EUV-initiated surface changes in polymers

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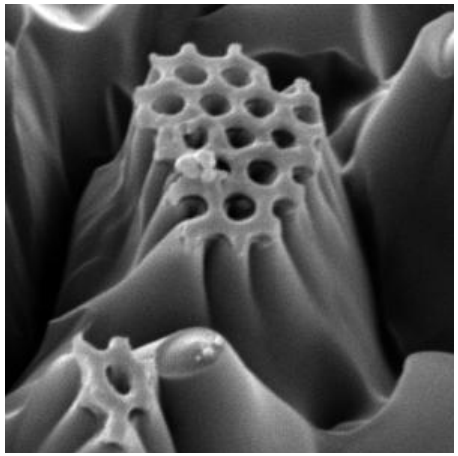
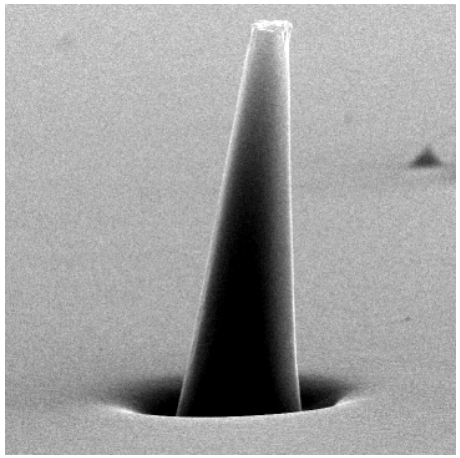




Outline

- motivations
- laser - plasma EUV source for surface modification
  - the source description
  - EUV parameters
- interaction with selected polymers
  - surface morphology - SEM measurements
  - chemical changes - XPS measurements
- summary

Motivations

• Surface processing- what for?

Change of some surface properties: wettability, roughness, optical and adhesive properties, biocompatibility

• How can be obtained?

Changing surface morphology and chemical structure

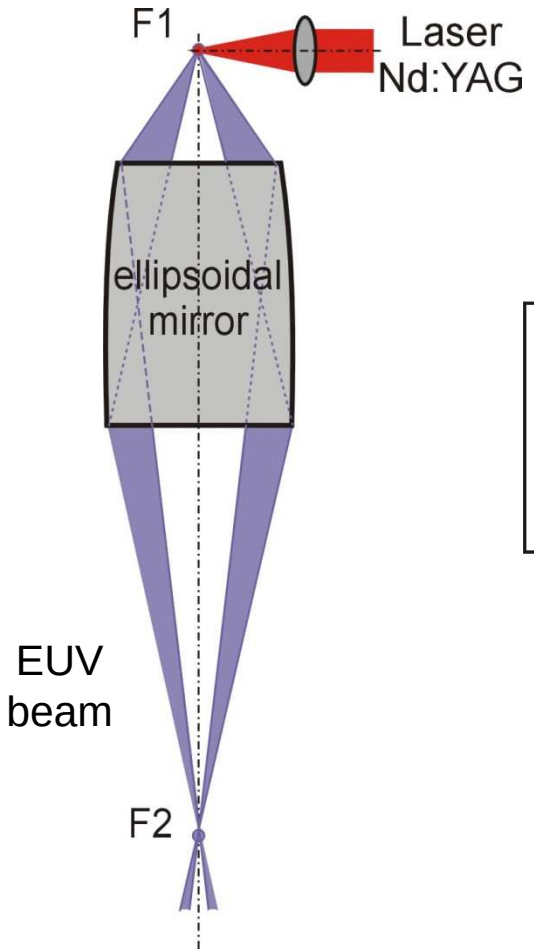
• Physical methods:

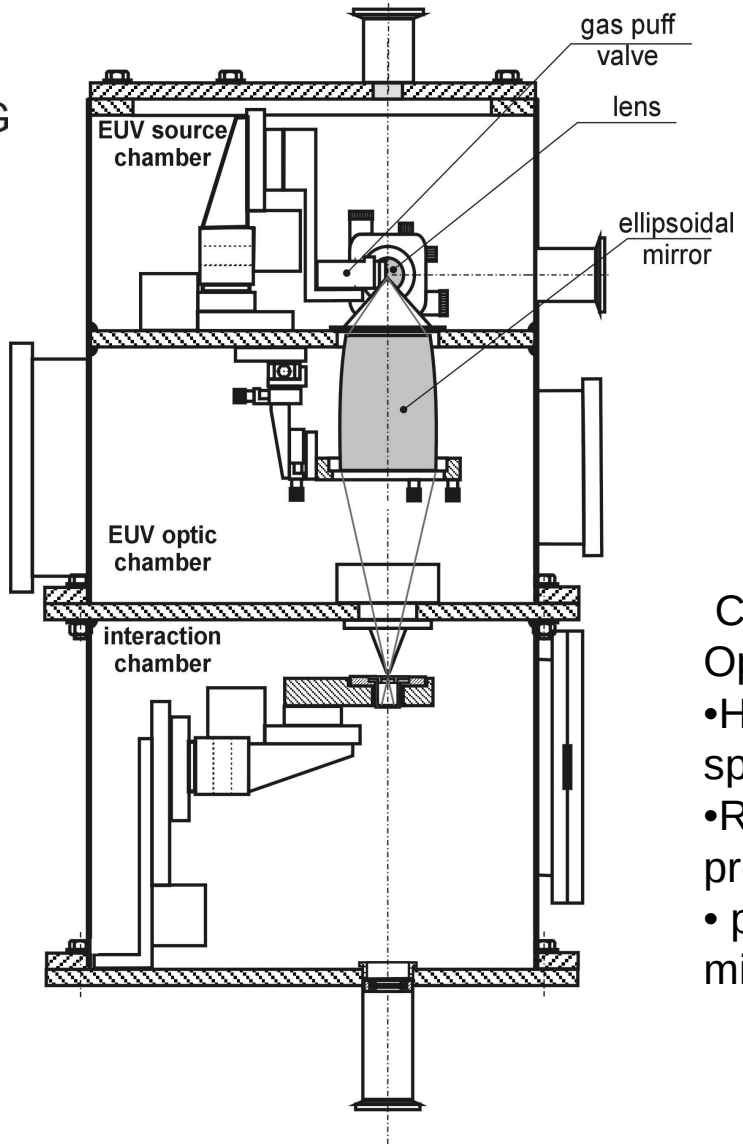
plasma treatment, ion implantation, UV irradiation

• Why EUV irradiation?

Additional method, very small penetration depth, applicable for any polymer

EUV source for surface processing





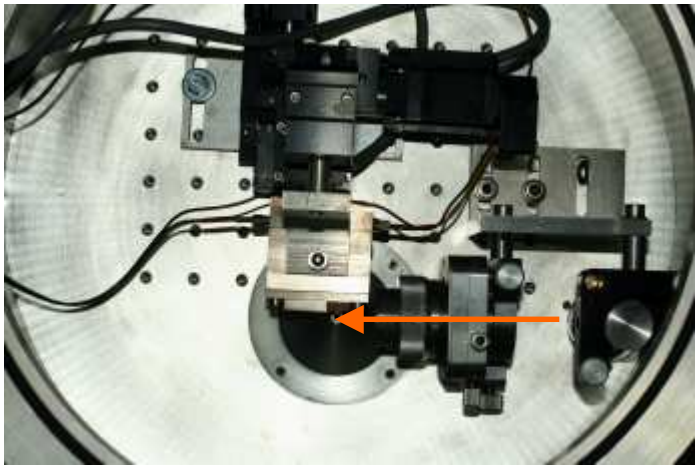
Laser-plasma
EUV source,
Gas-puff target,
Low vacuum

EUV collector,
Efficient turbo pump,
Differential pumping

Chamber for irradiation,
Options:
- High vacuum for mass spectrometry,
- Reactive gas under low pressure
- possible use for micromachining

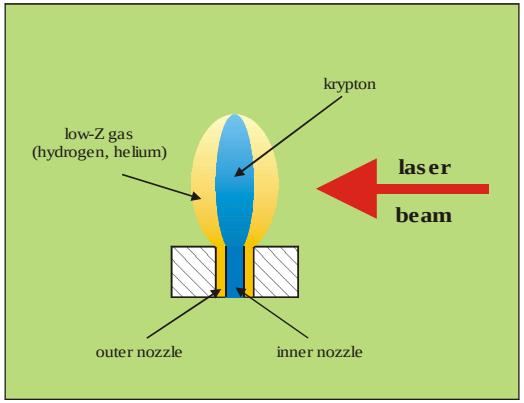
EUV source for surface processing

View of the EUV source for surface modification



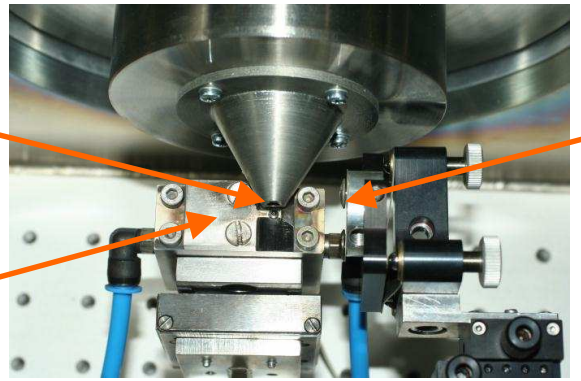
Source section, low vacuum

Laser
Nd:YAG
0.8 J, 4 ns,
10 Hz



Schematic view of the double stream gas puff target

Orifice for differential pumping

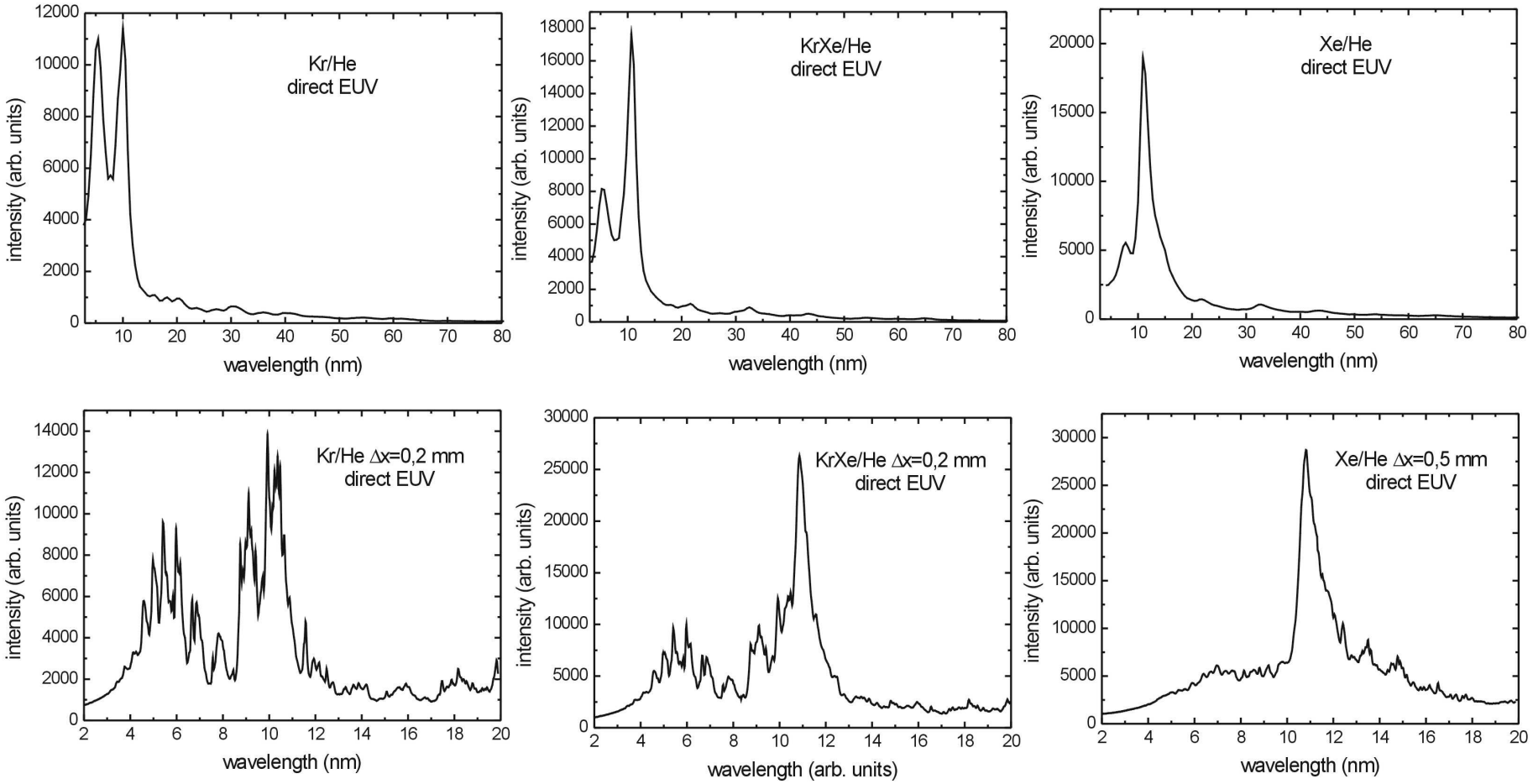


lens

Gas valve

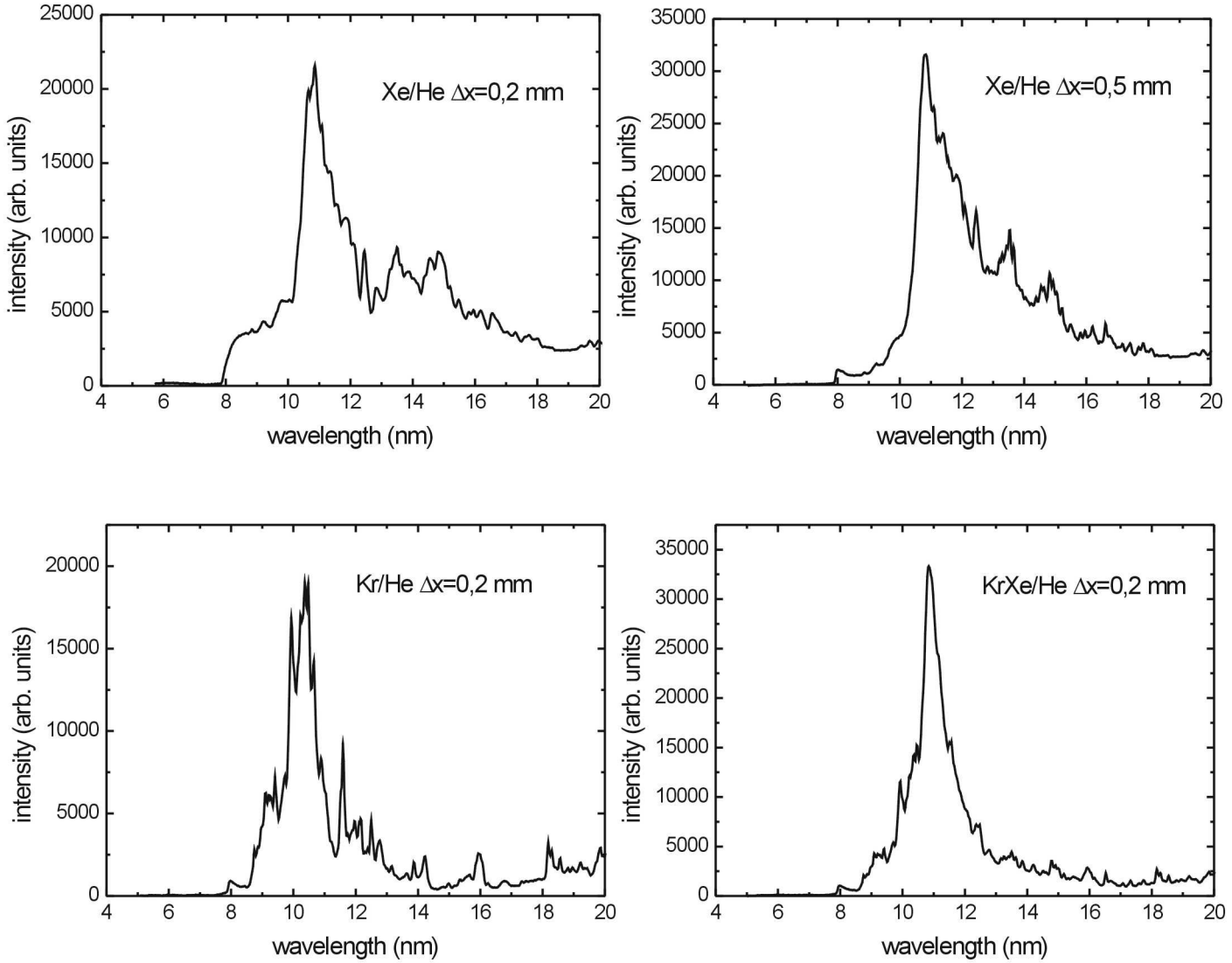
Gas puff target area

EUV spectra of Kr, Kr+Xe, Xe plasmas



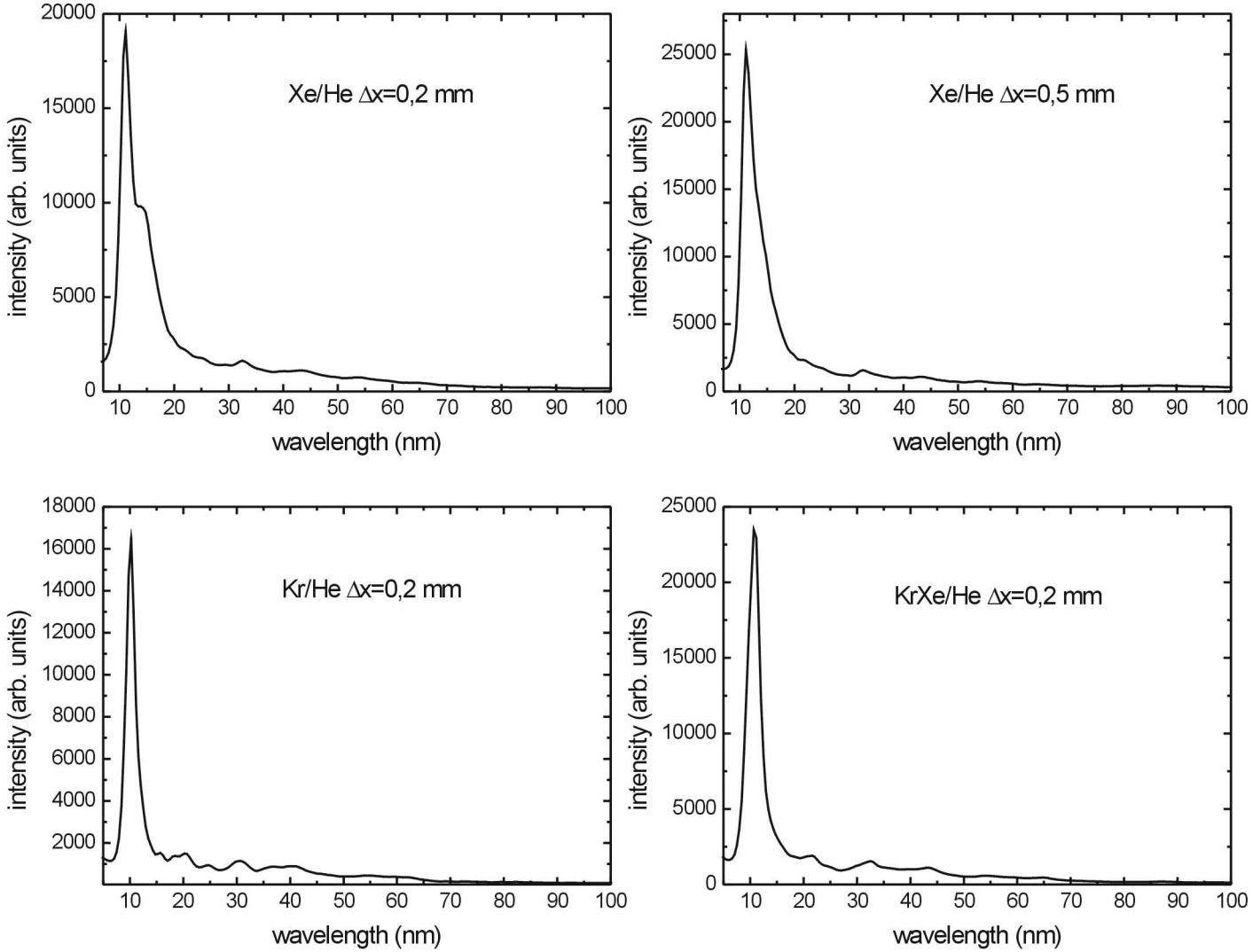
Spectra of Xe, Kr, Kr+10%Xe EUV direct radiation measured using a spectrograph with transmission grating TG 5000 lines/mm (high resolution) and 250 lines/mm (low resolution)

EUV spectra of Kr, Kr+Xe, Xe plasmas (reflected)



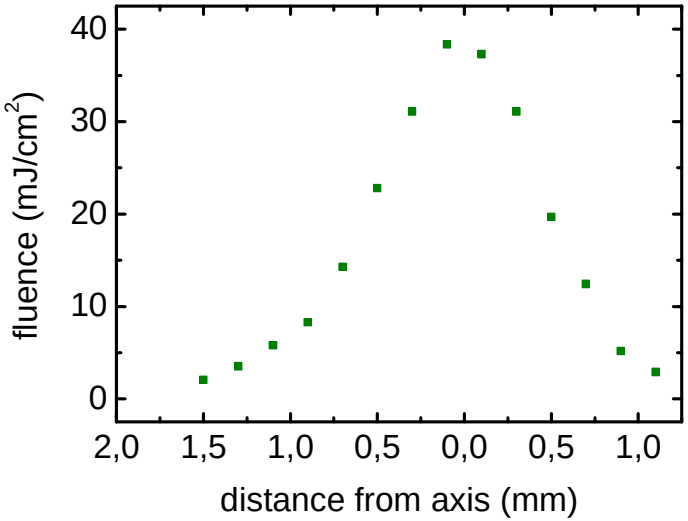
High resolution spectra of Xe, Kr, Kr+10%Xe EUV reflected from Au plated ellipsoidal collector, measured using a spectrograph with transmission grating TG 5000 lines/mm

EUV spectra of Kr, Kr+Xe, Xe plasmas (reflected)

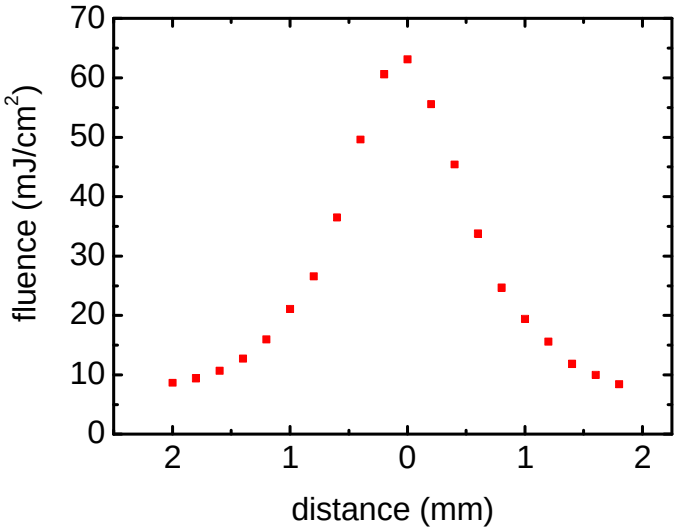


Low resolution spectra of Xe, Kr, Kr+10%Xe EUV reflected from Au plated ellipsoidal collector, measured using a spectrograph with 250 lines/mm transmission grating

EUV fluence in the focal plane for Kr plasma



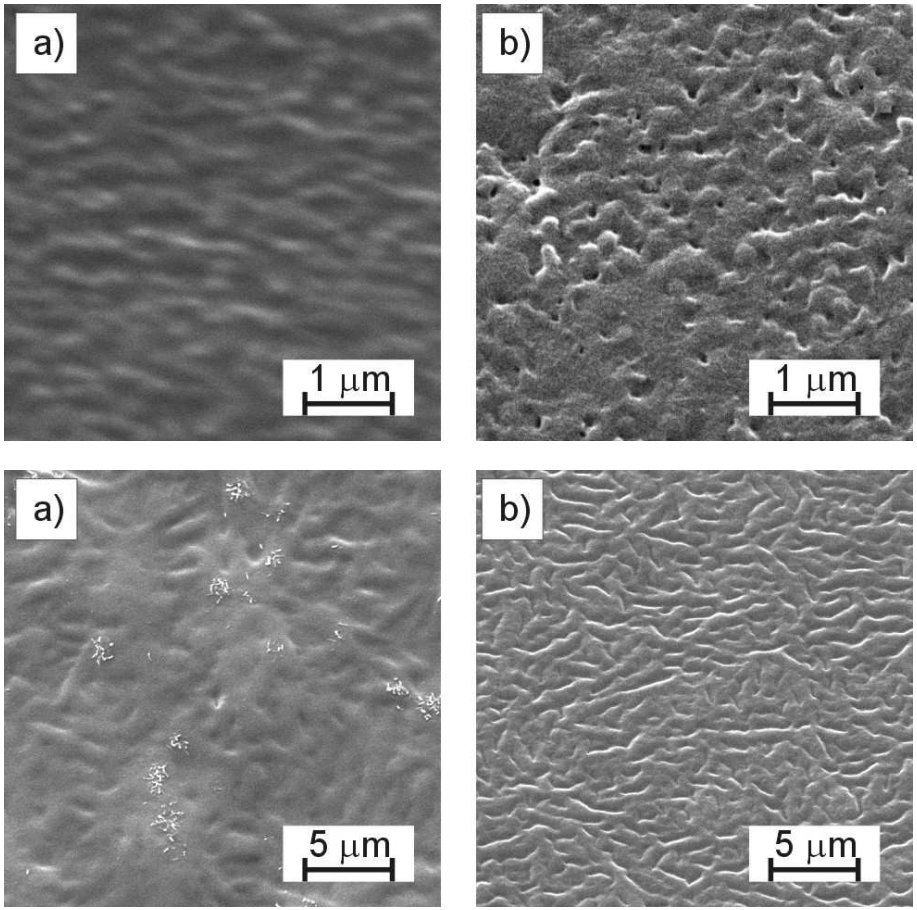
Intensity distribution close to 10nm in the focal plane of the EUV collector



Intensity distribution in the wide wavelength range in the focal plane of the EUV collector

EUV induced structures on PMMA and PA surfaces

Two opposite processes are possible: crosslinking and fragmentation of polymer chains.
Evidences of fragmentation shown here and in next slides

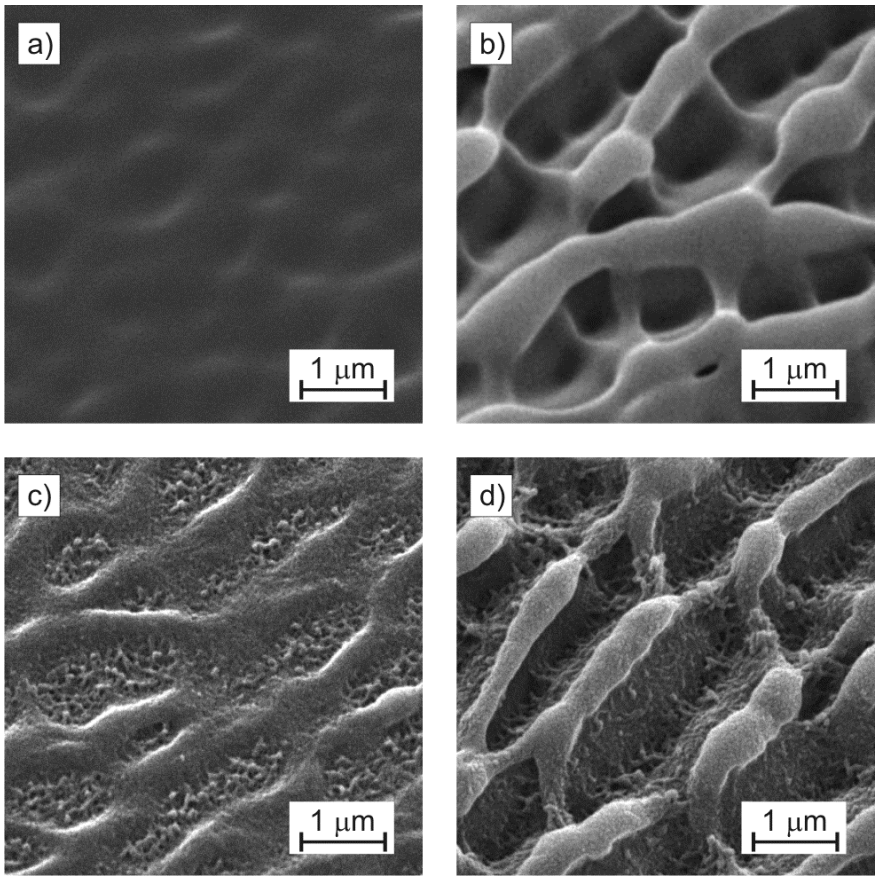


Poly (methyl methacrylate) PMMA
5 EUV pulses
a)no further treatment
b)soaked in PMMA developer (methyl isobutyl ketone + isopropyl alcohol)

Polyamide 6 (Nylon) 5 EUV pulses
a)no further treatment
b)soaked in isopropyl alcohol)

EUV induced structures on PET surface

SEM images of the microstructures formed under EUV irradiation with the fluence close to maximum, well above the ablation threshold, followed by acetone rinsing



Surface morphology of PET foil irradiated with different number of EUV pulses

with further acetone treatment:

a) 10 pulses,

b) 25 pulses,

without acetone treatment:

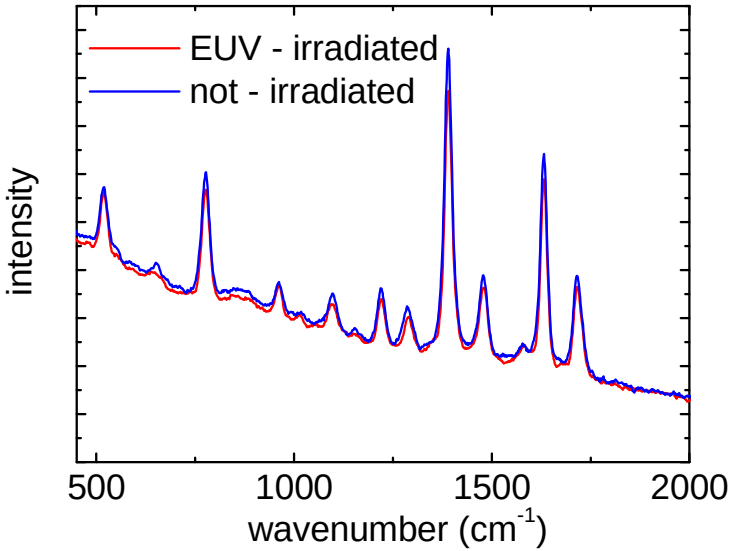
c) 10 pulses

d) 250 pulses

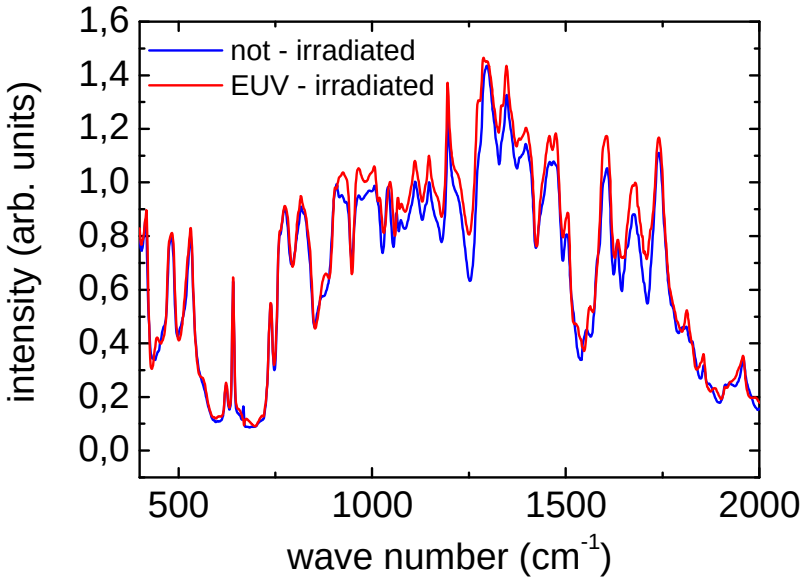
The acetone rinsing removes the light fractions revealing the nanostructures having the form of grains with the size of the order of tens nanometers. The general form of surface microstructures remains unchanged.

Measurements of chemical changes

- Raman scattering
- Infrared spectroscopy
- X-ray photoelectron spectroscopy



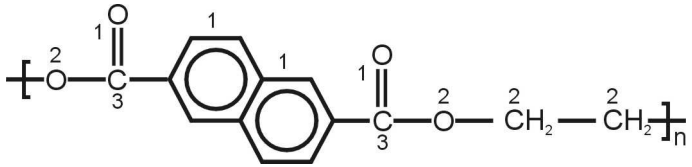
Raman spectra

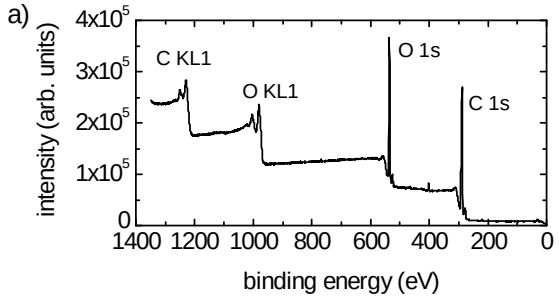


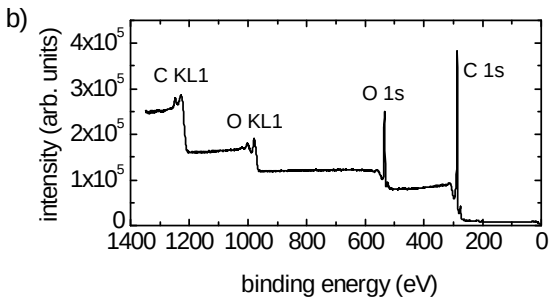
Infrared spectra

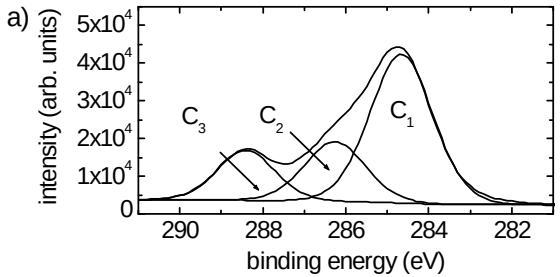
Signals come mainly from bulk with a very small contribution from the modified near surface layer. Hence the spectra before and after irradiation are almost identical.

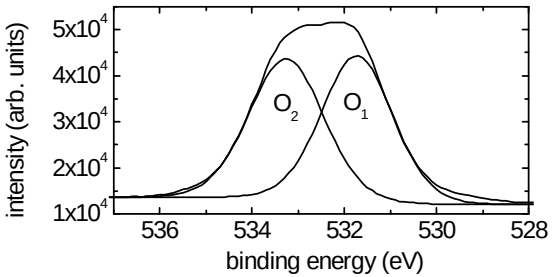
XPS spectra of PEN

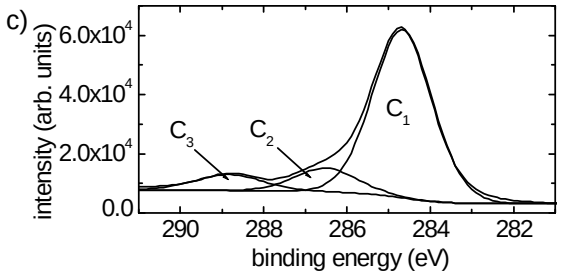


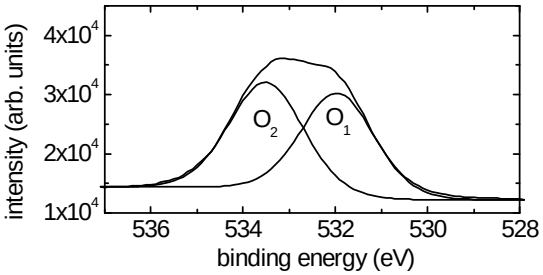












- Concentration of C_2 and C_3 remarkably decreased,
- Concentration of oxygen decreased
- O_1/O_2 ratio remained almost unchanged

oxygen is being removed as a whole O-C=O functional group

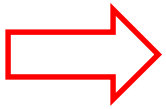
- Broadening of the peaks
- Shift of maxima of the peaks

each peak comes from more than one unique specie

XPS spectra of PET, PEN and PI

polymer	PET		PEN		PI		
component	C1s	O1s	C1s	O1s	C1s	O1s	N1s
non-treated	72,07	27,94	70,67	26,92	75,9	17,51	6,58
irradiated	80,23	19,77	82,16	17,85	82,92	12,31	4,77

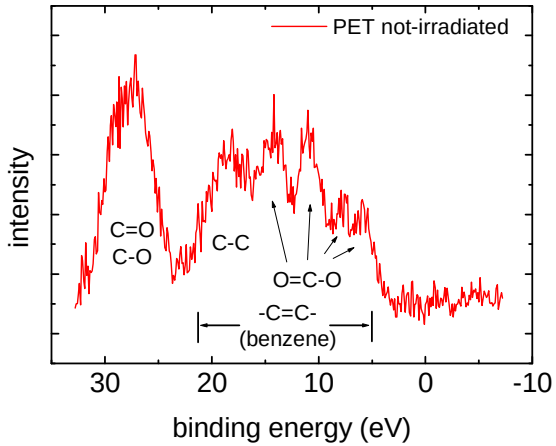
- Carbon enrichment in the near surface layer in all cases
- Concentration of O and N decreased



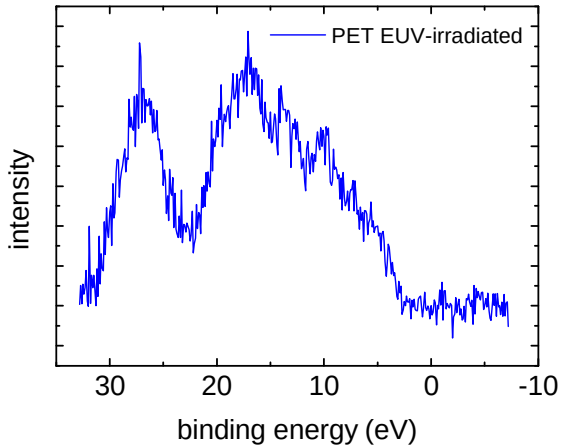
Changes in ablation and surface modification thresholds

XPS spectra of PET, PEN and PI

PET – valence XPS

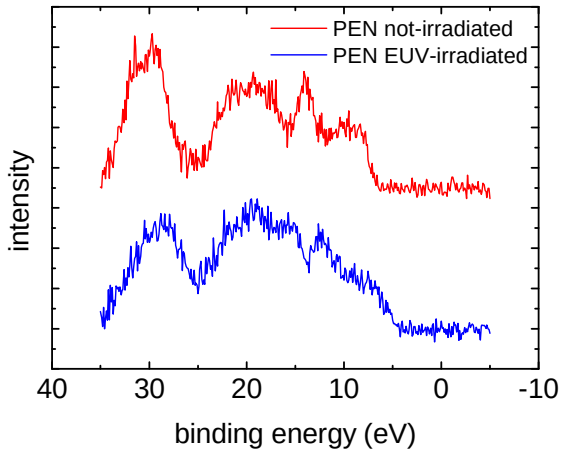


not-irradiated



EUV irradiated

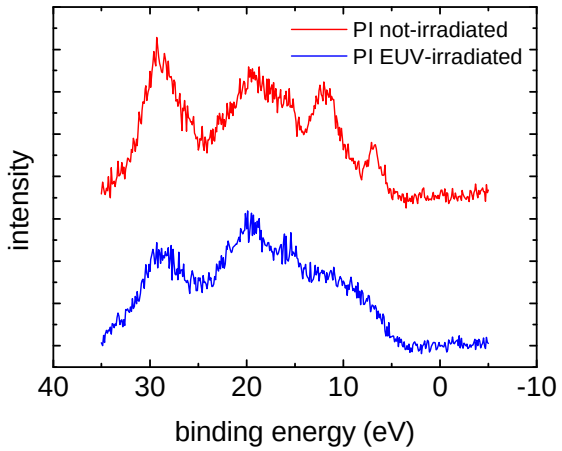
PEN – valence XPS



not-irradiated

EUV rradiated

PI – valence XPS



not-irradiated

EUV irradiated

Conclusions

- EUV source for surface modification was presented
- Parameters of the EUV source were measured
- morphology changes in selected polymers were presented
- chemical changes were proved
- results and interpretation of XPS measurements were presented

Acknowledgements

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