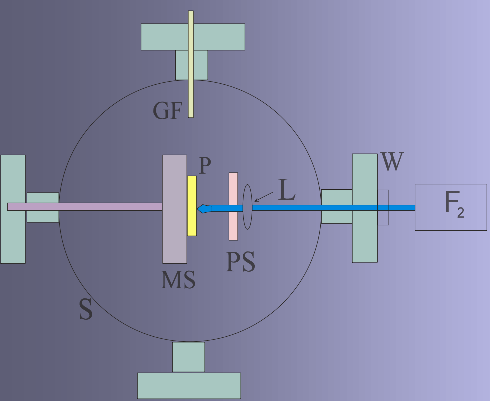
# Nano-scale spatial control over surface morphology of biocompatible fluoropolymers at 157 nm.

E. Sarantopoulou, Z. Kollia, A. C. Cefalas
National Hellenic Research Foundation. Theoretical and Physical Chemistry Institute
48 Vassileos Constantinou Avenue, Athens 11635 Greece
A. M. Douvas, M. Chatzichristidi, P. Argitis,
B. Institute of Microelectronics, NCSR Demokritos, 15310 Agia Paraskevi, Greece
S.Kobe
Josef Stefan Institute, Department of Nanostructured Materials, Jamova 39, Ljubljana SI-1000, Slovenia

## ABSTRACT

Specification of laser ablating parameters is important to fabricate micro-bio arrays with enhance sensitivity and speed. Optimum fabricated conditions occur when thin surface layers of bio-compatible fluoro- polymers, (2,2,2 poly trifluoroethyl methacrylate (PTFEMA) and Teflon), were ablated with nano-scale spatial resolution using laser at 157 nm. The surface ablation efficiency and morphology, and nano-volume ablation and other effects, such as the formation of nano-columns depend on the exposure conditions. Surface ablation is the main process for laser fluence less than 1 mJ/cm$^2$ and a laser spot-size smaller than ~ 10 μm.

## EXPERIMENTAL




❖Experimental set up for 157 nm laser surface treatment of bio-polymers. $F_2$: 157 nm laser. MS: X-Y-Z-θ computer controlled stage. S: Stainless-steel chamber. PS: Optical projection system. P: Polymeric thin films. L: Focusing $CaF_2$ projection system. W: $CaF_2$ window.

❖The micro-stepper was also equipped with a CCD imaging modulus that has been interfaced to the system in real –time feed back mode, through image processing software, which allows full automation of the system with improved speed and performance for polymer micro-array fabrication at 157 nm.

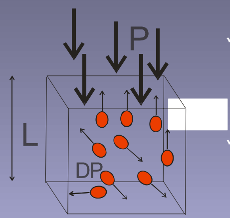
❖Thin films of Poly (2,2,2-trifluoroethyl methacrylate, PTFEMA), Mw=114,700, Mn=45,900, 80 nm thick, were synthesized by free radical polymerization of 2,2,2-trifluoroethyl methacrylate using 2,2´-azobis(2-methylbutyronitrile as initiator and then they applied by spin coating on a silicon wafer pre-coated with a thin gold film by sputtering.

❖The surface morphology of the films prior and after laser exposure was evaluated with an atomic force microscope (AFM).

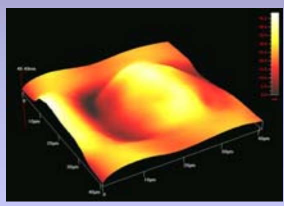
## RESULTS

Three different type of processes were observed during the interaction of 157 nm photons with thin films of the bio-compatible fluoropolymers PTFEMA and Teflon:

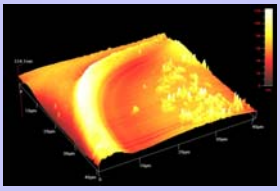
*3. 1 Volume ablation: Polymer surface swelling and dipping.*




- ✓ Volume ablation process, (left image). The laser radiation, (P), penetrates within the PTFEMA in a distance (L) specified by the absorption coefficient, (~ 7 μm for PTFEMA).
- ✓ Photo-dissociation is then following with sudden increase of the pressure within the polymer volume from the fast dissociated photo-fragments (DP).



When the pressure is not high enough to ablate the polymer volume, surface swelling is taking place as is clearly seen in the AFM image. The surface swells ~50 nm. Around the edges surface dipping can be clearly seen. The surface was illuminated with 100 laser pulse of 10 μm spot size at 1 mJ/cm$^2$.



Surface dipping from volume ablation. At lower laser fluence, the pressure is not high enough to support surface swelling and the dissociated photo-fragments escape from defects within the volume to the surface. As material is constantly removing the illuminated volume collapses with a 40 nm dipping. The area was illuminated with 100 laser pulses, having 100μm laser spot-size at 1mJ/cm$^2$ for each pulse.

***3. 2 Stacking of ablated dissociated products on the polymer surface.***

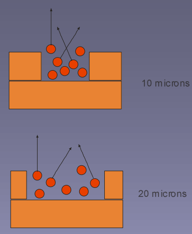
✓In the case of small laser spot size~10 μm, enhanced collision rate of the ejected photo-fragments within the plume above the surface and recombination of dissociated photoproducts and fast relaxation was taking place.

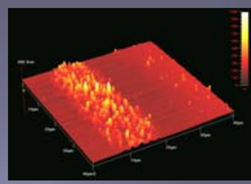
✓The size and the density of the pillars increased with increasing energy and fluence.

✓The photoproducts in this case were not removed from the surface, but they form agglomerations in the form of pillars.

✓The formation of the negative charged F-, $CF^{-1}$ photo-fragments in the ablative plume enhances the collision rate, in comparison to other polymers.

✓The formation of nano-pilars with dimensions ranging from 10 nm to 1 μm was observed for both polymers of PTFEMA and Teflon.

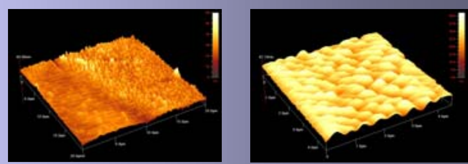


Stacking of dissociated products on the surface of the polymer. When the laser spot size was < 10μm, the dissociated products were stuck on the polymer surface forming pillars due to enhance collision rate, left image. The columns were vaied in length and size from the nano to micro scale. The area of the right image of PTFEMA, was illuminated with a 10 X 50 μm slit at 1 1mJ/cm$^2$.

***3. 3 Surface ablation.***

In the case of laser spot size > 20μm, , ablation was taking place predominantly from the surface of the polymer.



3D-AFM images of the edge between exposed and non exposed areas in Teflon at 157 nm.

Micro-array of PTFEMA spots , fabricated at 157 nm by surface laser ablation in PTFEMA. The dimensions of each one of the oval shaped spot was 10 X 20 μm.

## CONCLUSION

Three different type of processes were observed during the interaction of 157 nm photons with thin films of the bio-compatible fluoropolymers PTFEMA and Teflon:

1. Non-ablative Swelling /dipping of the illuminated polymer surface from volume ablation/dissociation in PTFEMA .
2. Stacking of the photo-dissociated moieties on the polymer surface from fast relaxation of the photoproducts in Teflon and PTFEMA was taking place with the formation of nano-pillars.
3. Surface ablation with well defined edges in PTFEMA was observed for laser fluence below 1 mJ/cm$^2$ per pulse. The efficiency of the processes depends not only on the irradiated conditions and the type of polymers, but on the laser spot size as well.

Polymer swelling and nano-pilling is the dominant laser ablation process in fluoro/ bio-compatible polymers for laser beam sport size < 10 μm, due to enhanced collision rate in the ablating plume. Definition of optimum surface treatment conditions allow biocompatible fluoropolymers micro array fabrication of 10 μm resolution.