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OPTICAL AND AFM MICROSCOPY STUDING OF THIN NLO ORGANIC FILMS DEPOSITED BY PULSED LASER DEPOSITION

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ABSTRACT

Bright field microscopy, Fluorescence microscopy and Atomic Force Microscopy (AFM) analysis of thin films from styrylquinolinium salts deposited by means of Pulsed Laser Deposition (PLD) technique, using high power UV Nitrogen laser are described. The thin films are deposited onto substrates from KBr, 316L SS alloy, optical glass and aluminium foil. The organic dyes: E-4-(2-(4-hydroxynaphthalen-1-yl)vinyl)-1-octylquinolinium iodide (**1**), (E)-1-ethyl-4-(2-(4-hydroxynaphthalen-1-yl)vinyl)quinolinium bromide (**2**), and 4-{(*E*)-2-[4-(dimethylamino)naphthalen-1-yl]ethenyl}-1-methylquinolinium iodide (**3**) are synthesized by Knoevenagel condensation. The thickness of the deposited films ranges between 80 – 300 nm, measured by interferometric method. Morphology and topology of deposited thin films in accordance with technological regimes and the type of substrates are discussed.

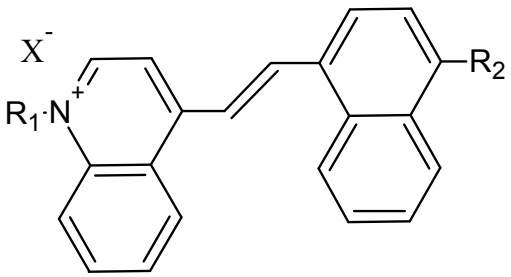
Keywords: Bright field microscopy, Fluorescence microscopy, AFM, morphology, PLD.

INTRODUCTION

Organic Non Linear Optical (NLO) thin films with preliminary designed properties and structure are very attractive in recent years for applications in various fields of science and industry including optoelectronics, lasers, optical recording and processing and sensors. The phenomena of Nonlinear Optics can be summarized as strongly interaction of electromagnetic field of laser light with the materials and observation of qualitative alteration in the propagation properties of the incoming light, such as frequency, phase and polarization. This applications of organic NLO materials as thin film, require high quality of the obtained films in relation to their functionality and their morphology (well-ordered films consisting of molecules of organic compounds with preliminary designed properties), topology, homogeneity (carefully aligned to each other and onto substrate) and thickness uniformity. The films have to

exhibit high stability without mechanical, thermal and chemical stress including solvent exposure and good adhesion onto substrate. Thin films of complex organic materials have been processed by means of conventional non-vacuum techniques, such as dip coating, spin coating, spray coating, electrochemical deposition, Langmuir–Blogett method usually and vacuum methods such as electron beam evaporation, thermally assisted vacuum evaporation, organic molecular beam epitacsy [1-4]. The preparation of thin films from single bulk complex organic target– polymers was first shown by Hansen and Robitalle in 1988 [5]. Recently developed laser based methods, such as Pulsed Laser Deposition (PLD) and Matrix Assisted Laser Evaporation (MAPLE) showed good results for deposition complex organic materials, including polymers, biopolymers, proteins and living cells, also [6,7].

Three new organic compounds, from merocyanine dyes group E-4-(2-(4-hydroxynaphthalen-1-yl)vinyl)-1-octylquinolinium iodide (**1**), (E)-1-ethyl-4-(2-(4-hydroxynaphthalen-1-yl)vinyl)quinolinium bromide (**2**), and 4-{(*E*)-2-[4-(dimethylamino)naphthalen-1-yl]ethenyl}-1-methylquinolinium iodide (**3**) have been synthesized by means of Knoevenagel condensation. The styrylquinolinium dyes with larger conjugated systems (naphthalene tail with different electron donor group) showed big potential as NLO materials [8].



(**1**): R_1= Octyl; R_2= OH; X= I
(**2**): R_1= Et; R_2= OH; X= Br
(**3**): R_1= Me; R_2= NMe_2; X= I

Figure 1. *Chemical structure of the investigated compounds*

The present work focuses on study by means of optical, optical fluorescent and AFM the ability of PLD to provide thin films from this new styrylquinolinium dyes with good quality in respect to their potential applications as NLO organic materials on different type of substrates.

EXPERIMENTAL

Pulsed Laser Deposition of NLO organic dyes

The experimental set–up used for thin films deposition is typical for PLD technique and is similar with [9]. The technological parameters of process deposition, by means of high power UV N_2 laser onto substrates from KBr, NaCl mono crystals, 316L SS alloy, optical glass – K5 and Al foil are described in [10]. The laser energy density has been selected from 350 mJ/cm^2 to 3.5 J/cm^2 in accordance with absorption spectrum spectra and chemical structures of deposited dyes. All experiments have been carried out at room temperature and vacuum of 10^{-3} mbar. The substrates have been cleaned in an ultrasound bath with pure acetone and ethanol, before deposition process and dried by means of technical nitrogen. The single bulk dyes targets

have been prepared with the aid of hydraulic press – (Perkins Elmer with diameter 1.2 cm and thickness from 0.3 cm to 0.5 cm). The choice of substrates is in accordance with the possible applications in field of NLO devices, as fast optical switches in waveguides systems, SGH (second generation harmonic) devices for lasers, rapid optical deflectors and as well as for the future developments of new organic/inorganic optical nanocomposites.

Bright field and Fluorescence microscopy measurements

An optical study was performed by means of Bright field/ Fluorescence microscopy Nikon Eclipse 80i with maximum magnification 400X and four standard filters, in the case of Fluorescent mode. Each Nikon triple band fluorescence set is optimized for use with DAPI [Ex (excitation filter) 340-380; DM (dichroic mirror) 400; BA (barrier filter) 435-485] and FITC (Ex 465-495; DM 505; BA 515-555) in combination with either TRITC (Ex 540/25; DM 565; BA 605/55) or Texas Red (Ex 540-580; DM 595; BA 600-660) probes. The microscopic images was performed by DS Camera Control Unit DS-U2 and DS camera Head DS-Fi 1 with use of imaging software NIS-Elements F 2.30.

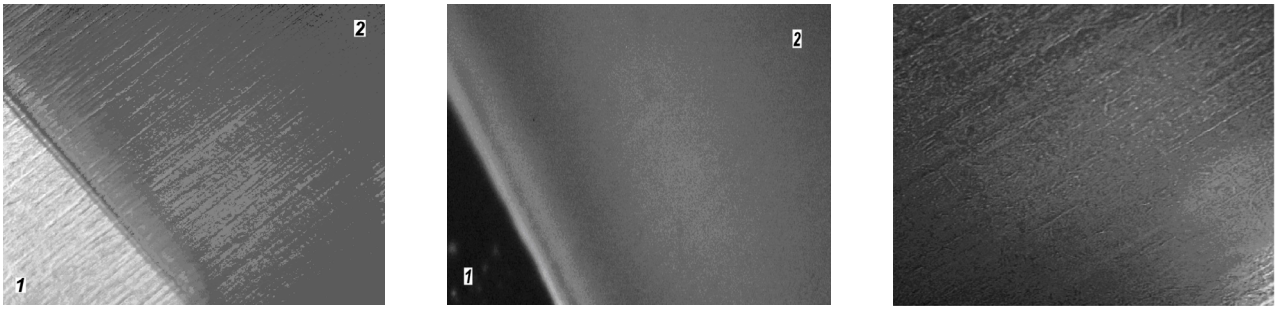
AFM measurements

AFM study in the present work was performed by means of Veeco DI Nanoscope MultiMode V system (contact mode) with scan size: 10μm x 10μm along XY axis and vertical range Z axis – of 2.5μm.

RESULTS AND DISCUSSION

An optical and optical fluorescent study was performed of thin films of the investigated new styrylquinolinium dyes (**1**) – (**3**) deposited onto substrates from KBr, 316L SS alloy, optical glass and aluminum foil.

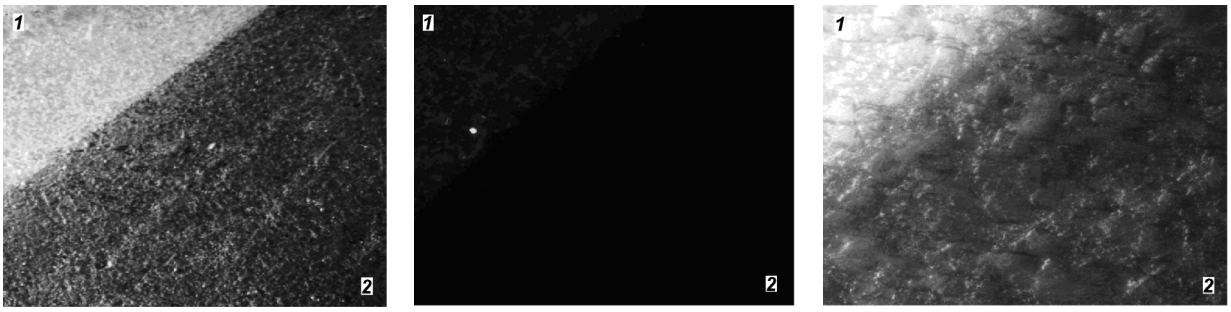
The surface quality of dye (**1**), as thin film with thickness 180 nm onto samples from stainless steel 316L are shown on Fig.2.



a) b) c)

Figure 2. *Bright field and fluorescence micrographs of dye (**1**) as thin film onto samples from stainless steel 316L: a) 100X; b) 200X by filter Texas Red; c) 200X by filter DAPI. On the micrographs with digit 1 was marked the substrate, with 2 – thin film.*

The images showed a very good homogeneity of thin films on surface area of 6 cm^2 without defects and any cracks. The surface quality of dye (**2**) as thin films with a thickness of 260 nm onto samples – substrates from KBr mono crystals are shown on Fig.3.



a) b) c)

Figure 3. *Bright field and fluorescence micrographs of dye (**2**) as thin film onto substrate KBr; a) 100X; b) 200X by filter DAPI; c) 400X. On the micrographs with digit 1 was marked the substrate, with 2 – thin film.*

The microscopy images from Fig.3 showed that the quality of thin films concerning topology and homogeneity followed surface quality of the substrates. The thickness of films is 150 nm.

Bright field and fluorescence images of dye (**3**) deposited on glass substrates are shown on Fig.4.

a) b) c)

Figure 4. *Bright field and fluorescence micrographs of dye (**3**) as thin films onto glass substrate; a) 40X; b) 100X; c) 200X. On the micrographs with digit 1 was marked the substrate, with 2 – thin film.*

Thin films from dye (**3**) are with thickness of 85 nm and showed a good adhesion onto substrates. The films are transparent in the visible spectrum. The droplets onto surface of films which are typical for PLD methods are no observed.

AFM is exceptionally useful tool for studying surfaces because it may provide real volumetric film morphology and nanostructures. Fig.5 and Fig.6 show the ability of AFM to visualize and characterize surfaces of studying styrylquinolinium dyes – dye (**1**) deposited by means of PLD on glass substrates and aluminium foils with thickness 220 nm, respectively.

The surface topology showed a different mechanism of the growing of deposited films in relation to substrates nature. The film is extremely uniform with deviation no more than 20 nm for glass substrate. The film deposited onto aluminum foil showed a deviation more than 30 nm and priority preference for of growing in vertical axis. The crystal structure of aluminum foil defines the direction of deposited film, most probably.

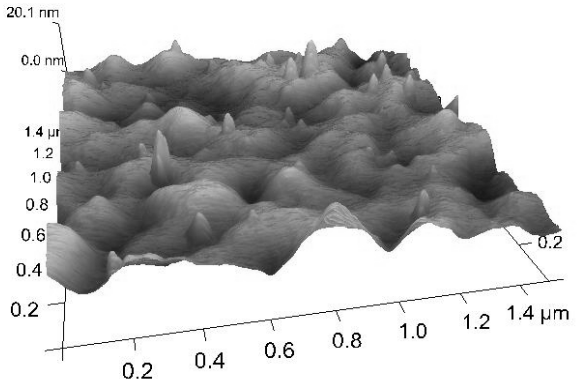


Figure 5. *AFM 3D image of a surface of the thin film of dye (**1**) deposited by means of PLD on glass substrates*

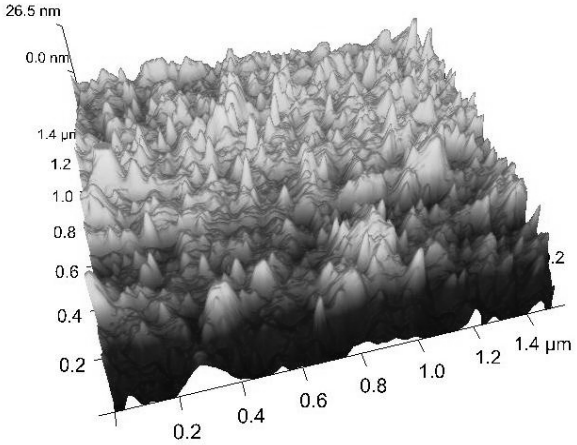


Figure 6. *AFM 3D image of a surface of the thin film of dye (**1**) deposited by means of PLD on aluminium foils*

X and Y axes are graduated in µm and show the area of the scanned sample. Z axis is graduated in nm and shows the roughness of the sample.

CONCLUSION

We have demonstrated successful deposition of thin films from styrylquinolinium dyes with larger conjugated systems by means of PLD technique using high power UV N_2 laser. The films are in highly ordered and uniform morphology with layered structure in which the organic molecules stand nearly vertical in the case of metal (aluminium foil) substrates and planar for in the case of dielectric substrates, such as optical glass and mono crystals from KBr and NaCl. The films are homogeneous and without any cracks and droplets on the surfaces. The laser energy density used in this work varies from 350 mJ/cm^2 to 3.5 J/cm^2 and laser repetition rate up to 20 Hz, respectively. The pressed micro crystal targets from complex organic NLO dyes are suitable for a PLD process at vacuum conditions in range 10^{-2} mbar to 10^{-3} mbar, as well. The films are amorphous and their surface morphology is characterized by small particles (with a dimensions about 20 – 30 nm) and roughness not more than 40 nm which is still enough and compatible for NLO applications. These first studies of the new deposition conditions have allowed for a future preparation of films with preliminary determinate properties and opened interesting possibilities to compose new styrylquinolinium dyes – inorganic nanocomposites for direct photonics applications.

Acknowledgements

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