Micro- and Nanoprocessing of Organic Polymers using a Compact Laser Plasma EUV source

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OUTLINE

• INTRODUCTION
  - extreme ultraviolet (EUV)
  - laser plasma EUV sources

• LASER PLASMA EUV SOURCE BASED ON A GAS PUFF TARGET
  - gas puff target approach
  - compact laser plasma EUV source
  - EUV optics

• MICRO- AND NANOPROCESSING POLYMERS USING EUV
  - synchrotron
  - laser plasma EUV source

• SUMMARY
INTRODUCTION

• extreme ultraviolet (EUV)


• motivation
  - nanometer resolution
  - nanometer penetration depth in solids

• generation
  - e-tubes
  - synchrotrons, FELs
  - plasma sources (discharge plasmas, laser plasmas)

• applications
  - nanoelectronics (EUV lithography)
  - micro- and nanotechnology (metrology, microprocessing)
  - biomedical technologies (microscopy, radiation damage)
LASER-PRODUCED PLASMA

- Solid target
- Shock wave
- Cold plasma (~10 eV), high density (10^{22} cm^{-3})
- Hot plasma (100-1000 eV), low density (10^{20} cm^{-3})
- Expanded low density plasma
- Focused laser beam
  - Nd:glass
  - Nd:YAG
  - KrF
  - CO₂
  - 10^{11}-10^{14} Wcm^{-2}
  - 1-10 ns/0.1-10 J

Graph showing:
- \( \rho/\rho_s \) vs. \( T_e, K \)
- \( \rho_c \)
- Laser

\( \rho \) vs. \( \rho_s \)
LASER PLASMA SOFT X-RAY/EUV SOURCES

Laser plasma soft X-ray sources \((\sim 1 \text{ nm, } \sim 1 \text{ keV})\)

- **ns laser pulses**: \(10^{13}-10^{14} \text{ Wcm}^{-2}, 1-5 \text{ ns/1-10 J}\)
- **fs laser pulses**: \(10^{16}-10^{18} \text{ Wcm}^{-2}, 50-100 \text{ fs/5 mJ-500 mJ}\)

Laser plasma EUV sources \((\sim 10 \text{ nm, } \sim 100 \text{ eV})\)

- **ns laser pulses**: \(10^{11}-10^{12} \text{ Wcm}^{-2}, 5-10 \text{ ns/0.5-1 J}\)
- **ps laser pulses**: \(10^{14} \text{ Wcm}^{-2}, 1 \text{ ns/1 J}\)
- **ps laser pulses**: \(10^{16} \text{ Wcm}^{-2}, 1 \text{ ps/1 J}\)
- **fs laser pulses**: \(10^{16}-10^{18} \text{ Wcm}^{-2}, 50-100 \text{ fs/5 mJ-500 mJ}\)

High harmonics (attosecond pulses)
COST Action MP0601
“Short Wavelength Laboratory Sources”

Action Co-ordinator: Professor Alan Michette
King’s College London

WG1 – Modelling and Simulation
WG2 – Source Development, Improvement and Characterization
WG3 – Integrated Systems: Sources, Optics, and Detectors
WG4 - Applications

6th WG Meeting – May, 2008, Kraków

www.shortwavelengthsources.net
LASER PLASMA EUV SOURCE

- SOURCE CHARACTERISTICS
  - high single pulse brightness
  - short pulse duration
  - easy tuning of wavelength
  - low investment costs

- MAIN DISADVANTAGES
  - laser target operation
  - target debris production

Vacuum chamber
Laser system
Oscillator
Amplifier
Focusing lens
Target system
solid (rod, tape, wire),
liquid (jet, droplet)
Sample
GAS PUFF TARGET

- schematic of a gas puff target

P > 1 bar

nozzle

laser beam

~ 500 μm

- electromagnetic valve to form a gas puff target

- power supply

nozzle
diaphragm
coil
gas reservoir

1 cm

Patent Nr 172027
GAS PUFF TARGET CHARACTERIZATION

X-ray pulsed radiography with a laser-plasma x-ray source

Typical x-ray shadowgram

Nd:glass laser beam 1 ns/10 J
GAS PUFF TARGET APPLICATIONS

- generation x-ray and EUV radiation
- high-resolution spectroscopy of multiply-charged ions
- x-ray contact microscopy
- laser-gas puff target interactions (self-focusing)
- x-ray lasers

Limitations:
- nozzle degradation
- self-absorption in cold gas

Fiedorowicz et al. Laser and Particle Beams 12, 471 (1994)
Khakhalin et al., JOSA B 79, 1203 (1995)
DOUBLE-STREAM GAS PUFF TARGET

- schematic of a double-stream gas puff target

- electromagnetic valve system

- X-ray backlighting images

SOFT X-RAY EMISSION STUDIES

- Nd:glass laser (Institute of Optoelectronics, Warsaw)

- x-ray pinhole images of gas puff laser plasmas

- x-ray spectra measured with the crystal spectrograph

EUV EMISSION STUDIES

- KrF laser (Institute of Plasma Physics, Nieuwegein, The Netherlands)

Schematic of the experimental setup

EUV signals

Patent No.: US 6,469,310 B1
EUV EMISSION STUDIES

- Nd:YAG laser (Institute of Laser Engineering, Osaka, Japan)

Schematic of the experimental setup

EUV spectra
EUV EMISSION STUDIES

EUV emission from a double-stream xenon/helium gas puff target irradiated with a Nd:YAG laser (0.5J/10ns)

ILE, Osaka
IOE, Warsaw

- Elimination of debris
- Operation with repetition
- Conversion efficiency improvement

LASER PLASMA EUV SOURCE

EUV spectrum

CE at 13.5 nm ~ 1.5 %
LASER-PLASMA EUV SOURCE

- a compact laser-plasma EUV source based on a gas puff target for metrology applications
EUV METROLOGY

- characterization of Mo/Si multilayer mirrors
- degradation of Mo/Si multilayer mirrors irradiated with EUV pulses

Collaboration with IOF, Jena, Germany

Collaboration with REFLEX s.r.o. Prague, Czech Republic
various techniques, including chemical and plasma etching, e-beam and ion-beam writing, photolithography, thin film deposition, and laser ablation, are used to produce mechanical or electromechanical parts in micro- or nanoscale from polymers, however, some polymers (i.e. PTFE) require special techniques for microprocessing,

so far, for microprocessing of PTFE the laser ablation techniques using UV lasers and ultrashort pulse lasers has been applied, however, it was difficult to make microparts with sub-micron structural accuracy and a high aspect ratio (the ratio of the depth and the pattern width),

it was demonstrated that direct photo-etching using synchrotron radiation (SR) can be applied in high aspect ratio microprocessing of PTFE.
Direct photo-etching of polymers with synchrotron radiation – a single photon carries enough energy to break any chemical bond and create small fragments of a polymer chain. Similar to photo-etching with UV light (UV laser ablation).

Synchrotron Aurora:
- electron energy: 575 MeV
- critical wavelength: 1.5 nm
- $3 \times 10^{17}$ ph/s/cm$^2$ at a sample surface

Non-thermal ablation of PTFE demonstrated:
- ablation depth: 240 μm
- aspect ratio: 11

Advantages:
- dry process
- soft x-ray radiation preferred (opposit to LIGA process) and no high-contrast masks required

PHOTO-ETCHING WITH SYNCHROTRON

High Aspect Ration Micromachining of PTFE (Teflon)

UVSOR at the Institute for Molecular Science, Okazaki National Research Institute, Japan.

- 1-mm-thick Teflon
- aspect ratio: 50
- 10 nm wavelength

M. Inayoshi, M. Ito, M. Hori, T. Goto, M. Hiramatsu,
Synchrotron CAMD Louisiana State Univ:
- electron energy: 1.5 GeV
- critical energy: 2.5 keV
- integrated power density 35 mW/horizontal cm

X-ray ablation of heated Teflon

Non-thermal x-ray ablation of PTFE demonstrated:
- ablation rate: 40μm/h
- strong temperature dependent
- photochemical changes of x-ray irradiated samples

M. Feldman, G. S. Lee, D. Noel, C. Khan Malek, R. Bass
PRAGUE ASTERIX LASER SYSTEM (PALS)

PALS, Prague

Soft X-ray emission studies

- Photoemission experiments
- Transmission grating spectrograph
- Vacuum chamber
- Valve system with double nozzle
- PALS laser
- Silicon photodiode
- Silicon photodiode

$E_L = 700 \text{ J}$
$\tau_L = 0.5 \text{ ns}$

J. Alloys & Compounds (2005)
SOFT X-RAY EMISSION FROM NITROGEN

PALS, Prague
IOE, Warsaw
APU, Remagen

$5 \times 10^{15}$ photons at 2.5 nm measured for laser energy 540 J

CCD camera readout

$24 \times 10^{15}$ photons at 2.5 nm measured for laser energy 540 J
SOFT X-RAY EMISSION FROM XENON

Soft X-ray spectrum for xenon/helium gas puff target irradiated with the PALS laser

X-ray emission measured with the silicon photodiode

- 0.5 nm 10 J 2%
- 1-2 nm 160 J 30%
- 3-7 nm 160 J 30% (?)
Depth profiles of the structures formed by X-ray photo-etching using LPXS

Ablation depth vs sample-source distance

X-ray ablation with multiple exposition

PHOTO-ETCHING USING LASER PLASMA EUV SOURCE

EUV spectra

EUV

Micro-grid

Polymer sample
X-ray fluence \(\sim 2-3 \text{ mJ/cm}^2/\text{shot}\)  
10 min exposition time

- Kr/Ar gas puff target, \(T=200^\circ\text{C}\)
- Xe/Ar gas puff target, \(T=200^\circ\text{C}\)
- Xe/He gas puff target, \(T=100^\circ\text{C}\)
- Xe/He gas puff target, \(T=200^\circ\text{C}\)

**Strong dependence on temperature**

[Graph showing etching depth vs. temperature for Xe/He and Xe/Ar targets]
Ellipsoidal mirror with Mo/Si coating

18 mJ/cm² at 13.5 nm for xenon

Collaboration with REFLEX s.r.o. Prague, Czech Republic (substrate) and IOF, Jena, Germany (multilayers)
Grazing incidence „lobster eye” multifoil mirror system

Two orthogonal stacks of ellipsoidal mirrors forming a double-focusing device. The ellipsoidal surfaces are covered by a layer of gold that has relatively high reflectivity at the wavelength range between 8-20 nm up to about 10 degrees of an incidence angle.

> 20 mJ/cm² for xenon

Collaboration with the Czech Technical University and Reflex s.r.o., Praha
EUV OPTICAL SYSTEM

Grazing incidence axisymmetrical ellipsoidal mirror

Spectrum of radiation from Xe target focused with the EUV collector

> 30 mJ/cm²

Au, Mo coated

Collaboration with RITE, Prague (former Reflex s.r.o)
EUV PROCESSING SETUP

Gas targets:
Xe/He
Kr/He,
(Kr+10%Xe)/He

Ellipsoidal collector

Focal plane

Irradiated sample

Distance

Motorized XYZ translation stage
PHOTO-ETCHING POLYMERS USING LASER PLASMA EUV SOURCE

High-aspect microstructuring polymers using EUV optics

50 μm PTFE foil
Exposition time 4 min. (40μm/h for CAMD)

front side  back side

X-ray fluence ~20-30 mJ/cm²/shot
Formation of granular (conical) microstructures

PTFE

with optics
Cone Formation Si₃N₄ Ceramics  - Institute of Applied Physics, University Linz, Austria

KrF laser

Macromolecules 1996, 29, 6301-6309
T. Lippert,*,† T. Nakamura, H. Niino, and A. Yabe

ArF*-laser, $\lambda = 193 \text{ nm}$

$\phi \approx 1.2 \text{ J/cm}^2$

N = 500

Inhomogeneities $\Rightarrow$ shadowing $\Rightarrow$ Cones

# EUREKA PROJECT E!3892- EULASNET II MODPOLEUV

## 1. General description

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<th>Project</th>
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<td>Title</td>
<td>Modification Of Polymer Foils With Euv (Extreme-Ultra-Violet) Radiation For Applications In Biomedical Technology</td>
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**Summary:**

New Methods And Techniques For Modifying Polymer Foils To Improve Their Bio-Functions Using Extreme Ultraviolet (Euv) Radiation From Laser Plasma Light Sources Which Will Be Developed During The Project For Biomedical Technology.

Institute of Applied Physics, Linz
Institute of Optoelectronics, Warsaw
Institute of Biophysics, Linz
REFLEX s.r.o, Prague
LASER PLASMA EUV SOURCE

Nd:YAG laser

Ellipsoidal EUV collector

Lens

Diaphragm for differential pumping

Gas puff valve
EUV photo-etching polymers

Smooth ablation accompanied by cones formation, 2 min irradiation, 10 Hz
SEM images

Polymer foils from Goodfellow, 50 µm thickness

Suggested explanations for cones formation:

• shielding by impurities,
• carbon enrichment
• local shift of the ablation threshold,

Polytetrafluoroethylene, PTFE

Fluorinated ethylene – propylene, FEP

Poly (methyl methacrylate), PMMA
EUV photo-etching polymers

SEM images of strongly modified surfaces with conical structures, 10 Hz EUV irradiation. Dashed yellow lines indicate borders between zones of different structures.

poly(ethylene terephthalate), PET

Structure coming probably from relaxation of frozen stress fields

Polyimide, PI

Higher fluence | Lower fluence
Conical structures details

Differences in the conical structures connected with EUV fluence shown for two kinds of polymers: poly(ethylene terephthalate) and polyimide.

Peeling of thin films covering the cone

Traces of a layered structure indicating dry photo-etching
Wavelength dependence

PMMA, 1 min, 10 Hz exposure

Kr plasma, 140 nm Zr filter

Kr plasma, 150 nm Al filter

FEP, 2 min, 10 Hz exposure
Wavelength and EUV dose dependence

Transition from smooth ablation with cones formation to a non-uniformly swelled structure in PMMA irradiated through an Al filter. No such transition with Zr filter.

Structure of the whole irradiated areas for increasing radiation dose

Microstructures in central part of the irradiated areas
Polymethyl methacrylate (PMMA)

SEM images of PMMA irradiated in the focal plane of Mo coated ellipsoidal collector, Xe plasma radiation, repetition rate 10 Hz

1 min exposure

2 mm

10 μm

2 min exposure

2 mm

2 μm

2 μm

10 μm
Polymethyl methacrylate (PMMA)

SEM images of PMMA irradiated in behind the focal plane of Mo coated ellipsoidal collector, Xe plasma radiation, 1 min exposure, repetition rate 10 Hz

8 mm behind a focal plane

12 mm behind a focal plane

2 mm

10 μm

2 μm

36
Polyvinyl fluoride (PVF)

SEM images of PVF irradiated in and out of the focal plane of Mo coated ellipsoidal collector, Xe plasma radiation, 1 min exposure, repetition rate 10 Hz
Polyvinyl fluoride (PVF)

SEM images of PVF irradiated 3 mm behind the focal plane of Mo coated ellipsoidal collector, Xe plasma radiation, repetition rate 10 Hz

5 s exposure

10 s exposure

30 s exposure
Polystyrene (PS)

SEM images of PS irradiated in the focal plane of Mo coated ellipsoidal collector, Xe plasma radiation, repetition rate 10 Hz

1 min exposure

2.5 s exposure
Polystyrene (PS)

SEM images of PS irradiated behind the focal plane of Mo coated ellipsoidal collector, Xe plasma radiation, 10 s exposure, repetition rate 10 Hz

3 mm behind a focal plane

5 mm behind a focal plane
Polyethylene terephthalate (PET)

SEM images of PET irradiated in the focal plane of Mo coated ellipsoidal collector, Xe plasma radiation, repetition rate 10 Hz

1 mm exposure

2 min exposure

500 μm
Polyethylene terephthalate (PET)

SEM images of PET irradiated behind the focal plane of Mo coated ellipsoidal collector, Xe plasma radiation, repetition rate 10 Hz

Central part

Close to an edge of the focal spot

1 min exposure

30 s exposure

10 s exposure
Sodium Chloride (NaCl)

SEM images of NaCl irradiated in the focal plane of the multifoil collector, Xe plasma radiation, 4 x 2 min exposure, repetition rate 10 Hz
Germanium (Ge)

AFM images of Ge irradiated in the focal plane of Au coated ellipsoidal collector, Kr+10%Xe plasma radiation, repetition rate 10 Hz

2 min exposure
3 x 1 min exposure
2 x 2 min exposure
Laser plasma EUV source for modification polymer surfaces – preliminary design

Dia 350 mm

600 mm
CONCLUSIONS

• laser-plasma EUV source based on a laser-irradiated gas puff target have been introduced,

• compact laser-plasma EUV source was developed,

• EUV optical systems were presented,

• microprocessing polymers using a laser plasma EUV source was demonstrated
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