

## Nanotopology of Polyimide Films Obliquely Treated by Plasma Beam and Liquid Crystal Alignment

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*The correlation between nanorelief of polyimide films obliquely treated by the beam of accelerated Ar plasma and liquid crystal (LC) alignment on these films is investigated. It is shown that the plasma beam treatment results in the change of films' roughness in a nanometer scale. In this case, the values of roughness in the directions parallel and perpendicular to the plasma beam projection on the films are different and dependent on the exposure dose. Clear correlation between the anisotropy of surface roughness and the direction of LC alignment is observed. This implies that topology is important, possibly decisive, factor of planar LC alignment on the surfaces obliquely treated by plasma beam.*

**Keywords:** alignment; atomic force microscopy; ion beam alignment; liquid crystal; plasma treatment

### 1. INTRODUCTION

Effect of liquid crystal (LC) alignment on the substrates obliquely processed by ion/plasma beam [1–5] roused big application interest. Avoiding direct mechanical contact with the aligning surface this method eliminates many intrinsic problems of rubbing alignment

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technique commonly used in modern LCD industry. These problems are deterioration of alignment films and surface electronic elements, microscopic alignment nonuniformity, electrical charging, dusting and complexity of alignment patterning. By contrast, ion/plasma beam alignment provides readily patterned highly uniform alignment with variable pretilt angle and anchoring energy. This process can be easily scaled up and applied for the non-flat surfaces.

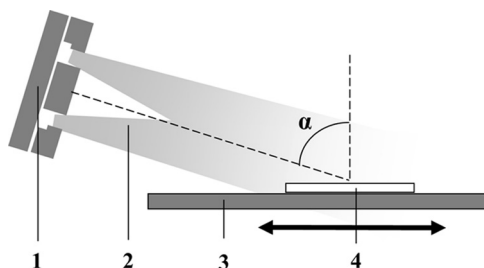
The mechanisms of LC alignment on the ion/plasma beam processed substrates are currently intensively discussed. The researchers using ion beam alignment process, usually based on Kaufman type ion source, uphold mechanism of selective destruction of molecular bonds by ion beam obliquely incident upon the alignment film [3,6]. Their arguments are based on results of NEXAFS or XPS studies of the treated films showing slight anisotropy of molecular bonds in the top layer of the film. In turn, authors using plasma beam alignment process, based on anode layer source, state that major alignment factor is anisotropy of surface relief [4,7]. Particularly, in work [4], we traced correlation between the anisotropy of surface relief of glass substrates and liquid crystal alignment. We detected that LC aligns in the direction corresponding to minimal roughness. However, it remained unclear, whether this correlation takes place for different exposure doses and different alignment materials.

In present work, topology of the aligning polyimide films is studied as a function of exposure dose of plasma beam. It is shown that anisotropy of surface relief of these films non-monotonically changes with the exposure dose and fully correlates with LC alignment. This additionally confirms important role of surface relief in LC alignment by plasma beam treated films.

## 2. EXPERIMENTAL

The samples were treated by means of anode layer source that was described in detail in [4,5]. The source was mounted in a vacuum chamber with a possibility of rotation around the horizontal axis. This allowed us to change the angle of plasma beam incidence onto the substrate. The basic pressure in the chamber was  $2 \cdot 10^{-5}$  Torr. The working gas was argon. Its pressure during the irradiation was  $4 \cdot 10^{-4}$  Torr. At this pressure and anodal potential 600 V the ionic current in the beam was 8–10  $\mu\text{A}/\text{cm}^2$ .

The scheme of irradiation is represented in Figure 1. Plasma beam was set at the angle of  $70^\circ$  to the normal of substrate. The substrates during irradiation were moved under the plasma beam in the back and forth directions with a speed of about 1.5 mm/s. This scanning mode



**FIGURE 1** Plasma beam irradiation scheme: 1 – source of plasma beam; 2 – plasma beam; 3 – sample holder; 4 – sample; 5 – direction of sample motion.

provided a few times passing of the substrate under the plasma beam that resulted in homogeneity of surface treatment.

The samples were glass plates covered with thin polyimide layers from one side. The polyimide layers were obtained by spin coating polyimide Al3046 (JSR, Japan) solution at 3000 rpm during 20–30 s. Then substrates were backed at 220°C for 2 h. Finally, polyimide layers were treated with plasma flux during different time.

A series of batches of substrates with different treatment times (from 0.5 to 30 min) was produced. The other treatment parameters were fixed. One substrate from each batch was selected for the nanorelief measurements before the plasma treatment. The other two samples were used to measure the nanorelief after the plasma beam exposure. These measurements were carried out by scanning atomic force microscope Nanoscope IIIa (Digital Instruments) working in the mode of periodic contact with a silicon probe. The fragments of surface with a size of  $1 \times 1 \mu\text{m}$  were analysed in all these cases. The scanning direction was parallel to the plasma beam projection on the substrate.

The residuary three samples from each batch were used for LC alignment tests. Symmetric (both substrates are treated with the plasma beam) and asymmetric (combination of plasma beam treated and rubbed polyimide substrates) LC cells were made for this purpose. The symmetric cells were used for evaluation of LC pretilt angle in the cells, while asymmetric ones were employed for identification of the alignment direction in the cell plane. Both types of cells were used for evaluation of LC alignment quality. The thickness of all cells was about  $20 \mu\text{m}$ . The cells were filled with nematic LC ZLI-2293 from Merck at room temperature. The quality and type of LC alignment were checked up by observation of LC cells between crossed polarizers or in polarising microscope.

### 3. RESULTS AND DISCUSSION

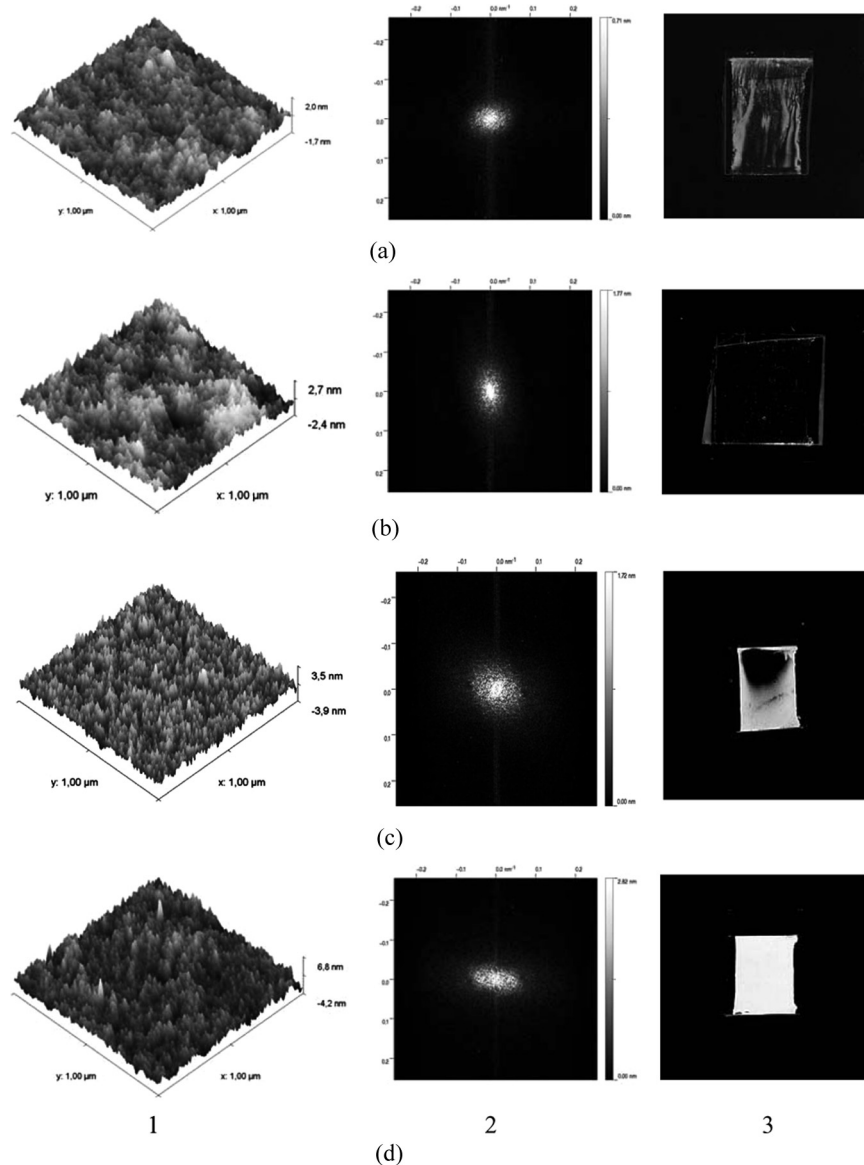
As said above, the substrates from each batch (each irradiation time) were used for nanorelief study and LC alignment tests.

The three-dimensional reconstructions of surface relief (column 1), fast Fourier transformation (FFT) of measured data (column 2) and photos of asymmetric LC cells (column 3) are presented in Figure 2. The photos demonstrate type and quality of LC alignment on the polyimide surfaces at different doses of irradiation.

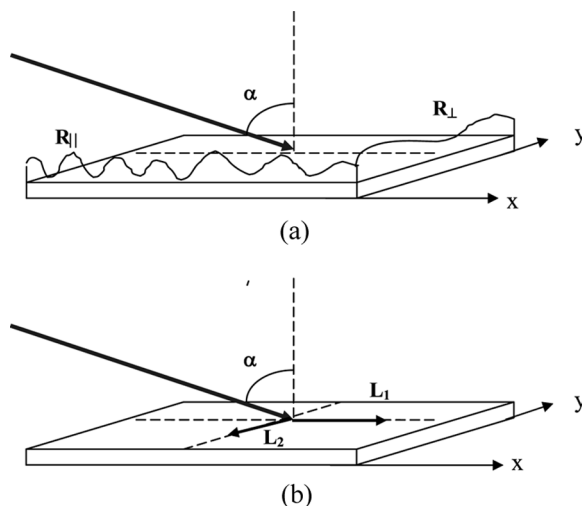
Comparing three-dimensional images it is possible to see that a surface irregularity (roughness) grows with irradiation time. This conclusion is supported by the direct calculation of roughness made by processing of AFM data by the program Gwyddion 2.8. The mean value of roughness was determined in the direction of beam projection on the plane of substrate ( $R_{\parallel}$ ) and in the direction perpendicular to the plane of substrate ( $R_{\perp}$ ) – see Figure 3a. The values of  $R_{\parallel}$  and  $R_{\perp}$  corresponding to different irradiation doses are presented in Figure 4. There is obvious that both parameters of roughness grow with the increase of irradiation time.

There is also evident from Figure 4 that  $R_{\parallel} \neq R_{\perp}$  in a general case. Interestingly that ratio between  $R_{\parallel}$  and  $R_{\perp}$  changes with exposure dose: while for the short irradiation times ( $\leq 10$  min)  $R_{\parallel} < R_{\perp}$ , for the longer times inequality changes to opposite one. In other words, with the increasing of time, the smoothest direction of surface changes from  $x$  to  $y$  (Fig. 3a). The same show Fourier transformations (column 2 in Fig. 2). The ranges of the exposure doses for which the ratios  $R_{\parallel} < R_{\perp}$  and  $R_{\parallel} > R_{\perp}$  are correspondingly observed are separated by narrow range for which the surface becomes almost isotropic ( $R_{\parallel} \approx R_{\perp}$ ) as before irradiation. However, the measurements in smaller scale reveal some local anisotropy of roughness.

Now we compare behaviour of roughness and LC alignment at the change of exposure dose. The unexposed samples demonstrate very poor LC alignment (some LC alignment is caused by the alignment in flow during filling of the cell). At small exposure doses (up to 10 min) homogeneous LC alignment in the incidence plane of plasma beam with the non-zero pretilt angle (easy axis  $\mathbf{L}_1$  in Fig. 3b) was observed. This type of LC alignment we called the first alignment mode. At the exposure doses greater than 15 min planar LC alignment in the direction perpendicular to the incidence plane (easy axis  $\mathbf{L}_2$  in Fig. 3b) was observed. In this case pretilt angle is intrinsically equal to zero. The second type of LC alignment was called the second alignment mode. Finally, at the intermediate exposure doses (10–15 min) the two-fold degenerated LC alignment with the easy axis  $\mathbf{L}$  forming angle



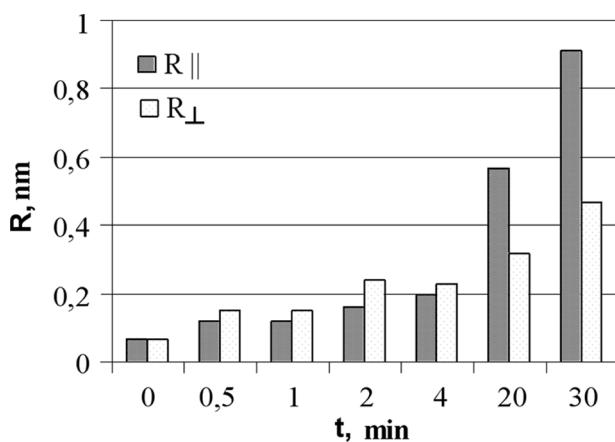
**FIGURE 2** The three-dimensional reconstructions of surface relief (column 1), fast Fourier transformation (FFT) of measuring AFM data (column 2) and photos of asymmetric LC cells (column 3). The photos demonstrate type of LC alignment. Projections of irradiation direction (upper substrate) and rubbing direction (lower substrate) are antiparallel. The cells are filled with LC ZLI-2293 (Merck). The time of plasma irradiation in case (a), (b), (c) and (d) is, correspondingly, 0, 2, 10 and 20 min.



**FIGURE 3** Schematic presentation of surface with anisotropic relief (a) and types of LC alignment (b).

about  $\pm 45^\circ$  with the beam incidence plane, coined as a transient alignment mode, was realized.

Thus LC alignment with exposure, same as anisotropy of surface roughness, undergoes several stages. In this case, clear correlation takes place between the anisotropy of roughness and the direction of LC alignment. For all exposure doses liquid crystal aligns in the



**FIGURE 4** Roughnesses  $R_{||}$  and  $R_{\perp}$  for different times of plasma treatment.

smoothest direction. The validity of this empiric rule was earlier confirmed with a number of studies in which substrates with anisotropic relief were employed for LC alignment [8–12]. Theoretically, this can be explained by minimization of free energy of LC in the direction with minimal roughness [13]. Also, clear correlation between surface relief and LC alignment takes place at the intermediate doses of irradiation: the transient state of the roughness anisotropy agrees well with intermediate multimode LC alignment. This altogether implies that anisotropy of surface relief is important, very likely decisive, factor of LC alignment on the surfaces treated by plasma beam.

## 4. CONCLUSIONS

Treatment of polyimide surface by plasma beam causes growth of surface roughness in the nanoscale range. In this case different changes occur in the direction of plasma beam projection on the treated surface and in the perpendicular direction. The clear correlation between the anisotropy of roughness and LC alignment is observed at different irradiation doses: LC aligns in the direction with minimal roughness. The latter proves important role of the topology factor in planar LC alignment on the surfaces treated by plasma beams. This alignment factor in case of plasma beam procedure seems to be more important than in case of ion beam procedure because of higher energy of particles causing surface modification. The discussed mechanism of in-plane alignment does not exclude contribution of the other factors, for instance, anisotropic destruction of molecular bonds [3,6]. Besides possible contribution to in-plane alignment, the interfacial chemical interaction in the LC-substrate interface is responsible for polar anchoring transitions and difference in alignment of LC with positive and negative dielectric anisotropy [5].

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