Original Research Article

Fullerene-doped polyimide materials treated via the vacuum ultraviolet irradiation: Novel possible approach to create the structured relief

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Abstract: Among the various surface reliefs obtained by the modification of the nanostructured materials used for the orientation of the liquid crystal molecules or applied as the possible way to extend the optical limiting mechanisms, the vacuum ultraviolet irradiation can provoke the novel approach with the varied contact angle and can be recommended for use in the development of the light- and electro-addressable liquid crystal spatial light modulators, switches, and limiters. The main accent in the current paper is connected with the study of an impact of the vacuum ultraviolet irradiation with the different wavelength and power densities on the fullerene-structured polyimide thin films. To support the proposed idea, the spectral measurements were carried out, the contact wetting angles of the structured surface were determined, and an atomic force microscopic analysis was performed. Based on the data obtained, it is proposed to effectively use such relief formed by the vacuum ultraviolet irradiation for the design of the modulators and converters of the laser radiation, some biomedicine devices and the solar cells as well where a liquid crystal mesophase is actively used as an electro-optical modulating layer. Some ideology of the current article is aimed that the polyimide materials, when irradiated in the vacuum ultraviolet, can perform a dual role, as a photo layer and as an orienting layer as well.

Keywords: Novel Approach to Coating Development; Vacuum Ultraviolet Irradiation; Polyimide Thin Films; Fullerenes; Relief to Orient the Liquid Crystal Molecules; Ablation; Spectra; Wetting Angle; Atomic-force Microscopy Analysis; Nanophotonica

Received: 13th March 2023; Accepted: 7th April 2023; Published Online: 23rd April 2023

1. Introduction

It is well known that so many scientific teams and practical engineers groups search for the novel ways in order to extend the approaches to orient the liquid crystal (LC) molecules in the planar, homeotropic or tilted position. The introduction of the different nanoparticles (fullerenes, carbon nanotubes, quantum dots, reduced graphene oxides, etc.) is considered both inside the LC mesophase to affect the orientation of the LC dipoles, and at the interface of the solid substrate-LC interface to lay the LC molecules in a certain directions[1–13]. It permits to develop the LC devises in the twist-nematic, IPS-switching, MVA, etc. constructions and to solve some complicated organic nanophotonics problems...
coincided with the increase of the speed, sensitivity, contrast and resolution of the display elements, LC spatial light modulators (SLM), biomedicine instruments, etc. devises. Thus, it can stimulate the re-search in the new methods designing for the materials surface modification for the LC area use. Why novel relief as the new coatings can be useful for the LC? It is due to great interest to study namely the LC mesophase, for example, nematic LC ones, because as it was shown before that the electro-optical nematic liquid crystal (NLC) is a good model in order to consider, from one side, the fundamental physical effects in the anisotropic intermediate media[14–20] and, from another side, to develop the realistic technical devices such as the membranes, laser radiation switchers, optical limiters, convertors, electrically- or optically- addressed SLMs, solar energy cells, gas storage systems, display elements, etc. technical useful systems[21–28]. Moreover, the structured relief for the LC dipoles orientation can be used in order to decrease the light radiation efficiently die to varying the Fresnel losses when the optical limiting devices can be constructed.

The physical-chemical phenomena in the LCs materials under an application of the different external fields, for example under the use of the bias voltage, connect with the weak intermolecular interaction of the structural elements of the LC media with the objectives added in the LC mesophase or placed on the interface. Thus, one of the more unique properties of the LCs is their orienting ability, which is used to develop new optoelectronic devices based on these LC composites. But it should be remarked that the relief at the interface, solid substrate-LC mixture influences dramatically on the basic parameters of the LC as well.

Oxides based on SiO2, SiO, CeO, etc. structures and polymers (PVA, polyimides, polyvinyl carbozole, etc.) obtained via the rubbing technique, imprinting process, photo lithography method, holographic grating recording in the VIS and near-infrared, etc. approaches were applied to create the perspective relief, which orient the LC molecules.

As the famous and the perspective way the photo-alignment can be taken into account, which has been shown in details in papers[29–38]. The photo-aligning technique for LC display applications has been used with good advantage by Prof. Chigrinov with colleagues. This technique includes the determination of the anchoring energy and the surface viscosity, modeling of various photo-aligning processes in the photo-sensitive films. Basically, the azo-dyes alignment materials have been used which are stabilized by the polymerization.

Some views of the reliefs obtained previously by Prof. Kamanina team at the polyimide thin films via different approaches are shown in Figure 1. Some views of these reliefs are shown in Reference [27].
Figure 1. Possible relief to orient the LC molecules obtained by us before. Relief established and observed at the surface of the polyimide materials doped with nanotubes (Carbon nanotubes (SWCNTs) type #704121 with the diameter placed in the range of 0.7–1.1 nm purchased from Aldrich Co. have been used), when the polyimide film has been placed on the glass substrate (a); relief observed at the surface of the polyimide materials doped with nanotubes when the film has been placed on the Si substrate (b). Relief observed in polyimide materials doped with fullerenes when the polyimide film placed on the glass substrate has been treated in an irreversible mode by the pulsed Nd-laser in the Raman-Nath diffraction conditions at the spatial frequency of 100 mm⁻¹ and at the wavelength of 532 nm with the power density of ~0.6 J·cm⁻² (c) and one obtained in the reversible mode with the power density of ~0.4 J·cm⁻² (d). Relief observed at the surfaces of the polyimide materials doped with fullerenes (e) when the polyimide film placed on the glass substrate has been treated by the CO₂-laser at the wavelength of 10.6 microns, with the power of 30 W and by the scanning speed of 1,000 mm·s⁻¹; and the same obtained before via AFM “Bio47-Smena” in the “share-force” mode (f).

In this paper, using the example of the nanoparticles-doped polyimide layers (namely PI + 0.5 wt.% C₇₀), which we previously studied by the laser methods in the visible and IR-spectral range at a wavelength of 532 nm; 1,047 microns; 1,315 microns, etc. [39-41], the data on the vacuum ultraviolet irradiation treatment of the doped polyimide thin film are presented for the first time. It makes it possible to orient the liquid crystal dipoles via the relief obtained by the vacuum ultraviolet irradiation with good advantage. Indeed, it should be remarked that the polyimide matrix is very good to model to vary the properties via the irradiation under the different conditions, such as: 1) Holographic recording gratings written at the different spatial frequencies, which can form the varied period of the gratings responsible for the different reliefs; 2) Rubbing approach, which permits to make the potential relief, provoked the regular orientation of the LC molecules; 3) Variation
of the dopant content in the polyimide body; some amount of the nanoparticles, due to their strong core, can develop the relief at the polyimide surface with good advantage; 4) Photo aligning process treated the polyimide surface can prepared the unique relief as well. It is important to note that different scientific teams have studied this type of the materials (namely the polyimide ones) up to now for the various applications\textsuperscript{[43–46]}.

2. Materials and methods

In this study, the photosensitive layers of polyimides (PI) with the general chemical formula previously shown in paper (Reference [42]) were used. A photosensitive layer of the polyimide was sensitized with the C\textsubscript{70} fullerene and chosen for the study, since such sensitization allowed to significantly expanding the spectral features of the polyimide matrix material from 380–400 nm up to a wavelength of 1.315 microns\textsuperscript{[39]}. The fullerene doping process influences on the surface of the PI matrix was previously shown in paper (Reference [11]).

Currently doped polyimide sample with a photo layer of PI + 0.5 wt.% C\textsubscript{70} was placed on a glass substrate made of the K8 crown material. The sample was divided into the 4 parts for the systematic experiments. General view of the samples with the area irradiated is shown in Figure 2(a).

The vacuum ultraviolet irradiation was applied using the standard excimer lamps at the wavelengths of 126 and 172 nm. The vacuum ultraviolet irradiation was carried out through a layer of an air with a thickness of \(d = 0.3\) mm. The view of the experimental scheme is shown in Figure 2(b).

The spectra of the studied materials were obtained by the FSM-1202 Fourier spectrometer operating in the spectral range of 1–2.5 microns; the OCA 15EC device purchased from LabTech Co. (St. Petersburg-Moscow, Russia) was used to measure the wetting angle (contact angle) at the surface. The modified surface was analyzed using the Solver Next AFM atomic force microscope (purchased from NT MDT Co., Zelenograd, Moscow Region, Russian Federation). The AFM instrument was operated in the semi-contact mode in the atmosphere of air.

3. Results and discussion

The basic results of the current experiments on an irradiation of the chosen polyimide in the vacuum
ultraviolet range with subsequent formation of the surface relief are given in Figure 3.

The main surface parameters are shown in Table 1. These data indicate the quantitative data of the statistic processing of the materials studied.

![Figure 3](image1.png)  
![Figure 3](image2.png)  
![Figure 3](image3.png)  
![Figure 3](image4.png)

**Figure 3.** AFM images of studied polyimide films doped with 0.5 wt.% C70, with the visualization area is 1 \times 1 \text{microns}: (a) pristine sample; (b) sample irradiated at $\lambda = 172 \text{ nm}$ with power density of $J = 130 \text{ mJ cm}^{-2} (t = 60 \text{ s})$; (c) sample irradiated at $\lambda = 172 \text{ nm}$ with $J = 400 \text{ mJ cm}^{-2} (t = 180 \text{ s})$; (d) the sample irradiated at $\lambda = 126 \text{ nm}$ with $J = 18 \text{ mJ cm}^{-2} (t = 60 \text{ s})$.

**Table 1.** Some data on the static processing of PI surfaces under the UV irradiation (initial with inclination)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Untreated PI</th>
<th>PI + UV ($\lambda = 172 \text{ nm}, J = 130 \text{ mJ cm}^{-2}$)</th>
<th>PI + UV ($\lambda = 172 \text{ nm}, J = 400 \text{ mJ cm}^{-2}$)</th>
<th>PI + UV ($\lambda = 126 \text{ nm}, J = 18 \text{ mJ cm}^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Root-mean square roughness, nm</td>
<td>19.952</td>
<td>26.523</td>
<td>15.817</td>
<td>20.839</td>
</tr>
<tr>
<td>Average roughness, nm</td>
<td>16.000</td>
<td>22.037</td>
<td>12.148</td>
<td>15.942</td>
</tr>
<tr>
<td>Maximum area peak height, nm</td>
<td>76.690</td>
<td>88.720</td>
<td>75.414</td>
<td>56.300</td>
</tr>
<tr>
<td>Maximum area valley depth, nm</td>
<td>33.092</td>
<td>59.086</td>
<td>40.062</td>
<td>70.017</td>
</tr>
</tbody>
</table>

It can be considered as the novel approach to make the perspective relief based on the structured polyimide. It is worth noting that the UV irradiation changes the surface of the polyimide material under the study, with the most distinct and regular change.
in the relief, which can be recommended for the orienting surfaces creating for the LC molecules laying when the LC SLMs designing. It should be taken into account that the relief generally used for the LC molecules orientation can be shown, as the classical ones, in Figure 4. It can be the planar, homeotropic and tilted one with the change of the angle of the orientation between 0 and 90°. These types of the LC molecules orientation permit to construct the LC cells in $S_-$, $B_-$, and Twist positions.

Let us to return to the case of the irradiation of the substrate with the polyimide matrix in the UV range shown via AFM images. It occurs first when the polyimide surface is processed at a wavelength $\lambda = 172$ nm for 60 s at an irradiation energy density at the level $J = 130$ mJ·cm$^{-2}$ (Figure 3(b)), and then it can be changed via an ablation process at a wavelength $\lambda = 172$ nm for 180 s at an irradiation energy density increase at the level of $J = 400$ mJ·cm$^{-2}$ (Figure 3(c)). When the irradiation wavelength was reduced from 172 to 126 nm, the ablation process became more obvious. One can see that the results of exposure to the vacuum ultraviolet radiation depend both on the wavelength (the smaller it is, the more pronounced they are) and on the radiation dose. Thus, it can be seen that this process makes it possible to create new coatings to develop the surface relief on the polyimides materials, which can be used to orient the LC molecules.

Let us to compare current results with the ones obtained by us via the laser irradiation at 532 nm with the varied energy density. For the fullerene-doped polyimide, this treatment by the second harmonic of the pulsed nanosecond Nd-laser at the energy density of ~0.5 J·cm$^{-2}$ corresponds to 350–400 kcal·mol$^{-1}$ taken into account the molecular mass of the PI units of 750. The rotation threshold for the polyimide structure is ~100–700 kcal·mol$^{-1}$[47]. Thus, this effect is likely to result in a better arrangement of the polyimide donor fragment (triphenylamine) and the fullerene planes, as an effective acceptor. Thus, it provokes an efficient intermolecular charge transfer process between them. The general PI formula and the possible intermolecular charge transfer complex formation process is shown in Figure 5.

It should be remarked that the electron affinity energy of an acceptor fragment of the polyimide matrix is close to 1.14–1.4 eV, that is significantly less than the one for the fullerenes (2.6–2.7 eV), as an intermolecular acceptor.

It is possible that when exposed to the vacuum ultraviolet radiation on the doped polyimide, the same process is observed at the wavelength of 172 nm when the energy density varies from 130 mJ·cm$^{-2}$ to 400 mJ·cm$^{-2}$.  

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**Figure 4.** Classical relief used for the LC molecules orientation: (a) the planar type of the LC molecules orientation; (b) the homeotropic type of the LC molecules orientation; (c) the tilted type of the LC molecules orientation.
In order to show a more probable possibility of using such a relief, the additional spectral measurements were performed, as well as an assessment of the change in the wetting angle of the surface were made.

The IR-spectral data of all four regions of the polyimide sample under this study are visualized in Figure 6. The IR spectra, namely 4 curves, connected with the treatment of the area shown in Figure 2(a). Thus, it is shown as following: 1, 2, 3, and 4 areas are connected with the curves 1, 2, 3, and 4: Untreated PI; PI + UV (λ = 172 nm, P = 130 mJ·cm⁻²); PI + UV (λ = 172 nm, P = 400 mJ·cm⁻²); PI + UV (λ = 126 nm, P = 18 mJ·cm⁻²).

Attention is drawn to the fact that the spectral measurements do not provide any significant information on the breaking of the bonds in the structural link of the polyimide films, but only visualize the change in the density of the material, which is most likely partially due to the ablation process. It should be noticed that the spectral changes do not correlate too well with changes in the surface controlled by the atomic force method; however, this is most likely due to the fact that a different spectral region of the transmission of the samples was chosen that was before used for their irradiation in the vacuum ultraviolet range. As an additional, the spectral pick is shown in Figure 6(b), which is support of the intermolecular charge transfer in this doped polyimide materials.

The measured wetting angles during the formation of the different reliefs on the irradiated polyimide are shown in Figure 7. The best images have been chosen.
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Figure 6. Spectral measurements of four areas of the studied polyimide sample measured by IR-spectrometer at the wavelength range of 1–2.5 microns (a); spectral pick in the IR-range for the polyimide doped with the fullerene C\textsubscript{70} (b).

Figure 7. Some data of the contact angles obtained at the samples studied: (a) pristine sample; (b) sample irradiated at $\lambda = 172$ nm with $J = 130$ mJ·cm\textsuperscript{-2} ($t = 60$ s); (c) sample irradiated at $\lambda = 172$ nm with $J = 400$ mJ·cm\textsuperscript{-2} ($t = 180$ s); (d) sample irradiated at $\lambda = 126$ nm with $J = 18$ mJ·cm\textsuperscript{-2} ($t = 60$ s).
### Table 2. Changes in the wetting angle of the studied doped polyimide sample after the vacuum ultraviolet irradiation

<table>
<thead>
<tr>
<th>The average value of the contact wetting angle (°)</th>
<th>Error rate</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>90.8</td>
<td>0.8–0.9</td>
<td>Non-irradiated area</td>
</tr>
<tr>
<td>63.7–64.0</td>
<td>2.07–2.45</td>
<td>Irradiated sample at $\lambda = 172$ nm, with $J = 130$ mJ cm$^{-2}$ ($t = 60$ s)</td>
</tr>
<tr>
<td>52.9–53.1</td>
<td>1.35–1.45</td>
<td>Irradiated sample at $\lambda = 172$ nm, with $J = 400$ mJ cm$^{-2}$ ($t = 180$ s)</td>
</tr>
<tr>
<td>57.3–57.3</td>
<td>0.51–0.63</td>
<td>Irradiated sample at $\lambda = 126$ nm with $J = 18$ mJ cm$^{-2}$ ($t = 60$ s).</td>
</tr>
</tbody>
</table>

The average data of this processing to estimate the contact angle (wetting angle) are placed in **Table 2**.

Analyzing the data in **Table 2**, one can say that the change in the angle of an inclination of the water molecules on the surface of the studied samples is most significant (the contact angle changes by ~1.7 times) under the action of the UV irradiation at a wavelength of $\lambda = 172$ nm with an energy density at the level of $J = 400$ mJ cm$^{-2}$ for $t = 180$ s, which are coincided with the presented AFM data (**Figure 3(c)** and **Figure 7(c)**) on the study of the surface on an atomic force microscope. Regular structuring of the surface of the thin polyimide film under the influence of the UV irradiation begins at $\lambda = 172$ nm with an energy density at the level of $J = 130$ mJ cm$^{-2}$ (**Figure 3(b)** and **Figure 7(b)**); the contact angle changes by 1.4 times. After reducing the acting wavelength, the angle of an inclination of the water molecules on the surface of the polyimide practically does not change dramatically. In **Table 2**, the contact angle has been changed via change of the wavelength and energy density of the irradiation. The angle has been varied from 90.8 to 63.7–64.0 to 52.9–53.1 to 57.3–57.3. Thus, if we have discussed the display application of the novel relief, we can propose to use it for the vertical alignment of the LC molecules and for the tilted ones. It permits to illuminate the direct alignment layers and used the polyimide for the two roles: as the photolayer and as the alignment layer.

### 4. Conclusions

Analyzing the results of the current first study, we can testify the following points:

Really it is important to note that polyimide matrix is very good materials to observe some structural and surface change after the external field, including the vacuum UV irradiation.

The ideology of the whole article was aimed at showing that when irradiated in the field of the vacuum ultraviolet polyimide materials that are used as photolayers in SLM, as well as the independent orienting coatings in the display technology, it is possible to create a new surface relief for LC molecules alignment. This relief is controlled by both a change in the irradiation wavelength and a change in the energy density. In such a system of a SLM, a direct orienting layer can be removed. In a polyimide photolayer, it can perform a dual role: as a photo layer and as an orientant.

1) It is shown for the first time that the modification of the surface relief created on the doped polyimide sample irradiated in the vacuum ultraviolet range depends on the irradiation time, energy density and wavelength.

2) It is proposed to use the procedure of the UV polyimide treatment in the LC molecules orientation process for the first time.

3) For the first time in the field of the vacuum ultraviolet, doped polyimide thin-film layers were studied for the purpose of the possible application of
such processing to create a surface relief on the photosensitive layer itself when designing the electrically- or optically-addressed LC SLM.

4) The IR spectra of the polyimide samples irradiated in the vacuum ultraviolet region were studied for the first time as well, but they were not revealed the essential information on the change of the polyimide structures.

5) The contact wetting angles of the surface of the resulting relief were determined and shown for the doped polyimide samples treated at the different ultraviolet range.

6) Based on the experimental studies carried out, it is proposed to use such developments to orient LC molecules at the polyimide coatings for the biomedicine area in order to visualize the configuration of the human erythrocytes, for example.

7) It can be possible to apply the relief obtained for the LG, Samsung, Philips, etc. display Co., which used different display technologies due to the reason that the current procedure can be considered as the alternative technique for the rubbing one or for the VA technique.

8) Novel approach can be useful in the engineering area to develop the optical limiters operated in the VIS and IR ranges.

9) The results shown can be possibly used in the education process as well to extend the students the methods, which can modify the different materials surfaces in order to make the novel coatings.

**Author contributions**

Conceptualization, resources, formal analysis, writing—original draft preparation: NK; investigation, methodology: GZ.

**Funding**

The current study was made as the initiative investigation.

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**Acknowledgments**

The authors would like to thank their colleagues from Vavilov State Optical Institute, LETI University and Nuclear Physics Institute for the useful discussions at the scientific seminars. We acknowledge the graduate student AS Toikka (adviser for him is Prof. Kamanina NV) for the help with the figure’s preparations. Partially, this research datum have been discussed at the Applied Optics conference in the framework of the Nanotechnology in Optics (Saint-Petersburg, December 2022).

**Conflict of interest**

The authors declare no conflict of interest.

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246–252.


doi: 10.18282/mpc.v6i1.3319