Enhancement of sensing properties of thin poly(methyl methacrylate) films by VUV modification

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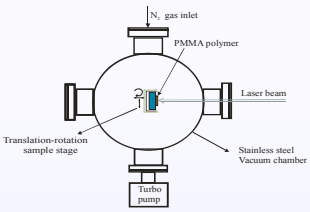
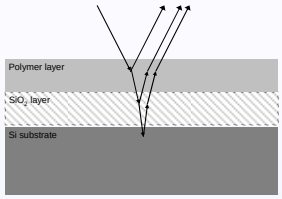
Abstract

Surface modification of polymeric films by VUV light is an efficient method to tailor their properties and functionality for a variety of applications. Laser irradiation at 157 nm of poly(methylmethacrylate) (PMMA) thin films deposited on SiO_2 layer, demonstrates a considerable increase of surface and bulk **swelling** during water vapour sorption in comparison to the non irradiated film areas. AFM images of surface morphology of the irradiated_areas reveal that surface roughness depends on the irradiation conditions. Besides morphological changes, X-ray photoelectron spectroscopy (XPS) suggest chemical modification of the irradiated film areas. The enhanced surface swelling and the chemical modification increases the detection efficiency of water analyte in gas phase by many orders of magnitude **(400%)**. This method can be used to fabricate a polymer based sensor array and to engineer its detection efficiency.

Experimental set up



The experimental set-up for VUV exposure



The principle of operation of the white light reflectance spectroscopy (WLRS) for measuring polymer swelling.

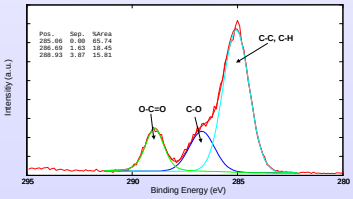
❖PMMA with M_w=120K (Sigma-Aldrich) solution was prepared from PMMA polymer (6% w/w) in propyl glycol mether ether acetate (PGMEA) after 96 hours stirring and subsequent filtering. The substrates were Si wafers, 1 μm thick, where the SiO_2 layer was thermally grown (1100 ºC, 200 min, and wet oxidation). The solution was spin coated on the SiO_2 layers and further baked on a hot plate at 160 ºC for 60 min. The initial PMMA film thickness was ~ 345 nm.

❖The experimental set-up for VUV exposure of the polymeric films consisted from the 157 nm molecular fluorine laser, (Lambda Physik, LPF 200), the all stainless steel vacuum chamber containing the computer-controlled X-Y-Z-θ translation stage where the polymer substrates were placed (Fig 1).

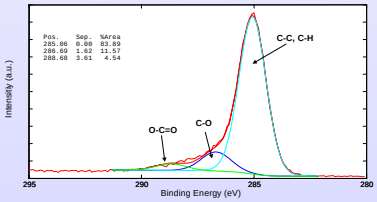
❖ AFM imaging of the surface morphology of both non-irradiated and irradiated areas was performed using a ¨Quesant - Qscope 250¨.

❖The X-ray photoelectron spectroscopy (XPS or ESCA) analyses were carried out on the PHI-TFA XPS spectrometer (Physical Electronics Inc). The analyzed area was 0.4 mm in diameter and the analyzed depth was about 3 - 5 nm.

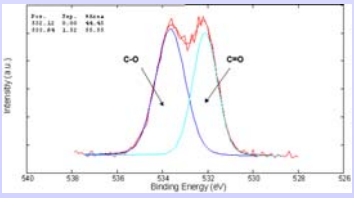
Results



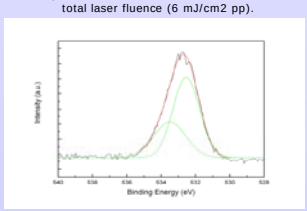
C 1s XPS spectrum from the surface of the non-irradiated PMMA areas.



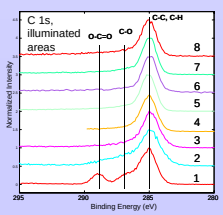
C 1s XPS spectrum of the 157 nm irradiated area 16.2 J/cm2 total laser fluence (6 mJ/cm2 pp).



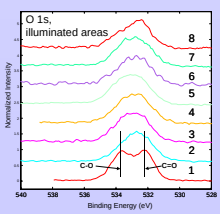
O 1s XPS spectrum from the surface of the non-irradiated PMMA areas.



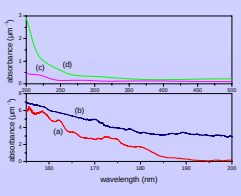
O 1s XPS spectrum from the surface of the irradiated PMMA areas16.2 J/cm2 total laser fluence (6 mJ/cm2 pp).



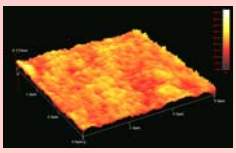
Normalized C 1s XPS spectra obtained on the illuminated areas of the PMMA films with increasing the laser fluence.



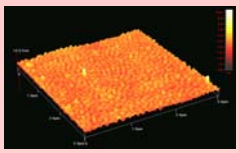
Normalized O 1s XPS spectra obtained on the illuminated areas of the PMMA films with increasing the laser fluence.



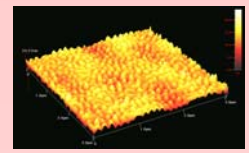
VUV, UV and visible absorbance of the PMMA film at 157 nm. **(a), (c)** prior to the irradiation and **(b), (d)** after irradiation.



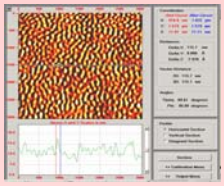
AFM image of a non irradiated area of the PMMA film. The Z_{av} value is ~ 1.9 nm



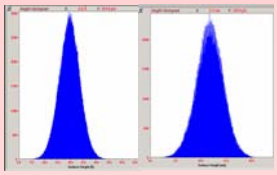
AFM image of the PMMA film following 157 nm irradiation with 0.27 mJ/cm^2 total laser fluence. The Z_{av} value is 3.22 nm.



AFM image of the PMMA film following 157 nm irradiation with 0.54 mJ/cm^2 total laser fluence.



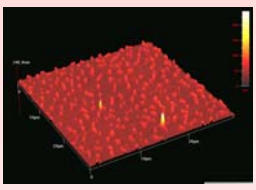
2D AFM image of the PMMA film following 157 nm irradiation with 0.54 mJ/cm^2 total laser fluence. The average size of the self -assembled structures is 116nm.



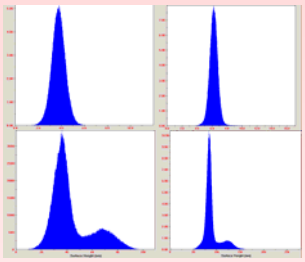
Height histogram for a scan area of 3 μm X 3 μm. The left histogram is for the non irradiated area, and the Z_{av} value is 1.9 nm. The right histogram is for the irradiated area with total fluence of 0.54 mJ/cm^2.

	0.00 J/cm²	0.27 J/cm²	0.54 J/cm²
Z_{ave} (nm)	1.5	3.2	5.5
Rq (nm)	0.2	0.5	1.0
Rp (nm)	1.5	2.3	4.2
Rv (nm)	1.5	3.2	5.5
Rt (nm)	2.9	5.9	9.7

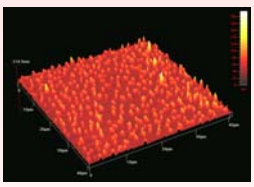
Surface parameters of the irradiated areas at different irradiation fluence obtained by the analysis of the AFM images.



AFM image of the PMMA film following 157 nm exposure (13.5 J/cm2). Surface was modified indicated micro/nano structure domains within the illuminated area. The surface roughness was increased to ~ 40 nm.



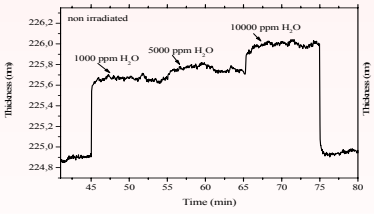
Height distribution histogram of the observed structures for an area 30 μm X 30 μm under different exposure conditions (Non-irradiated, 4.5 , 13.5, 67.5 J/cm2).



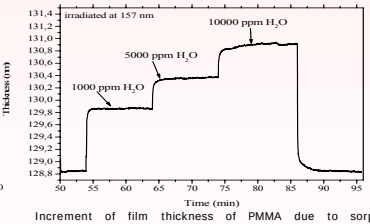
AFM image of the PMMA film following 157 nm exposure (67.5 J/cm2). Surface was modified indicated micro/nano structure domains within the illuminated area. The surface roughness was increased to ~ 80 nm.

	4.5(J/cm²)	13.5(J/cm²)	67.5(J/cm²)
Average Height (nm)	6.0	43.0	88.0
RMS deviation (nm)	0.7	16.0	18.0
Rp (Max. peak, nm)	11.0	65.0	191.0
Rv (Max. valley, nm)	6.0	43.0	88.0
Rt(Max peak – valley, nm)	17.0	108.0	280.0

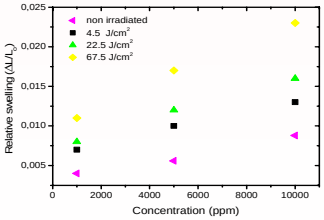
Surface characteristics of the irradiated areas at different irradiation time obtained by the analysis of the AFM images. Z_{ave} is the average of the Z values within the given area; R_q (root mean square) is the standard deviation of the height values; Rp is the maximum height of the profile roughness above the mean plane; Rv is the lowest point bellow the mean image plane; Rt is the sum total of the maximum peak and maximum valley measurements.



Increment of film thickness of PMMA due to sorption (absorption / desorption) with different concentrations of water (vapor) (1000, 5000 and 10000ppm) for the non-irradiated sample.



Increment of film thickness of PMMA due to sorption (absorption / desorption) with different concentrations of water (vapor) (1000, 5000 and 10000ppm) for the 157 nm irradiated sample (13.5 J/cm^2).



Relative swelling values of PMMA for irradiated samples at different 157 nm exposure doses (4.5, 13.5, 22.5, 45, 67.5 J/cm^2) for water vapors. The relative swelling of the non-irradiated samples is indicated as well for comparison.

Conclusions

✓PMMA thin films were processed with laser light at 157 nm.

✓The irradiated films indicated enhanced swelling during water vapour absorption in comparison to the swelling of the non-irradiated films.

✓The higher swelling was due to surface chemical modification and porosity increment following laser treatment.

✓XPS, AFM and absorption imaging indicate enhanced carbonization and porosity of the illuminating areas.

✓The irradiated polymer becomes more hydrophobic causing relatively higher swelling in comparison to the non-irradiated areas.