

Simultaneous treatment of polymer surface by EUV radiation and ionized nitrogen

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Abstract In this paper chemical modification of a poly(vinylidene fluoride) surface by extreme ultraviolet (EUV) irradiation in a presence of ionized nitrogen was demonstrated for the first time. Nitrogen gas, injected into an interaction region, was ionized and excited by the EUV radiation from a laser-plasma source. The ionization degree and excited states of nitrogen were investigated using EUV spectrometry and the corresponding spectra are presented. Chemical mod-

ification of polymer after combined EUV and ionized nitrogen treatment was investigated using X-ray photoelectron spectroscopy. A significant contribution of nitrogen atoms in near-surface layer of the polymer after the treatment was demonstrated.

Polymers are widely used in industry because of good mechanical properties and their resistance to environmental factors. For some applications, however, surface properties of polymers must be modified. The modification may concern hydrophobicity, wettability, adsorption, adhesion, optical or other surface properties and is associated with some changes in physicochemical structure of the near-surface layer. Different methods can be employed for surface structuring, including chemical [1], plasma [2], or radiation treatment. In the last case, ultraviolet (UV) lamps or UV lasers are mainly used [3–5]. Photons emitted from these sources can excite electrons from the valence band of polymer materials. Molecular electronic structure of the materials has some resonances, hence, excitation rate depends on energy of the irradiating photons and strongly influences the absorption depth. The excited states can relax through radiative or non-radiative processes. In case of polymers one of the possible radiationless channels corresponds to bond breaking of the polymer chain. This can result in formation of volatile fractions or in changes in chemical structure and composition of the polymer molecules. Some volatile fractions are released from irradiated layer resulting in smooth ablation or modification of the surface morphology due to a preferential dry etching of an amorphous polymer. For some applications incorporation of some functional groups into the polymer molecules is necessary. In such cases irradiation is being performed in a reactive atmosphere [4].

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In our previous work we proposed an extreme ultraviolet (EUV) treatment, as alternative method for surface modification, using a laser-plasma EUV source (for details see [6–8]). Interaction of EUV photons with polymers is quite different compared to UV interaction because of much higher photon energy. A single EUV photon carries sufficient energy to ionize any atom or molecule. Resulting photoelectrons have sufficient energy for further excitation or ionization of the polymer molecules. Apart from that, the relative probabilities of triplet states formation are greatly enhanced compared to excitation with electromagnetic radiation, which means that radiationless de-excitation processes, including bond breaking, are predominant. The absorption depth in this case is very short, of the order of 100 nm, and is hardly dependent on the polymer structure. Using this method we demonstrated modification of both surface morphology and chemical structure in the near-surface layer. A main advantage of the EUV treatment is preservation of bulk properties of irradiated material due to a strong EUV absorption in a very thin near-surface layer. For the same reason, however, EUV radiation propagates only in vacuum, hence, irradiation of polymer samples in gaseous environment requires a special arrangement.

In this work our recent results concerning EUV irradiation of polymers in nitrogen environment are presented. Interaction of the EUV radiation with nitrogen resulted in gas ionization and excitation. The ionization state of nitrogen was determined based on the EUV emission spectrum. Chemical changes in irradiated near-surface layer were investigated using X-ray photoelectron spectroscopy (XPS). A possibility of incorporation of nitrogen atoms into the molecular structure of poly(vinylidene fluoride) PVDF was demonstrated.

In our experiments, a 10-Hz laser-plasma EUV source, based on a double-stream gas-puff target, irradiated with the 3 ns/0.8 J Nd:YAG laser pulse, was used. The target was formed by pulsed injection of krypton–xenon (90/10 %) gas mixture into a hollow stream of helium by employing an electromagnetic valve system, equipped with a double nozzle set-up. Focusing conditions and plasma parameters were adjusted to obtain maximum intensity in the EUV spectral region. The radiation was focused using a gold-plated grazing incidence ellipsoidal collector, manufactured by Reflex s.r.o., Czech Republic. The collector allowed for effective focusing of radiation, emitted from Kr/Xe plasma, in the wavelength range $\lambda = 9\text{--}70$ nm. The most intense emission was in the relatively narrow spectral region centered at $\lambda = 11 \pm 1$ nm. The spectral intensity at longer wavelength range was much smaller, however, spectrally integrated intensities in both wavelength ranges were comparable. The EUV fluence in a focal plane of the collector exceeded 60 mJ/cm^2 at the center of a focal spot. FWHM diameter of the intensity distribution in the focal spot was

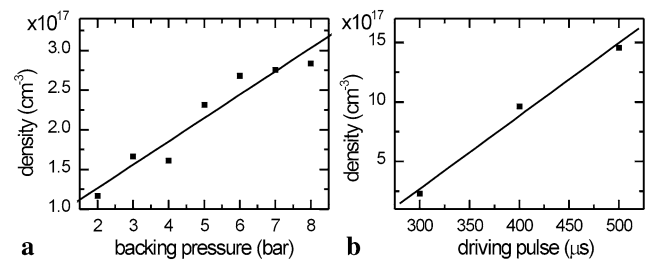


Fig. 1 Nitrogen density in the interaction region: (a) backing pressure dependence, driving pulse duration of 300 μs , (b) dependence on time duration of driving pulse, corresponding to the gas-puff valve opening time, backing pressure 5 bar

1.4 mm. Detailed description of the source and parameters of focused EUV radiation can be found elsewhere [9].

Nitrogen was injected into the interaction region, perpendicularly to optical axis of the irradiation system, using an auxiliary gas-puff valve. The valve was equipped with a tube-shaped nozzle, 30 mm long with an inner diameter of 0.9 mm. The nozzle outlet was located 2.5 mm from the optical axis. Nitrogen gas density in the interaction region was controlled by adjustment of either backing pressure or opening time of the valve. Density measurements were performed using a backlighting method [10], and the results are presented in Fig. 1. It can be noticed that the density is of the order of 1–10 % of the atmospheric density and is similar to NH_3 gas density employed in experiments performed using an excimer lamp for polymer irradiation [4]. Irradiation of N_2 , injected into the interaction region, by EUV photons results in ionization and excitation of the gas. A single EUV photon carries sufficient energy for photoionization of molecular or atomic nitrogen, releasing an electron from 2s or 2p subshell. Taking into account that the EUV photon energy, in this case, is equal to 112 eV, corresponding to maximum intensity of the EUV spectrum [9], the energy of subsequently released photoelectron is close to 100 eV, thus is sufficiently high for further ionization or excitation. This value corresponds to a maximum cross section for electron impact ionization of molecular nitrogen $\sigma(\text{N}_2^+, \text{N}^+ + \text{N}_2^{2+})$, which in this case, reaches value of $\sigma = 2.5 \times 10^{-16} \text{ cm}^2$ [12]. Taking into account the lowest gas density, used in the experiment, it results in a mean free path of photoelectrons equal to ~ 0.4 mm. A total cross section for excitation of electronic states in molecular nitrogen is also of the order of 10^{-16} cm^2 [13], thus, the released electrons are incapable of escaping from the interaction region. EUV photon energy is also sufficient for simultaneous ionization and excitation of nitrogen molecules.

The degree of ionization can be deduced from the EUV emission spectrum. The spectra were measured using a grazing incidence, flat-field spectrometer (McPherson, model 251), equipped with a 450 lines/mm toroidal grating. Spectral distributions, obtained for different N_2 densities,

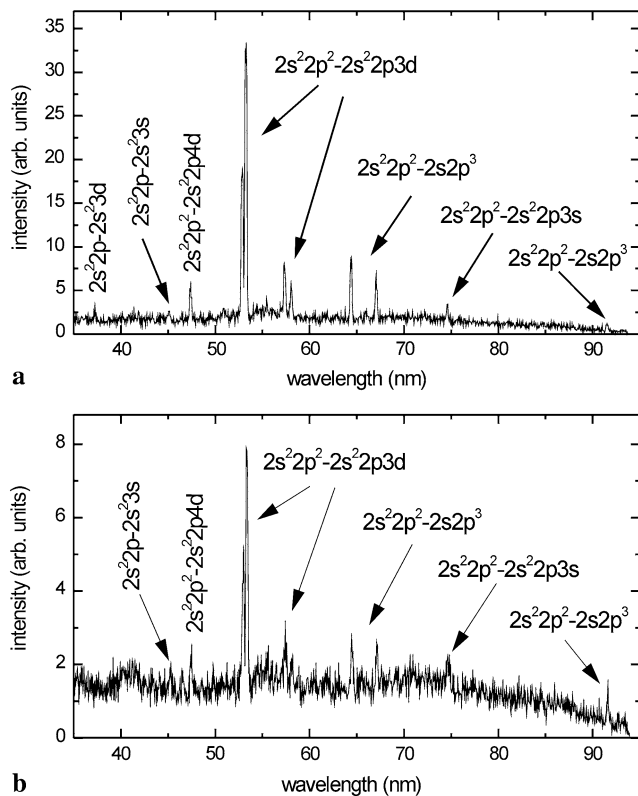


Fig. 2 EUV spectra of N II and N III ions acquired at different densities of nitrogen gas in the interaction region: (a) for 10^{17} cm^{-3} density, (b) for $1.5 \times 10^{18} \text{ cm}^{-3}$ density

are similar, however, their intensities decrease with increase of the gas density. The decrease can be associated with strong absorption of the EUV radiation in neutral molecular nitrogen surrounding the interaction region. Typical spectra for N_2 densities equal to 10^{17} cm^{-3} and $1.5 \times 10^{18} \text{ cm}^{-3}$ are shown in Fig. 2. The most intense spectral lines at 52.9 nm and 53.3 nm wavelengths, correspond to $2s^2 2p^2-2s^2 2p3d$ transitions in a singly ionized nitrogen (N II). The other emission lines, with much smaller intensities, correspond to other transitions in N II ions, except two very weak lines at wavelengths of 37.4 nm and 45.2 nm. These lines are $2s^2 2p-2s^2 3d$ and $2s^2 2p-2s^2 3s$ transitions in N III ions, respectively. No spectral lines corresponding to radiative transitions in N I were detected within the measured wavelength range. This is due to very low relative intensities of N I spectral lines emitted in this wavelength range [11]. Strong N I emission lines are located within the range $\lambda = 113\text{--}174 \text{ nm}$ and most of the EUV emission spectrum of N_2 molecules is also located beyond the spectrometer range [14].

Significant emission outside the wavelength range of the spectrometer was demonstrated using pinhole imaging. Images of the photoionized gas were acquired using a pinhole camera coupled to a back illuminated CCD detector, without any filter or protection plate. In this case radiation in a wide wavelength range, from EUV to visible light, was recorded.

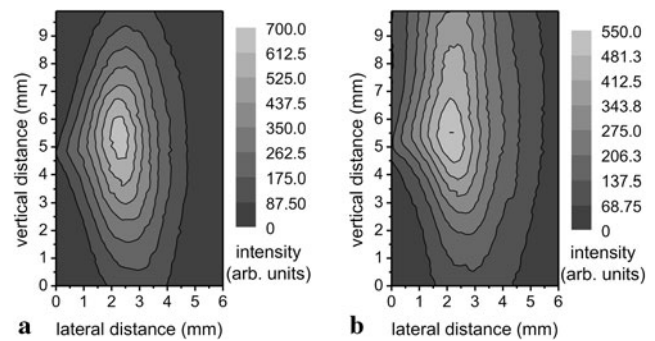


Fig. 3 Intensity distributions corresponding to pinhole images of the ionized region acquired at different densities of nitrogen gas without any filter: (a) for 10^{17} cm^{-3} density, (b) for $1.5 \times 10^{18} \text{ cm}^{-3}$ density

Intensity distributions, corresponding to typical images obtained at different nitrogen densities, are presented in Fig. 3. It can be noticed that the ionized region is elongated in vertical direction, along the optical axis of the EUV collector. In case of low gas density the region is quite symmetrical in respect to the focal plane with transversal FWHM width of approximately 2 mm. The ionized region induced in higher density nitrogen gas has similar size, however, is distorted. Maximum emission from this area is about 20 % less, compared to a corresponding region in the low density nitrogen. Additional images were acquired using either a 100 nm thick Al filter or a glass plate. The intensity obtained with the Al filter, having approximately 80 % transmission in the wavelength range 17–70 nm, was hardly detectable. Maximum intensity in this case was about two orders of magnitude lower compared to images obtained without any filter. Also images acquired in an optical region, with the glass plate acting as a filter, were several times weaker. It means that majority of the emission, recorded by the pinhole camera, originates from the intermediate wavelength range $\sim 70\text{--}300 \text{ nm}$.

The ionized nitrogen was used for chemical modification of near-surface layers of polymers. The polymer samples were located 3 mm downstream the focal plane of the EUV beam and nitrogen gas was injected into the focal plane, as mentioned above. EUV absorption in the nitrogen stream was about 5–50 % depending on the gas density, thus, dual action of the EUV radiation and the ionized gas was possible in this case. In our previous work we have shown a possibility of chemical modification of polymer structure by the EUV irradiation [7, 8]. Combined EUV and ionized nitrogen treatment, presented in this work, allows for additional incorporation of N atoms into polymer chains. In this experiment poly(vinylidene fluoride) (PVDF) foils from Goodfellow were exposed. Irradiation was performed at 10 Hz repetition rate for N_2 density equal to $\sim 5 \times 10^{17} \text{ cm}^{-3}$ with different exposure times up to 20 s. Chemical changes in the near-surface layer of PVDF were investigated using X-ray photoelectron spectroscopy (XPS). The XPS spectra were

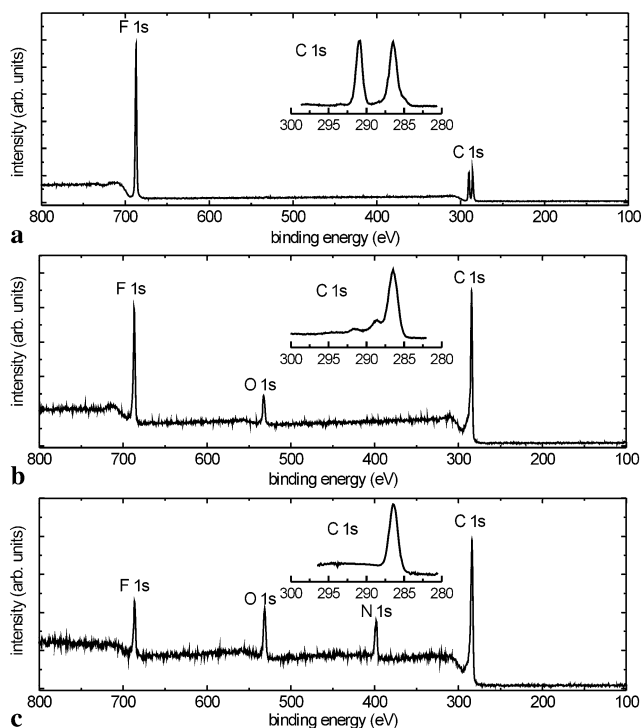


Fig. 4 XPS survey spectra of PVDF surface: (a) pristine sample, (b) sample irradiated with 150 EUV pulses, (c) sample irradiated with 150 EUV pulses in presence of nitrogen. *Sub-images* show the high-resolution XPS spectra of C 1s

acquired for polymer samples exposed to a different number of EUV pulses. For comparison the XPS measurements were performed also for a pristine PVDF sample. Typical XPS survey spectra obtained for the pristine sample and samples irradiated with 150 EUV pulses with and without N_2 are presented in Fig. 4. In all spectra two main peaks, which are characteristic for fluorine (F1s) and carbon (C1s), are present. Relative atomic concentration (AC) of carbon and fluorine, evaluated from these spectra, fits the theoretical value of 50:50 AC% in case of the untreated polymer sample (Fig. 4a). The XPS spectrum, shown in Fig. 4b, corresponds to irradiation of the polymer with a low fluence, below 10 mJ/cm^2 . In this case the C1s peak is much stronger compared to F1s peak. The calculated fluorine concentration decreased to 12.5 % while carbon concentration increased to 79.7 %. Also high-resolution C1s spectrum, recorded using pristine sample, changes significantly as a result of irradiation (compare enlarged C1s spectra in Figs. 4a and b). The C1s spectrum of untreated PVDF contains two peaks corresponding to $-\text{CH}_2-$ at the binding energy (BE) of 286.44 eV and $-\text{CF}_2-$ at BE of 290.9 eV [15]. The last peak strongly decreased for the polymer irradiated with low fluence. In case of the polymer irradiated with low fluence the peak corresponding to binding energy of 290.9 eV strongly decreased. It means that irradiation of PVDF with low fluence results in carbon enrichment in the near-surface

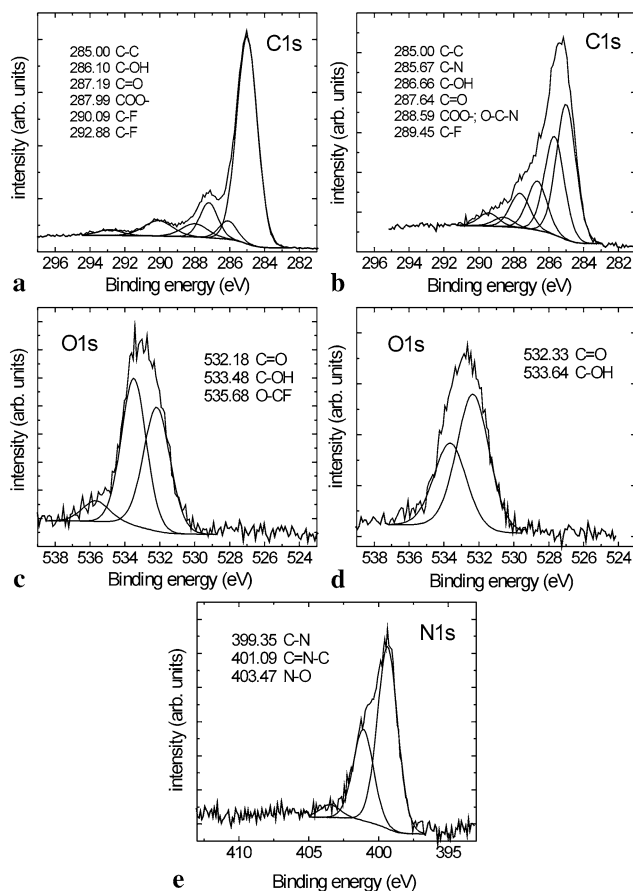


Fig. 5 High-resolution XPS spectra of PVDF: (a) C1s—EUV irradiated sample, (b) C1s—sample irradiated in presence of nitrogen, (c) O1s—EUV irradiated sample, (d) O1s—sample irradiated in presence of nitrogen, (e) N1s—sample irradiated in presence of nitrogen

layer. An additional O1s peak reveals small oxygen contents (7.5 AC%), which was incorporated into the polymer surface, exposed to air after irradiation. The XPS spectrum, shown in Fig. 4c, corresponds to a combined treatment of PVDF with the EUV radiation and ionized nitrogen. The calculated fluorine concentration decreased, in this case, to 9.4 %, while carbon concentration increased to 66.1 %. Two additional peaks of O 1s (11.5 AC%) and N 1s (13.0 AC%) were found in addition to the main C 1s and F 1s peaks. As before, oxygen atoms came from the atmosphere exposure, while nitrogen was incorporated during the EUV and nitrogen ions treatment.

More detailed analysis was based on high-resolution C1s, O1s and N1s XPS spectra shown in Fig. 5 and BE shifts corresponding to different functional groups reported in the XPS databases [15, 16]. The C1s spectrum for the EUV irradiated PVDF sample (Fig. 5a) was fitted with six peaks corresponding to different types of carbon bond: a C–C peak at 285 eV, a C–OH peak at 286.10 eV, a C=O peak at 287.19 eV, a COO– peak at 287.99 eV, C–F peaks at 290.09 and 292.88 eV. As could be expected from the sur-

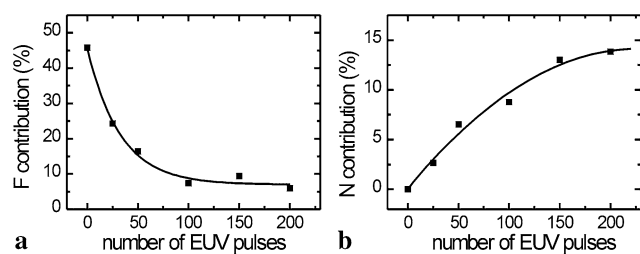


Fig. 6 Changes of chemical composition in the irradiated layer versus number of irradiation pulses: (a) decrease of fluorine atoms, (b) increase of nitrogen atoms

vey spectra, relative intensity of C–F peaks is much lower compared to the C–C peak, confirming defluorination of the irradiated polymer. The O-containing functional groups are formed in the polymer near-surface layer exposed to air after irradiation, due to interaction of the polymer molecules with O₂ or H₂O always present in air. Similar peaks, however, with different relative intensities, can be seen in the C1s spectrum (Fig. 5b) acquired for the PVDF sample irradiated in the presence of nitrogen. As could be expected there is an additional peak at the binding energy of 285.67 eV attributed to C–N bond formed during irradiation. Also a peak at 288.59 eV was partially attributed to O–C–N bond. Presence of the O- and N-containing functional groups was also confirmed in the O1s and N1s spectra shown in Figs. 5c–e. The O1s spectra were fitted with two intense peaks corresponding to C=O and C–OH functional groups. It can be noticed that peaks visible in the spectrum acquired with the presence of nitrogen (Fig. 5d) are approximately 30 % broader compared to the peaks shown in Fig. 5c. It suggests that each peak comes from more than one unique specie. An additional peak of low intensity visible in the O1s spectrum acquired without nitrogen can be attributed to a O–CF functional group. The N1s spectrum was fitted with three peaks: a C–N peak at 399.35 eV, a C=N–C peak at 401.09 eV and a N–O peak at 403.47 eV. Lack of the N-containing functional groups in PVDF irradiated without presence of nitrogen in the interaction region proves that the nitrogen atoms cannot be incorporated directly from air, but have to be ionized first.

The chemical composition of the modified surface layer changed with a number of irradiation pulses. The corresponding dependence is presented in Fig. 6. A strong decrease of fluorine contribution can be noticed for the first 100 EUV pulses to the value of approximately 10 %. Nitrogen contribution increases from 0 % to about 14 % for 200 pulses. Further irradiation does not change significantly the chemical composition.

In conclusion, a possibility of chemical modification of polymer surfaces by dual action of the EUV radiation and ionized nitrogen is presented for the first time. EUV induced ionization of N₂ was investigated and the EUV spectra of N II and N III ions are shown. Chemical modification was investigated using XPS method and the corresponding spectra are presented. Incorporation of nitrogen atoms into the polymer chains was obtained.

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