8]). It was shown that aligning micro relief could create nematic oriented structures, which are defect less at the microscopic level [9]. On SiOx films deposited at incident angles larger than 72°, the liquid crystal molecules align obliquely in the evaporation plane while SiOx/SiO2 films deposited at angles less than 60° induce an alignment normal to the evaporation plane or vertical to the glass plates depending
on the sign of LC dielectric anisotropy [10–12]. At incidence angles greater than 60° and less than 72° a bistable orientation between planar and oblique orientation is induced for SiOx films of the thickness comparable with the molecular length [13].

A technique was developed which uses polyvinyl alcohol (PVA) to cover SiOx layers evaporated under incident angles higher than 80° (e.g. [14–16]). PVA film, deposited by dip coating from aqueous solution, allows obtaining alignment angles for liquid crystal molecules from 27° (for PVA concentration of 0.25%) down to 7° (for solution concentration of 1.65%). For concentrations of 1.7% or higher the PVA film ceases to present alignment properties.

On the other hand, unidirectionally rubbed polymer layers have aligning properties [17] parallel to the rubbing direction; rubbing the polymer films was thus imposed as the most widely used technique in the display devices. There were also found polymer films which induce an alignment perpendicular to the rubbing direction for nematic liquid crystals with a cyan-end group, for example polystyrene (PS) [18], polyvinylimidazole (PVI) [19,20] or polyvinylcinnamate (PVCi) [19, 21]. Rubbing a layer of polyvinylcarbazole (PVK) (which is in addition an excellent film-forming material) induces homogeneous alignment of LCs with their director axes perpendicular to the rubbing direction [22].

In order to obtain new knowledge on the alignment mechanisms of liquid crystal molecules, we combined the orienting properties of thin polymer layers and those of SiOx layers obliquely evaporated in vacuum. Polymers with bulky or polar side chains as PVK, PVI or PVCi were thus chosen and deposited over SiOx by dip or spin coating. The withdrawing direction was chosen either parallel with the evaporation plane of SiOx or making an angle with this plane. For the cells made of plates with SiOx evaporated at 82° and coated with PVK from toluene solution with concentration between 0.25 and 1.50%, we found that the final alignment of liquid crystal was perpendicular to the evaporation plane, whereas uncoated SiOx evaporated at 82° induced alignment in the evaporation plane. The nematic LC used was a mixture of cyan-end group components (named E7); its behavior was compared with that of another nematic which has a methoxy-end group and imine structure. Over layers of fullerene (C60) doped PVK [23] does not show this found perpendicular alignment.

2. EXPERIMENTAL

2.1. MATERIALS

The liquid crystal (LC) used in this study was E7 (from Merck), a mixture of four cyanobiphenyl components. This LC was selected among the nematics for
having suitably low transition temperatures such as melting point at 263 K, nematic-isotropic transition at 331 K and a glass transition at 211 K. Behavior of E7 was compared with that of MBBA (N-(methoxybenzilidene)-4-buthylaniline) from Aldrich. MBBA has a negative dielectric anisotropy. The transition temperatures from solid to LC and from LC to isotropic liquid are 293 and 316.9 K respectively.

PVK was obtained from the corresponding monomer (Polysciences Inc.) at the Institute of Macromolecular Chemistry “Petru Poni” (Iassy, Romania). PVK has the molecular weight of ca. 40000, while PVCi, ca. 200000, both were purchased from Polysciences Inc.

Glass plates were soda-lime type, either standard Cole-Parmer microscope slides or ordinary float plates.

Other reactants and the solvents (toluene, chloroform, etc.) were of very high purity and used as purchased.

2.2. ALIGNMENT LAYERS

Non-stoichiometric silicon oxide (SiOx) layers were obtained on glass plates by obliquely evaporation in vacuum of SiO (Balzers), at incident angle of 82° or 60° in a B30.2 equipment (Hochvakuum Dresden) at 10^-8 bar as already described [24–26]. The SiOx deposited layers were subsequently coated with the polymeric layer mostly by dip coating but in some cases (mentioned in the following) by spin coating. For a few experiments, SiOx was subsequently covered with fullerene C60 [27, 28] by spinning from a 0.1% toluene solution.

PVK was deposited by dip coating: toluene solutions of 0.25, 0.50, 0.75 and 1%, were used; the withdrawing speed was of 10 mm/min. After deposition, the glass plates were thermally treated 30 min at 363 K, then 60 min at 453 K. PVK was used as such or doped (0.1%) with C60 fullerene.

PVI was also deposited by dip coating (with a vertical withdrawing speed of 3 mm/min) from 1% or 1.5% aqueous solution. The lifting set-up was used in a hut atmosphere. The withdrawing direction was usually parallel with the incident plane of SiOx evaporation; the sense was thus that the end of plate closer to the vapor source was the last to leave the solution. Aqueous solutions of 0.5% PVI were used for spin coatings. After PVI deposition the glass plates were backed at 373 K for 30 min.

PVCi was spin coated from a solution 1% in chloroform.

In the following, the samples were labeled by noting the type of polymer deposited, the SiOx evaporation angle, the substrate nature; for example PVK/SiOx82/G means a glass (G) plate containing a layer of SiOx deposited at 82° and an over layer of PVK; the “G” support was usually dropped.
PVK/(SiOx82+C60) means that the first layer (of SiOx deposited at 82°) was covered with C60 layer; the plates were dried and the layer of PVK was deposited. The liquid crystal cells (see further) made from such plates have the notation of the corresponding plates.

2.3. CHARACTERIZATION OF DEPOSITED LAYERS

Composition of glass deposited SiOx layers was investigated by X-ray photoelectron spectroscopy (XPS) in a SPECS Multimethod Surface Analysis System. The photoelectron spectra were obtained using a Phoibos analyzer with monochromatic X-rays emitted by an anti-cathode of Al (1486.7 eV), operating in the constant energy mode with a pass energy of 20 eV and in ultra high vacuum conditions (3·10⁻⁹ mbar). The energy scale of the spectrometer has been calibrated using C1s (285 eV) line. The spectra were processed using Spectral Data Processor v 2.3 (SDP) software.

The thickness of the layers was evaluated by spectroscopic ellipsometry. The layers for these measurements were deposited either onto the glass plates or especially onto silicon wafers by dip coating using the withdrawing system of a Langmuir Blodgett (LB) equipment (KSV Instruments) in order to have the best control of the withdrawing. The ellipsometric angles \( \psi \) and \( \Delta \) were measured on each sample, with a Woollam DUV-VIS-XNIR Variable Angle Spectroscopic Ellipsometer, in the spectral interval 400-1000 nm, at incidence angles of 60, 65 and 75°. The experimental data were fitted with an adequate uniaxial optical model, consisting of two Cauchy dispersions: one perpendicular and the other parallel to the substrate.

2.4. OBTAINING THE LIQUID CRYSTAL CELLS

The cells were made of rectangular glass plates provided or not with transparent electrodes of ITO, which were subsequently covered with alignment layers. The thickness of the cells was ensured with 15 \( \mu \)m strips of Mylar. The assembled cells were immobilized with binder clips or with epoxy resin on the cell perimeter. The filling with liquid crystal in the isotropic phase was made by capillarity, to avoid the appearance of a privileged alignment related to the direction of the flow during the filling. However, this type of filling may produce point-like or linear discontinuities of the orientation, when the anchoring to the alignment layer is weak. When polymer layer was deposited by withdrawing from solution, a three-region-structure of assembled cells was obtained as shown in Fig. 1a. The evaporation direction on the cell plates is shown in Fig. 1b, together with the alignment direction in the case of the cell deposited only with SiOx; these cells are so-called symmetric ones.
PVK changes the orienting upon obliquely deposited SiOx

Thus, in the central region of the cell the alignment properties are defined by identical orientation at the two surfaces covered with SiOx and polymer layer. The two lateral regions might have hybrid alignment properties determined by the possible different orientations at the surface layers: a reference region, covered only with SiOx and the studied region, covered with a combined layer of SiOx and the polymer.

After filling, the alignment in the cells was checked either by direct visual inspection (between parallel or crossed polarizers, in a parallel beam of light) or by conoscopy (between crossed polarizers in a convergent beam of light). The experimental setup includes as usually a polarizing microscope (Zeiss Amplival PolU or Leitz Ortoplan) with an adapted digital photo camera (Panasonic DMC-FZ8) or a video camera.

3. RESULTS AND DISCUSSION

3.1. CHARACTERIZATION OF DEPOSITED LAYERS

XPS investigation of SiOx layers was performed because it was found that SiOx layer horizontally aligns liquid crystals when the value of $x$ is in the range from about 1.0 to about 1.5, but vertically aligns the liquid crystals when the value of $x$ is in a range from about 1.5 to about 2.0 [29]. Representative high resolution spectra are given in Fig. 2 for silicium and oxygen. Both spectra are decomposed into several components. The highest Si2p peak belongs to Si$^{4+}$ in SiO$_2$ species [30, 31] while the peak of medium intensity, to SiO species. The highest O1s peak shows O$^2-$ species [32] while the second one, shows species OH$. The various suboxides cannot be differentiated using this O1s photoelectron peak [32].
From the intensities of Si2p and O1s photoelectron peaks in combination with the different sensitivity coefficients of each element it was possible to determine the chemical composition of the surface. Thus, the estimated value for the Si/O atomic ratio is 1.50, a limit value corresponding to the alignment imposed by SiOx layers deposited in vacuum under 60° incidence angles to MBBA and E7 molecules.

![Graph](image)

Fig. 2 – High resolution photoelectron Si2p (a) and O1s (b) spectra (empty symbols), their deconvolution into Gaussian components (dashed lines) and their sum (continuous line) for the sample SiOx82.

Representative spectroellipsometric measurements of the sample PVK/Si and their fit with the biaxial model are given in Fig. 3: a rather good agreement can be observed. The estimated values for the thickness of studied layers are presented in Table 1. SiOx layers have in average up to 100 nm (as expected from the deposition conditions), while PVK layers have a thickness of a few nm. The parallel and perpendicular refraction indexes of the deposited layer as obtained by the applied model (not shown in Fig. 3) are a bit smaller than those of a SiO2 glass [33] predictable on the basis of a smaller density of the “porous-like” structure of the deposited material. Since the uniaxial model gave the best fitting results, we can suppose that the SiOx layer is composed of SiO2 matrix with tilted and elongated nanopores inside.

Refractive index of PVK in the film deposited onto silicon is also a bit smaller than that of a bulk material but roughly one can say its value agrees with literature data.
PVK changes the orienting upon obliquely deposited SiOx

Fig. 3 – Ellipsometric data (empty symbols) and the corresponding fit (line) for the sample PVK/Si in the case of incidence angle of 75°. Dotted lines belong to Si substrate.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Layer of interest</th>
<th>Layer thickness* (nm)</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiOx82/Si</td>
<td>SiOx</td>
<td>63.4</td>
<td>Biaxial model</td>
</tr>
<tr>
<td>SiOx82/G</td>
<td>SiOx</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>PVK/SiOx82/G</td>
<td>PVK</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>PVK/Si</td>
<td>PVK</td>
<td>2.7</td>
<td>PVK deposited in LB cuvette</td>
</tr>
</tbody>
</table>

* In the case of columnar structure, the values are mediated.

3.2. ALIGNMENT PROPERTIES OF SiOx COVERED WITH POLYMER LAYERS

Since it was known that SiOx evaporation at 60° incidence angle provides an alignment normal to the evaporation plane for cyanobiphenyls [34, 35] and MBBA [25], we have focused mainly onto plates deposited with SiOx by evaporation at 82° and covered with polymer layers and obtained some reference cells.

In the antisymmetric cells (see Fig. 1b) made with plates deposited only with SiOx a homogeneous tilted alignment of liquid crystal molecules in the incident plane of evaporation can be obtained. One of the polarizers has the axis parallel to the evaporation plane (Fig. 4a). The conoscopic image of the same cell (Fig. 4b) supports the tilted orientation of LC molecules in the evaporation plane.

Representative images of the cells containing a PVK over layer made with plates deposited with SiOx82 and dipped into PVK solution (0.75%) are shown in Figs. 4c,d. The lateral light stripes (Fig. 4c) correspond to zones where the glass plates are covered with SiOx without PVK over layer, whereas the central zone has SiOx layer which is PVK covered. The cell aspect indicates a twisted structure in the lateral stripes, while in the central part the molecules are homogeneously
oriented perpendicular to the evaporation plane, imposed by PVK over layer. The alignment observed is quite stable (more than 2 months). PVK layers obtained from the other PVK concentrations behave similarly.

The cells obtained from PVK solution doped with C60 show alignment tilted in the incidence plane, as one can see from Figs. 4e,f.

At this stage of investigations, we can only speculate on the mechanism acting in the case of the surface alignment properties of our samples. For the liquid crystal cells made with plates with SiOx evaporated at 60° and coated with PVK, by cooling the liquid crystal from the isotropic phase one ends in a state aligned perpendicularly to the evaporation plane, as in the case of bare SiOx (not shown here).

![Fig. 4 – Up: Images of cells made from SiOx82 plates (a,b) or from PVK/SiOx82 plates (c,d) between crossed polarizers (a,c), by conoscop (b) or between parallel polarizers (d). Down: Images of a cell made with (PVK+C60)/SiOx82 (e,f) or PVK/(SiOx+C60) plates (g,h) between crossed polarizers (e,g) or by conoscop (f,h). LC was E7 in all the cases.](image)

In Fig. 5a the aspect between crossed polarizers of a representative LC cell assembled from SiOx82 glass plates subsequently covered by a PVI layer from a 1.5% solution is shown. As in the case of PVK over layered cells (Fig. 4c). The lateral light stripes correspond to zones where one of the glass plates has the SiOx layer uncovered by dipping in PVI solution, whereas the central zone has SiOx layer covered with PVI. The cell aspect clearly indicates a twisted structure. Taking into consideration that the alignment of LC molecules on SiOx is in the evaporation plane (parallel to the long side of the cell) the E7 molecules are aligned perpendicularly to the evaporation plane on the PVI layer. Therefore in the central zone of Fig. 5a, the LC molecules are uniformly aligned and perpendicular to the evaporation plane. In Fig. 5b, the image between crossed polarizers of a cell with the SiOx82 glass plates withdrawn from PVI solution at 30° to the evaporation plane is presented. It can be seen that the withdrawing direction does not influence
PVK changes the orienting upon obliquely deposited SiOx

the obtained alignment imposed by the polymer layer. This is definitely proved by Fig. 5c where PVI layer was deposited (also from a 1.5% solution) onto SiOx by spin coating.

The alignment obtained in all these LC cells made with different layers on the plates is summarized in Table 2. One can see the change of the alignment of E7 molecules when passing from plates deposited only with SiOx layer to those with a polymer over layer. It is noteworthy that fullerene C60 does not change the orientation plane when covers directly the SiOx layer. In the case of PVK layer, there are three situations: PVK covering SiOx changes the orientation, while PVK with C60 does not change the orientation plane as in the case of PVK covering (SiOx+C60) deposition. For PVI layers onto SiOx, the alignment remains normal to the evaporation plane. It results from Table 2 that MBBA molecules are always in the evaporation plane no matter which is the treatment of SiOx layer.

![Images between crossed polarizers](image)

**Fig. 5** – Images between crossed polarizers of a cell made from PVI/SiOx plates (a,b) or with one PVI/SiOx plate and the other PVA/SiOx plate (c). The withdrawing direction is: a) parallel; b) at 30° to the evaporation plane. The long side of the plate is parallel to the evaporation plane. The rubbing and evaporation directions for the cell in c) are at 90°. LC was E7.

**Table 2**

<table>
<thead>
<tr>
<th>Layer(s) \ LC</th>
<th>E7</th>
<th>MBBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiOx82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiOx82+C60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVK/SiOx82</td>
<td>⊥</td>
<td></td>
</tr>
<tr>
<td>PVI/SiOx82</td>
<td>⊥</td>
<td></td>
</tr>
<tr>
<td>PVCi/SiOx82</td>
<td>⊥</td>
<td></td>
</tr>
<tr>
<td>PVA/SiOx82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVK/(SiOx82+C60)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVI/(SiOx82+C60)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(PVK+C60)/SiOx82</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The symbols mean: || - parallel, ⊥ - perpendicular to the evaporation plane.

**3.3. DISCUSSION**

The mechanisms proposed to explain the alignment of LCs on substrate surfaces take into consideration the effect of the topography [5], steric hindrance,
order electricity [36, 37], van der Waals interactions [10, 11] and even \(\pi-\pi\) electron coupling in the case of some polymer layers [38, 39].

Alignment layers of the rubbed polymers either obtained from PVA, polymethyl methacrylate (PMMA) or from polymers exposing aromatic rings in the lateral groups (PVI, PVK, PVCi) induce molecular ordering of LCs having a methoxy-end group (MBBA), following a direction parallel to the rubbing direction. When LC has cyan-end groups, LC molecules adopt an orientation parallel to the rubbing direction onto PVA, PMMA layers while on the PVK, PVI, PVCi substrates the orientation is perpendicular to the rubbing direction [20]. Birefringence measurements [17], polarized absorption spectra [39], NEXAFS [38] and surface specific sum frequency vibrational spectra [39] proved that the rubbing process effectively aligns polymer main chains and lateral groups. Therefore the alignment of LCs by unidirectionally rubbed polymer layers is usually attributed to the interactions between LC molecules and polymer layer ordered by rubbing.

The alignment of cyanobiphenyl LCs onto polymers having lateral groups PVI, PVK, PVCi [20] perpendicular to the rubbing direction might be related to the interaction of the cores of nematic molecules with polymer lateral groups [40] via \(\pi-\pi\) interactions as it was reported for PVCi [39].

Covering SiOx with polymer layers has shown that the alignment strongly depends on the polymer structure. For PVA covering SiOx deposited at 82°, the decreasing the tilt angle of pentyl cyanobiphenyl molecules with increasing the PVA concentration in the dip coating solution of SiOx was explained [14, 15] by assuming that the variation of the alignment angle is due to the alteration of the initial columnar topography of SiOx surface. PVA molecules would be deposited preferentially on the hollow of SiOx micro-columnar surface, thus reducing the height of these columns and modifying the aspect ratio of the evaporation topography.

The results presented in this paper clearly show that the different alignment of E7 and MBBA on rubbed PVI, PVK, PVCi and PVA as function of the terminal (cyan or methoxy) group is also manifested onto the same polymer layers covering SiOx82 substrates.

MBBA molecules are tilted in the evaporation plane onto PVK or PVI layers deposited onto SiOx82, like onto bare SiOx82 substrate, showing that the changes in the SiOx topography by polymer covering process do not lead to the change of the alignment plane. In addition, doping of PVK with C60 leads to the alignment of E7 molecules tilted in the evaporation plane as in the case of bare SiOx82 additionally supporting the idea that the topography changes by PVK covering of SiOx82 are not responsible for the alignment perpendicular on the evaporation plane observed in the cells with PVK/SiOx82 layers. Therefore we may suppose the alignment of E7 molecules perpendicular on the evaporation plane onto PVK or PVI covered SiOx82 substrate cannot be related to changes in the SiOx topography by polymers deposition. It rather might reflect an ordering of the polymer lateral
PVK changes the orienting upon obliquely deposited SiOx group planes and implicitly, of the polymer main chains in the presence of the SiOx anisotropy known to consist in a tilted columnar structure [41]. Such an ordering could be favored by bulkiness of carbazole group, which compels the polymer chain of PVK to form stiff rods [42] and hindered by the presence of C60 groups on the SiOx surface. In fact, the polymers and C60 interact weakly [43].

4. CONCLUSIONS

Alignment layers of polyvinylcarbazole were obtained by withdrawing glass plates with SiOx nanostructured layers (obliquely evaporated in vacuum) from PVK solutions in toluene, of different concentrations. Other polymer layers (PVI, PVCi) were investigated for comparison.

A new alignment effect of nematic liquid crystals was revealed, that consists in the change of alignment direction of liquid crystal molecules imposed by SiOx layers evaporated at incidence angles of 82° or more, when they are coated with PVK (or PVI). This effect is inhibited by doping the PVK with C60 (0.1%), when the liquid crystal orientation is that specific for SiOx obliquely evaporated substrates.

The observed alignment is quite stable.

It was supposed that the alignment of E7 molecules perpendicular on the evaporation plane onto PVK (or PVI) covered SiOx82 substrate reflects an ordering of the polymer lateral group planes and implicitly, of the polymer main chains in the presence of the SiOx.

MBBA molecules do not show the same behavior as the E7 ones when comparing the orienting properties of SiOx82 substrate and those of PVK (or PVI) covered SiOx82 substrates.

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