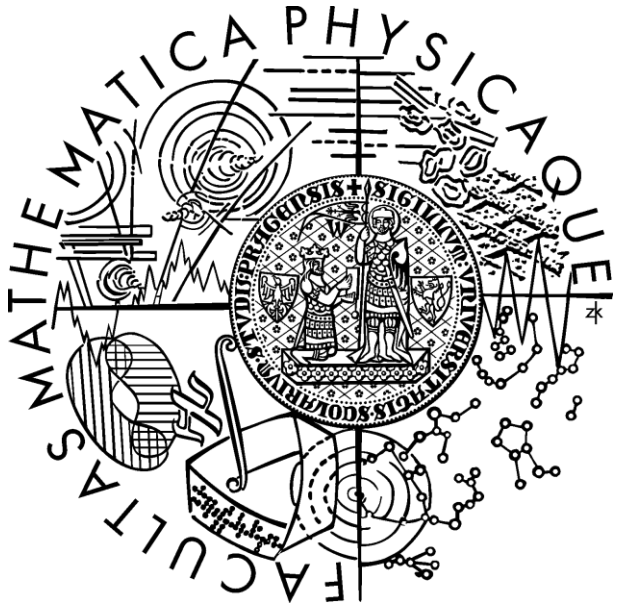


Low-temperature plasma for production of nanoscale dispersed solids

A. Choukourov, J. Hanus, J. Kousal, O. Kylian, P. Solar, O. Polonskyi, A. Shelemin, M. Vaidulych, D. Nikitin, A. Kuzminova, D. Slavinska, H. Biederman

Charles University
Faculty of Mathematics and Physics
Department of Macromolecular Physics

choukourov@kmf.troja.mff.cuni.cz

Outline

- Gas Aggregation cluster Source (GAS)

- Metallic NPs

  Pt, Au, Ag, Ti, Al, Cu

- NPs of plasma polymers

  C:H, Si:C:H:O, nylon-sputtered, PTFE-sputtered

- NP-based nano-composite coatings

- 2D nanoislands of plasma polymers

- Glancing Angle Deposition (GLAD)

- Conclusions

Charles University in Prague

Founded on April, 7, 1348 by Charles IV

First building,Karolinum, 1383
by Wenceslaus IV

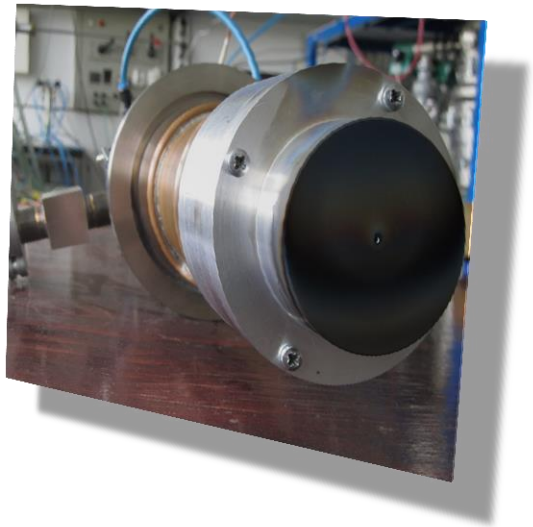
Charles University in Prague

Faculty of Mathematics and Physics
Department of Macromolecular Physics
Group of Plasma Polymer Physics

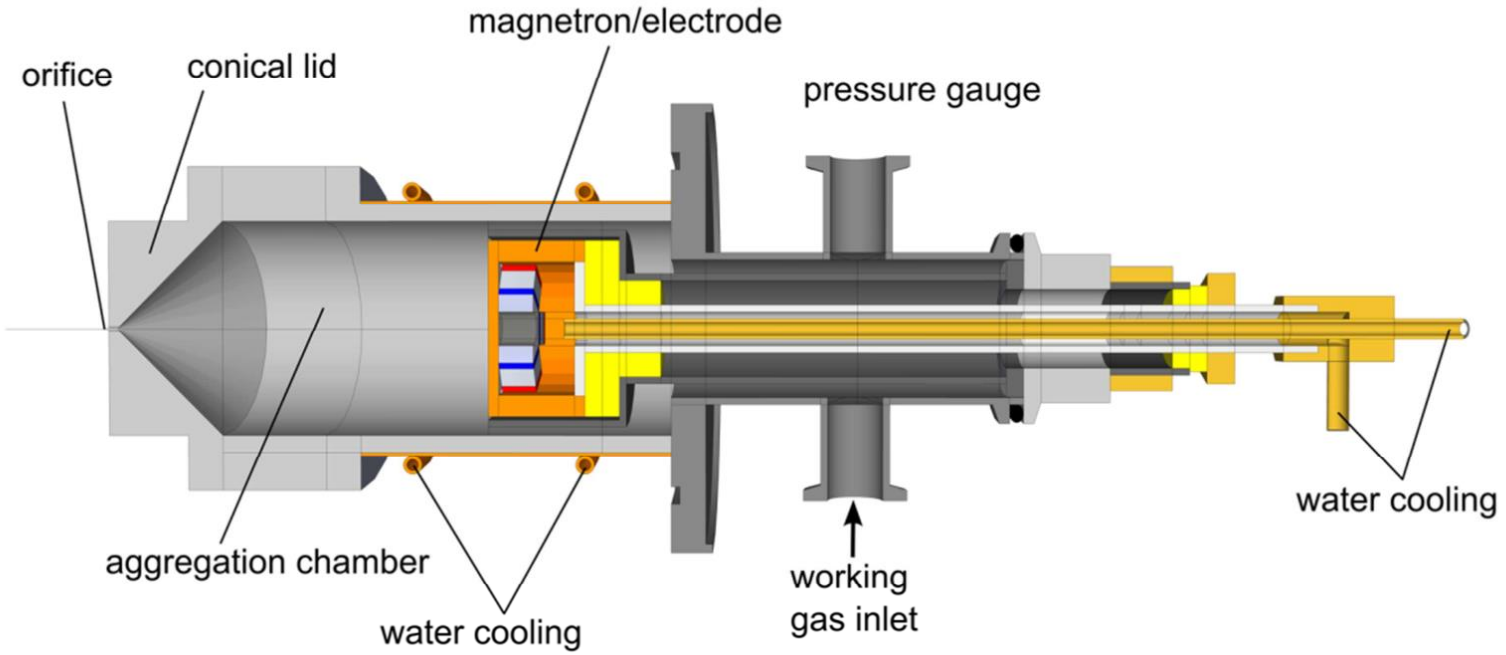
Main research activities:

- Fundamental research on nano-structuring of surfaces including fabrication of metallic and plasma polymerized nanoparticles

- Development of different vacuum based sources of nanoparticles



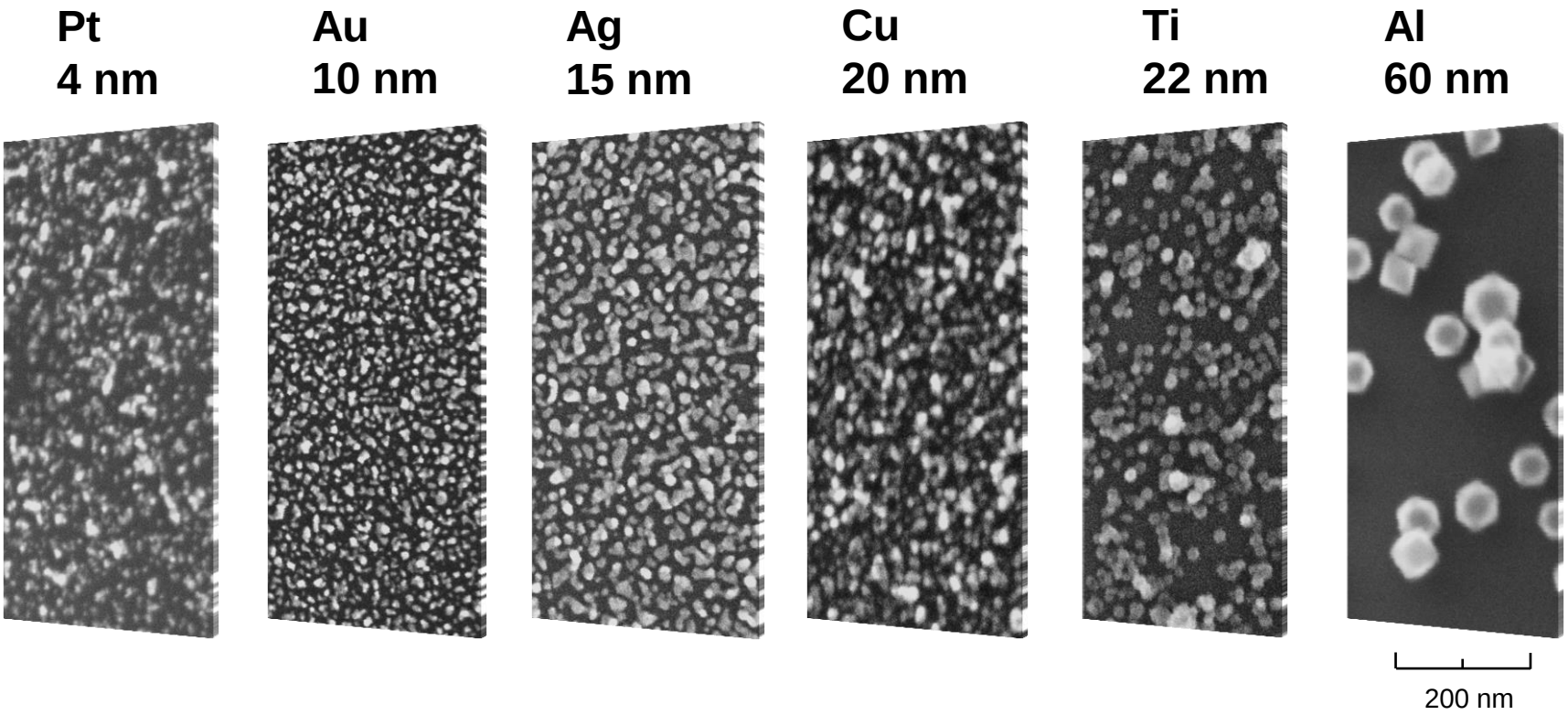
Simple Gas Aggregation cluster Source (GAS)



+ simple
+ possibility to control independently size and number of nanoparticles

inspired by:
H. Haberland et al., J. Vac. Sci. Technol. A 10 (1992) 3266.

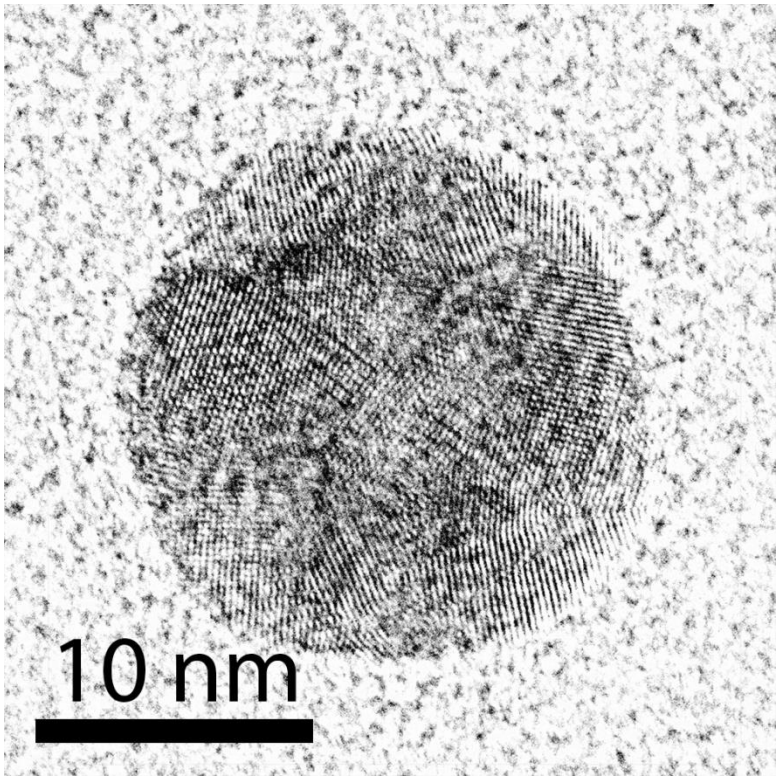
Metallic NPs



We are able to produce a wide range of metallic NPs by GAS.

Solar et al. Surface Coat. Technol. 2011, 205, S42
Drabik et al., Plasma Proces Polym, 2011, 7, 544
Kylian et al., Material Letters 2012, 79, 229
Polonskyi et al., J. Phys D. Appl. Phys. 2012, 45, 495301

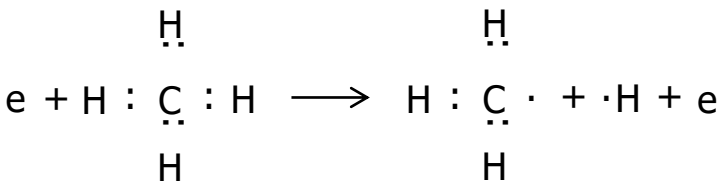
Ag NPs



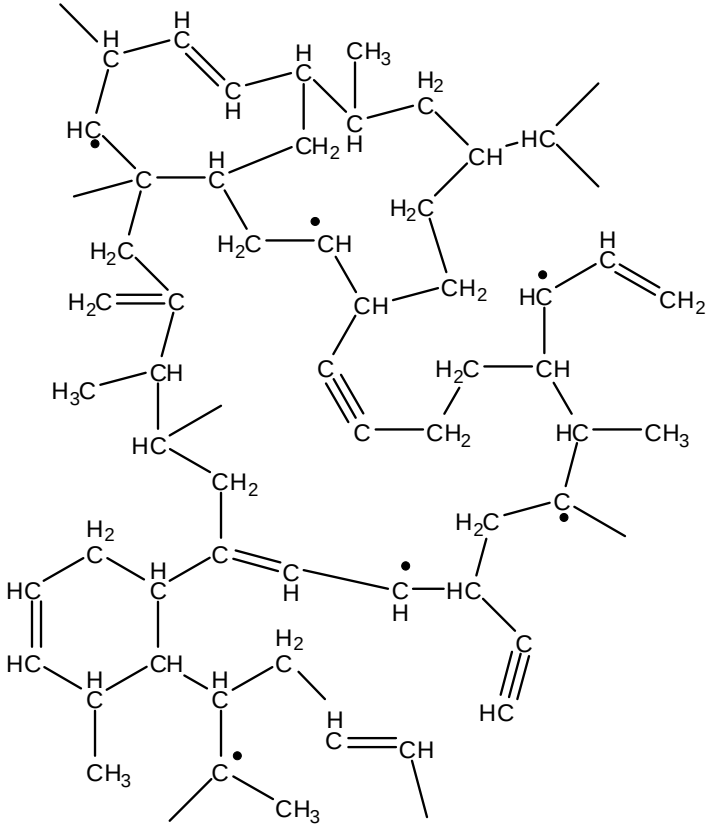
Solar et al. Surface Coat. Technol. 2011, 205, S42
Drabik et al., Plasma Proces Polym, 2011, 7, 544
Kylian et al., Material Letters 2012, 79, 229
Polonskyi et al., J. Phys D. Appl. Phys. 2012, 45, 495301

NPs of plasma polymers

Dissociation by electron impact



conventional poly(ethylene)



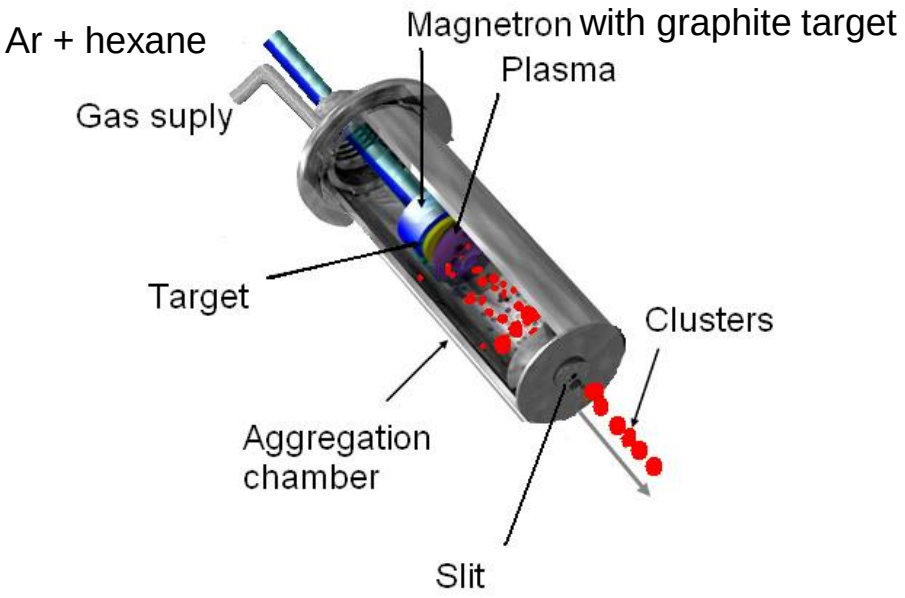
Scheme of a hydrocarbon plasma polymer
(Tibitt, Yasuda)

Glow discharge at low pressure (<100 Pa)
high MFP, low collision rates→heterogeneous growth is favoured→**thin films**

With rising pressure (>1oo Pa), powder formation occurs and the ‘‘polymer’’ formation is located in the gas phase → **NPs**

NPs of plasma polymers

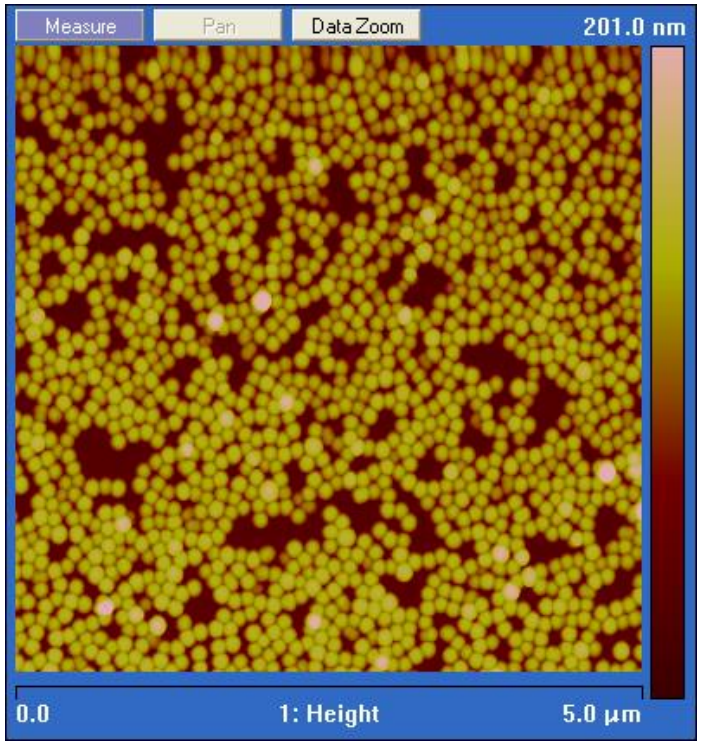
C:H plasma polymer NPs



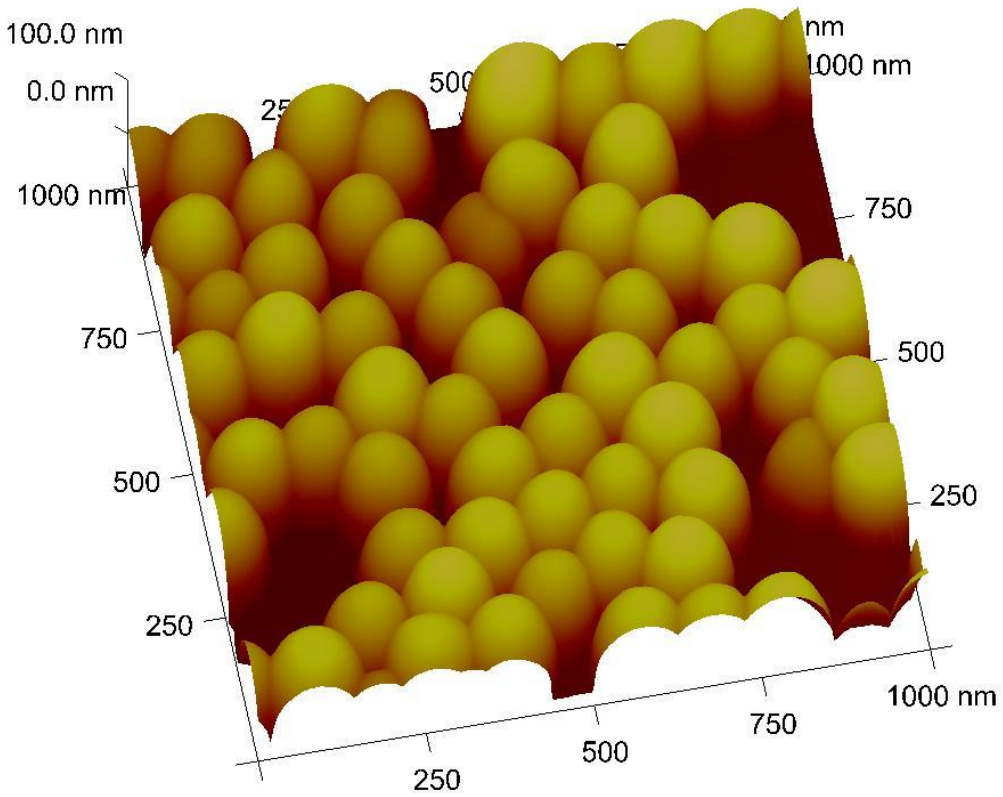
NPs of plasma polymers

C:H plasma polymer NPs

AFM top view



AFM 3D view



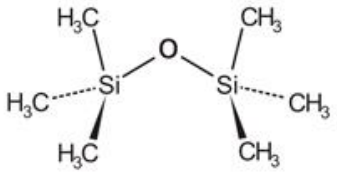
∅100 nm

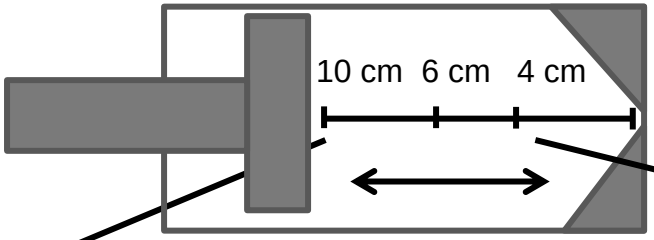
Pressure in the cluster source
Ar – 130 Pa, hexane – 30 Pa;
Power of discharge – 100W;
Time of deposition – 10 min.

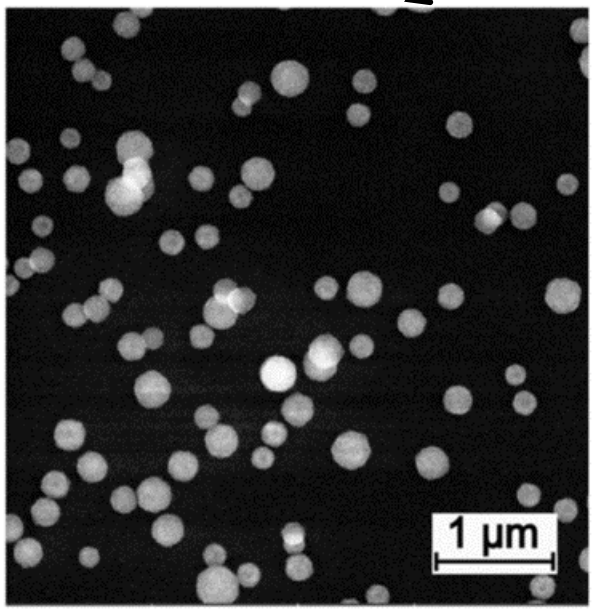
P. Solař, et al., Surf. Coat. Technol., ***205****, S42-S47, 2011*

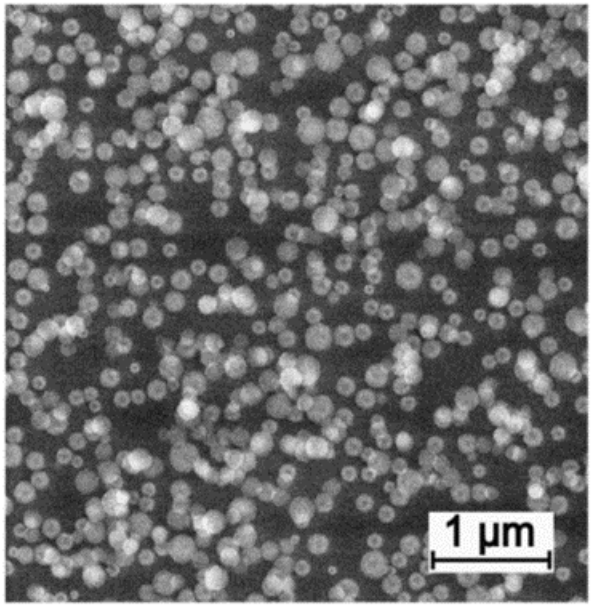
NPs of plasma polymers

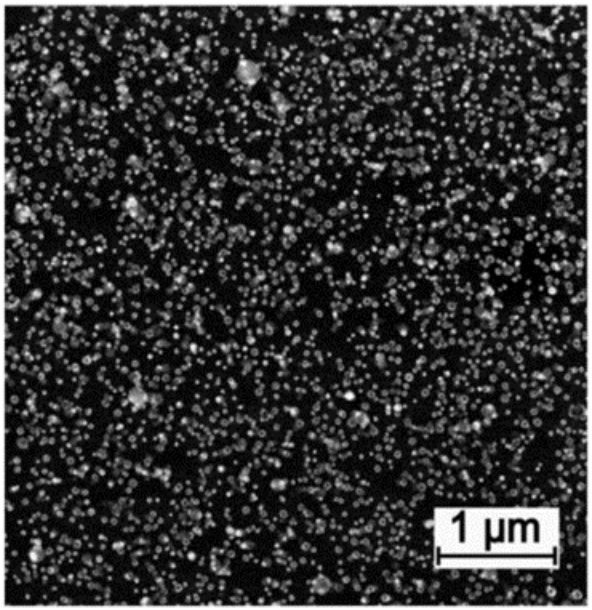
HMDSO plasma polymer NPs











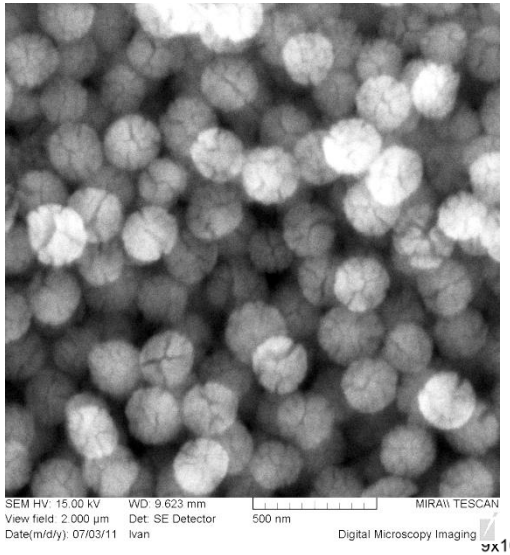
a) b) c)

SEM images of ppHMDSO NPs deposited at different aggregation lengths. a) 10 cm b) 6 cm and c) 4 cm. Pressure is 45 Pa, the power is 30 W.

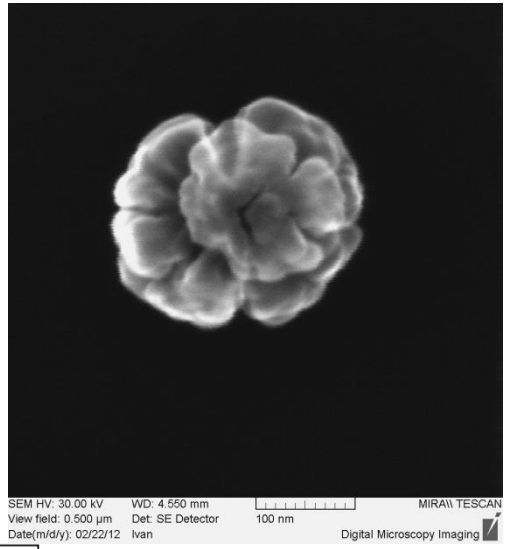
A. Shelemin, et al., J. Phys. D, 2016 accepted

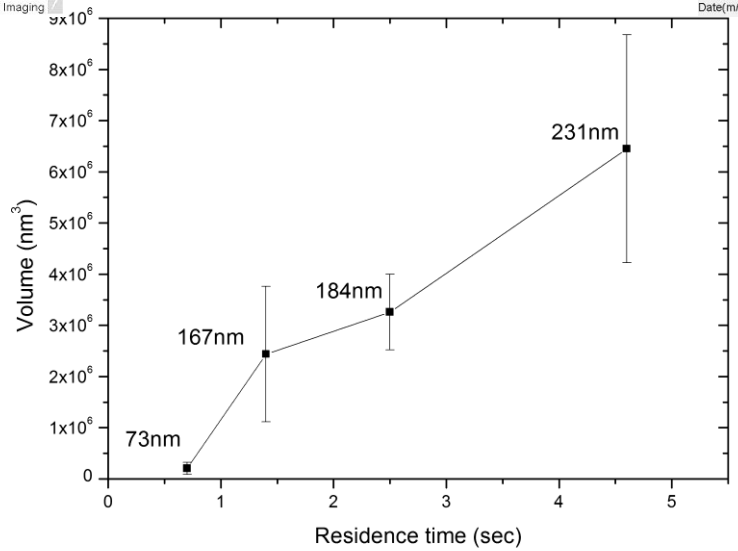
NPs of plasma polymers

nylon-sputtered plasma polymer



We are able to adjust the size of NPs by changing their residence time in the GAS.

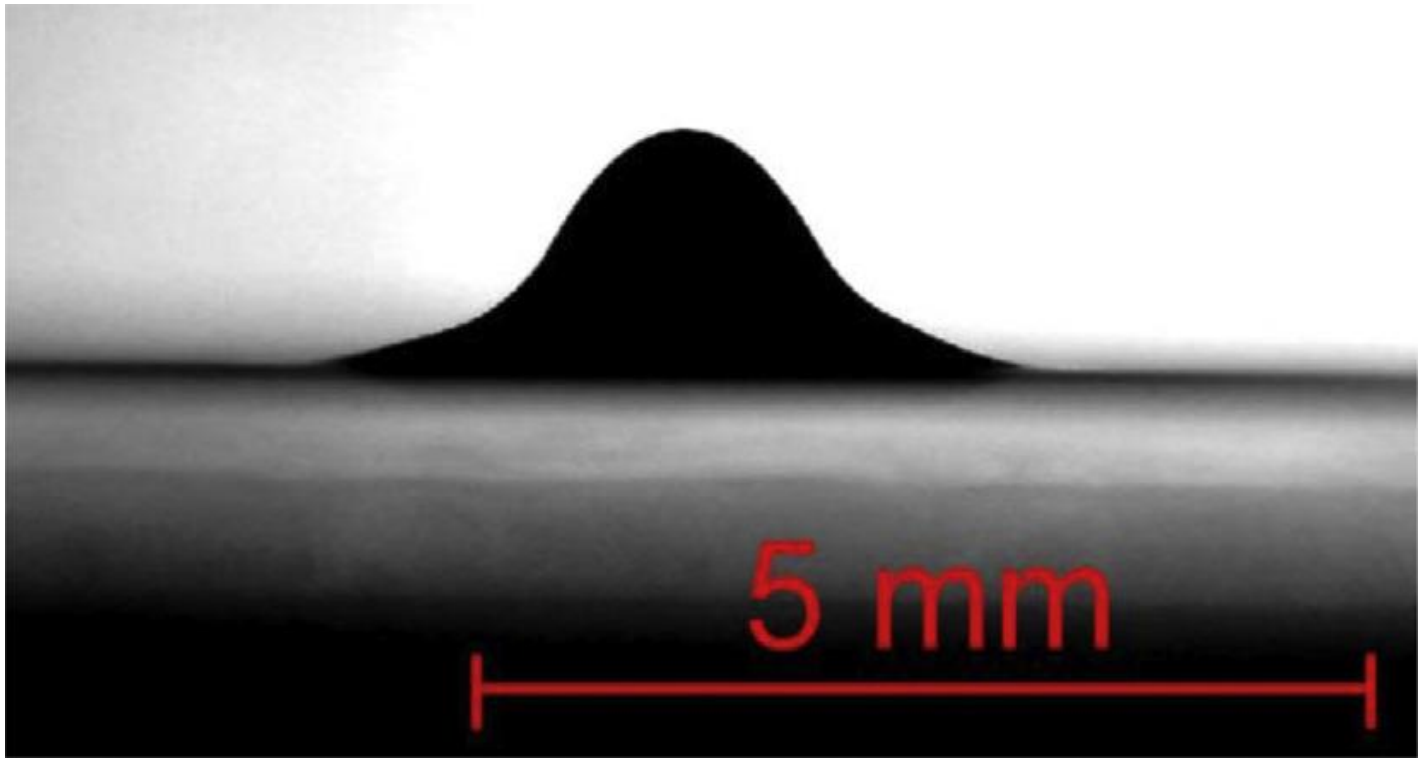




O. Polonskyi, et al., J. Phys. D, 45 (2012) 495301.

NPs of plasma polymers

nylon-sputtered plasma polymer

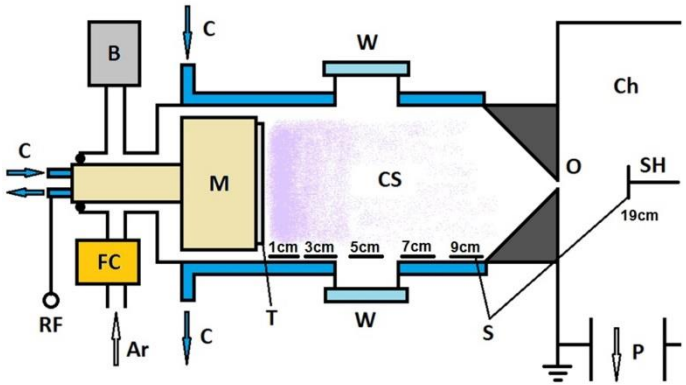


The side view of the macroscopic deposit of the nylon-sputtered particles deposited for 20 min

P. Solar, et al., Vacuum, 111 (2015) 124.

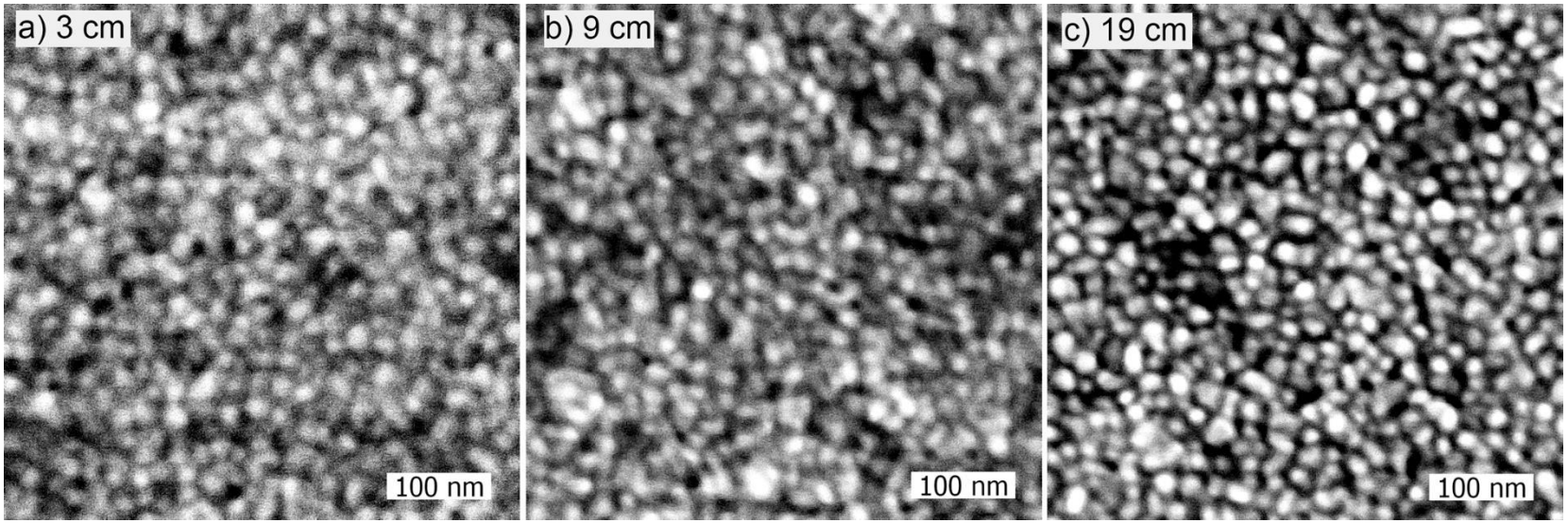
NPs of plasma polymers

PTFE-sputtered plasma polymer



A. Serov, et al., Surf. Coat. Technol., 254 (2014) 319.

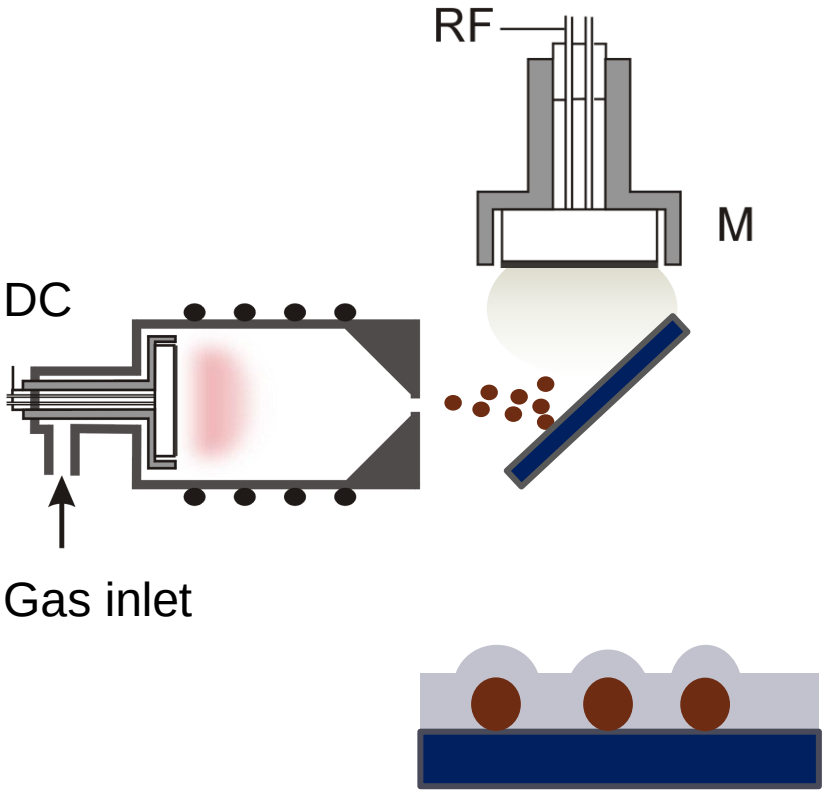
NPs are formed in vicinity of the magnetron and then get transported by the gas flow without changing their 20-30 nm size.



SEM images of PTFE-sputtered NPs

Nano-composites

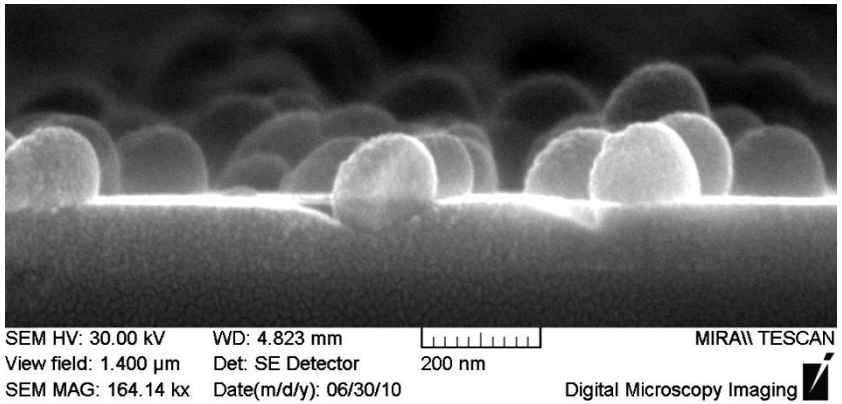
Embedding of NPs into plasma polymers



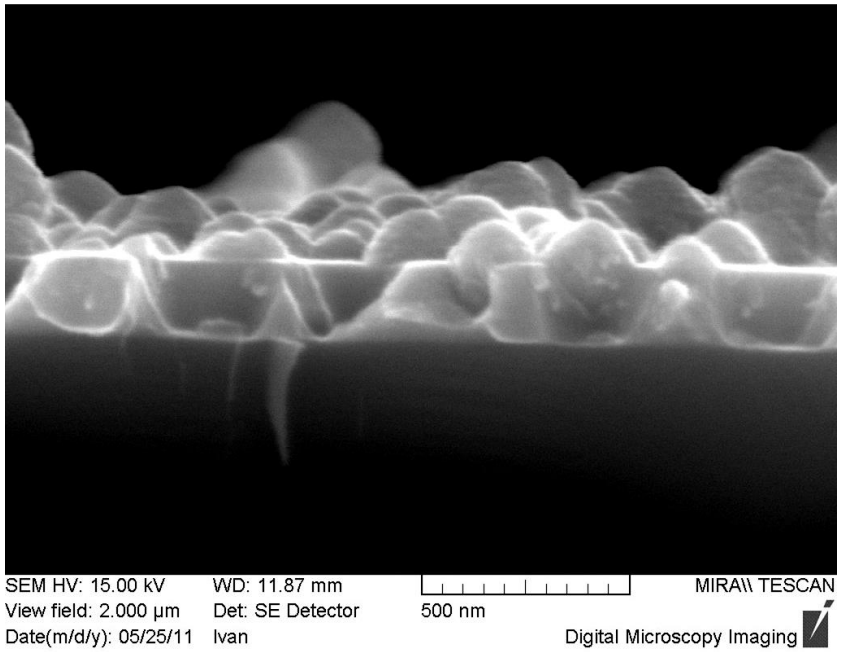
Nano-composites

C:H NPs overcoated by different films

C:H plasma polymer particles overcoated with a C:H plasma polymer matrix



C:H plasma polymer particles overcoated with Ti

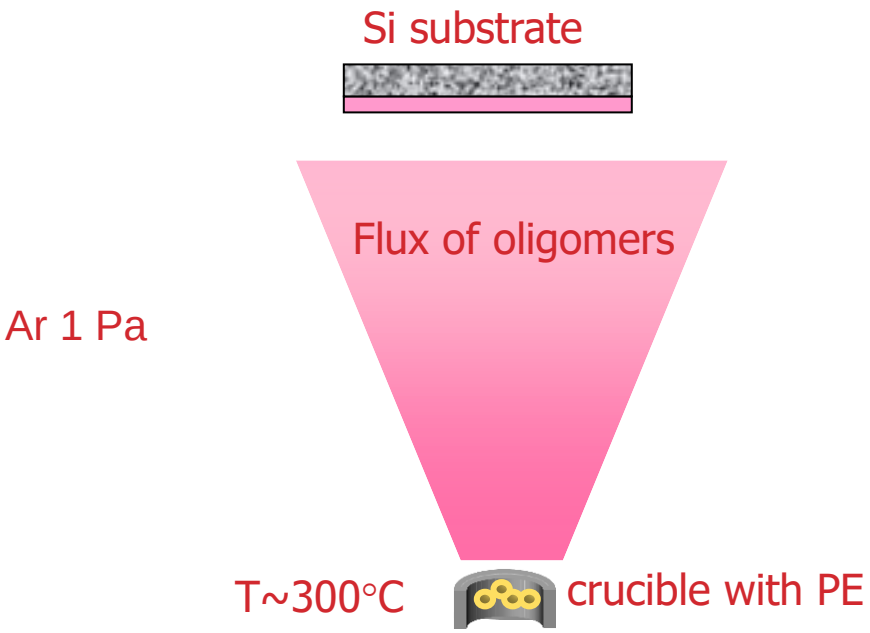


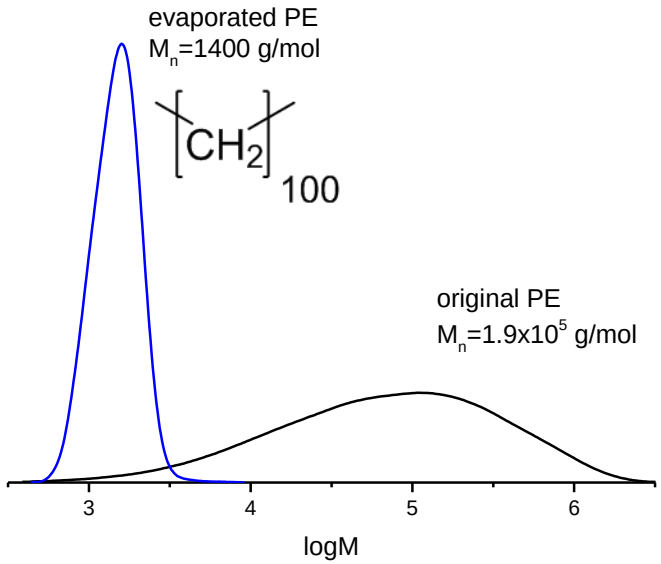
Independent control of surface roughness and chemistry

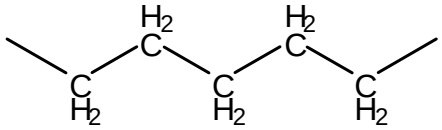
Plasma-Assisted Vapor Phase Deposition

2D nano-islands of plasma polymers

Vapor Phase Deposition of polyethylene (PE) over Si





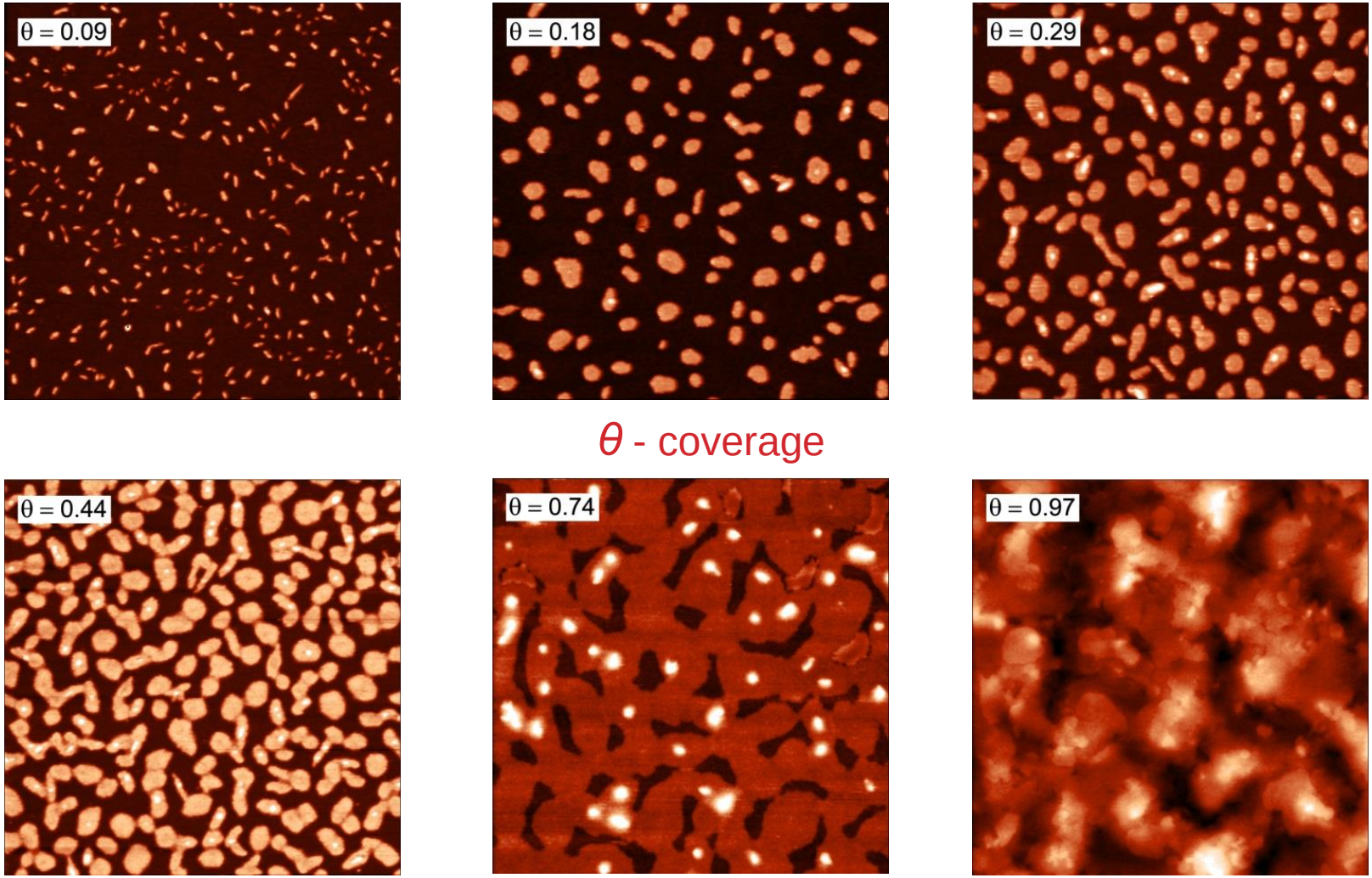


Melnichuk et al., Appl. Surf. Sci. 351 (2015) 537

Vapor Phase Deposition of polyethylene (PE) over Si

no plasma

The AFM height images (5x5 μm) of the films prepared by PVD of PE on Si without activation by the plasma in dependence on deposition time

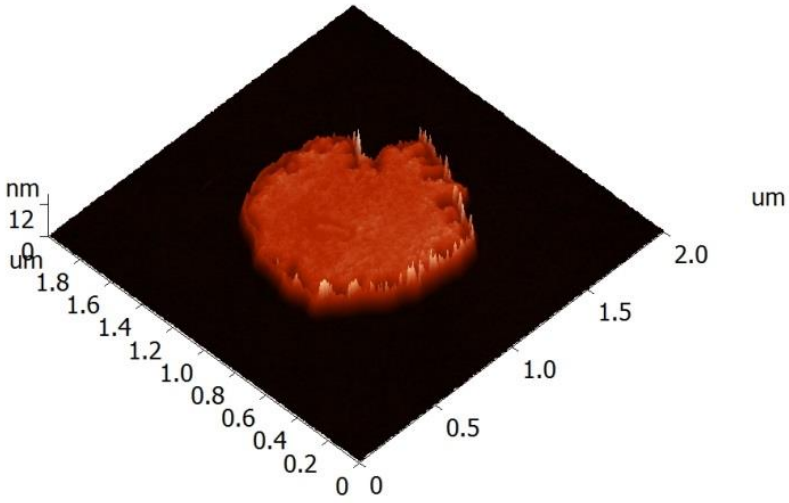


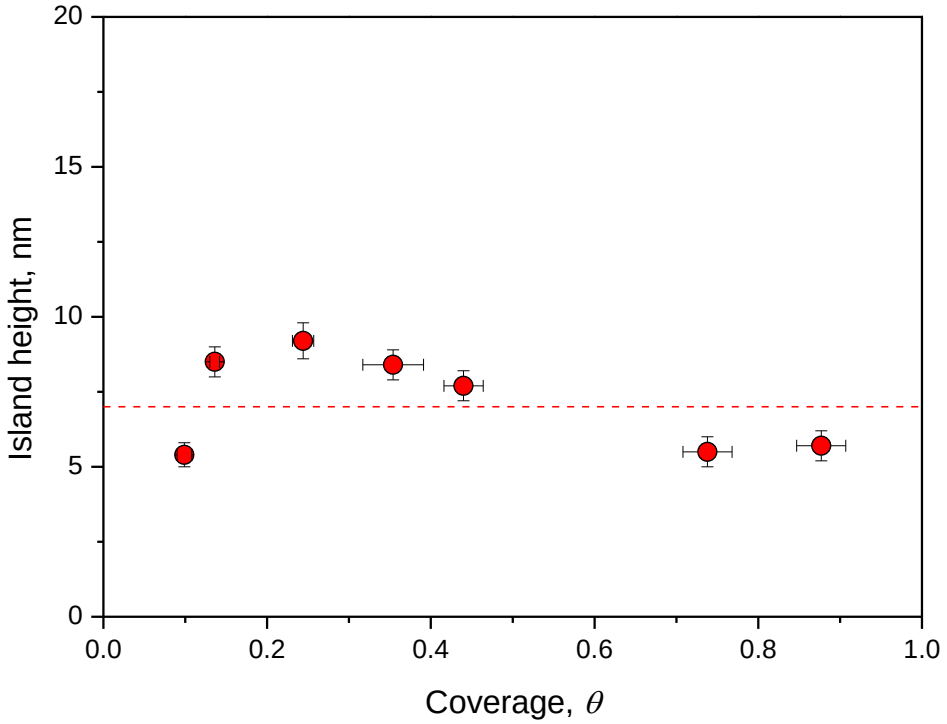
θ - coverage

Vapor Phase Deposition of polyethylene (PE) over Si

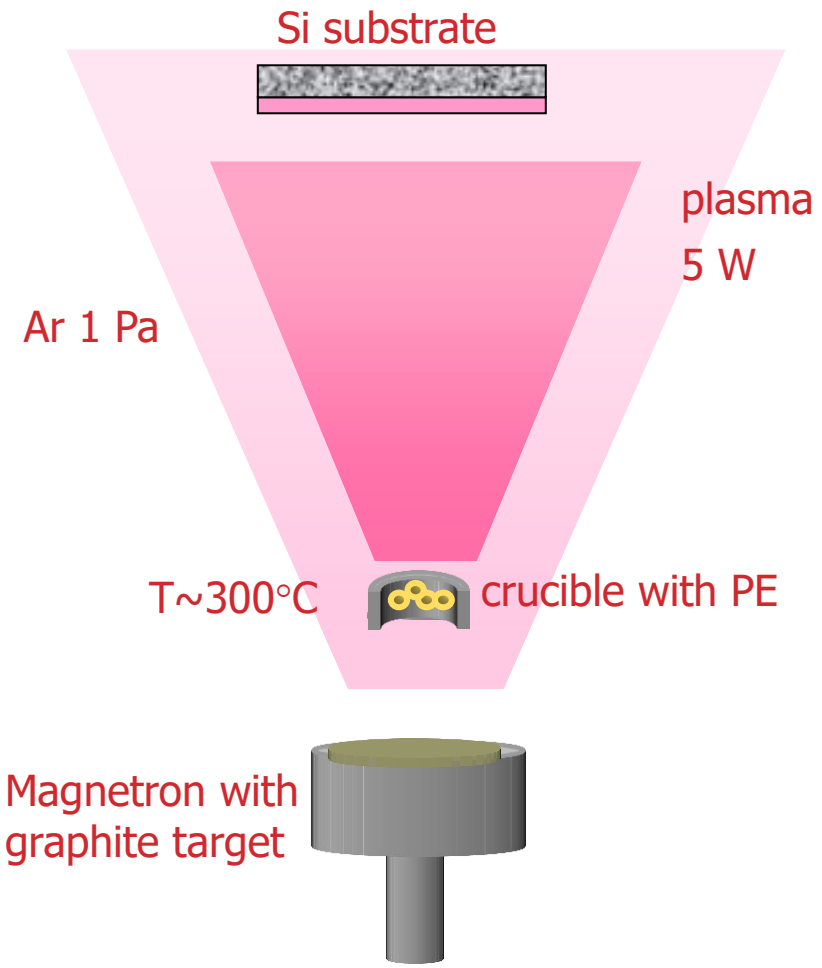
no plasma

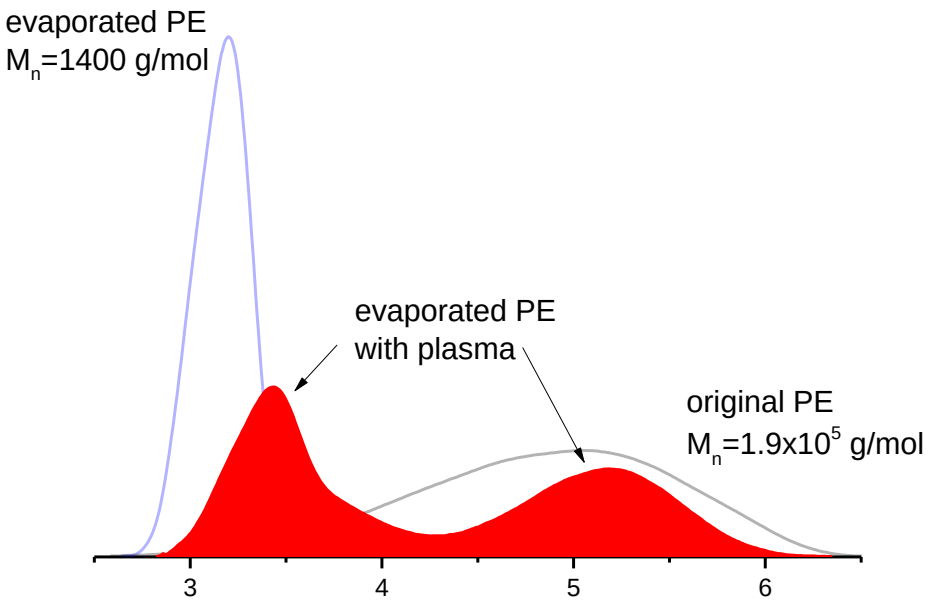
Thickness of islands stays constant at 7 nm; 2D growth





Plasma-Assisted Vapor Phase Deposition of PE



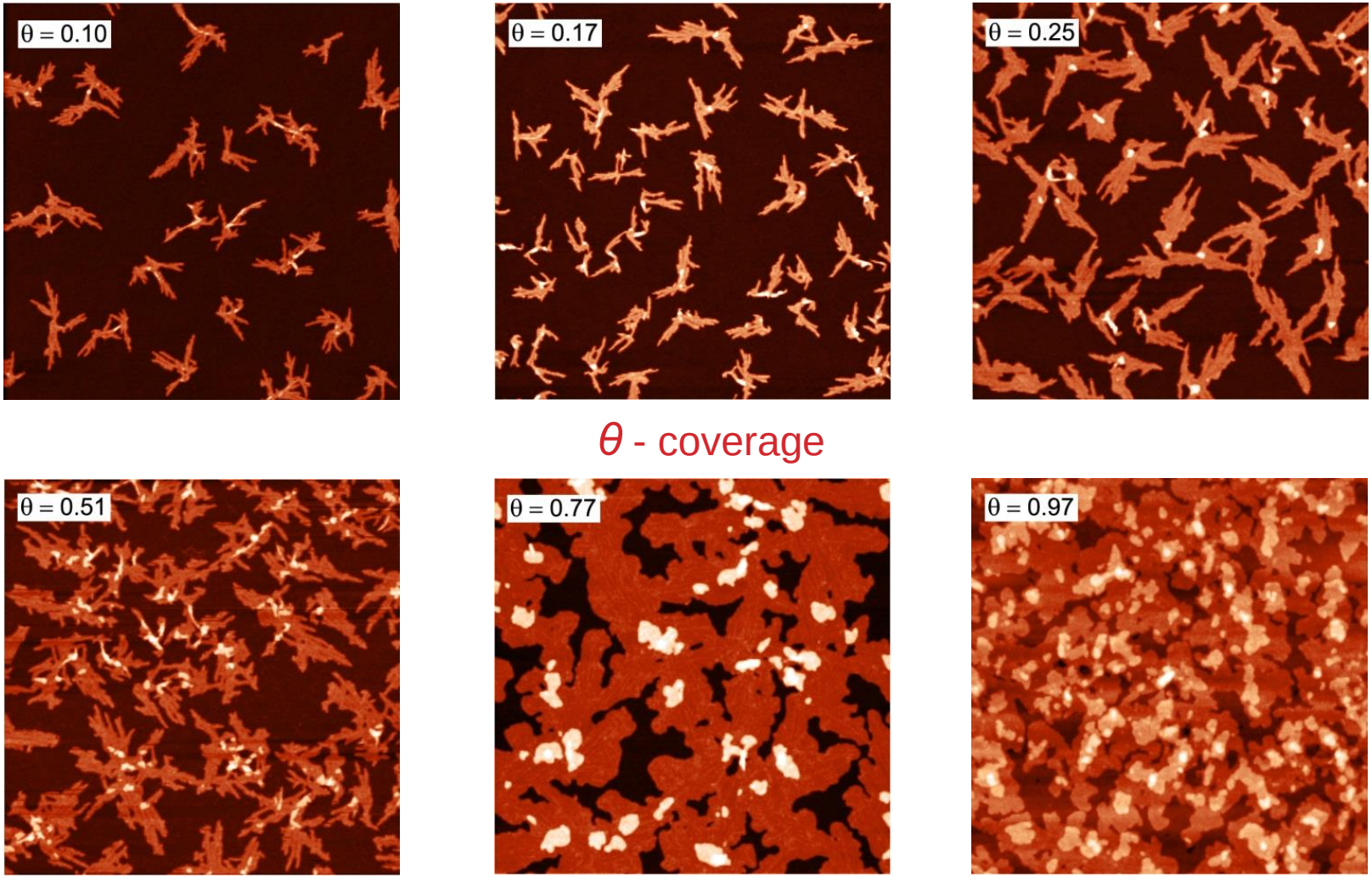


Radical-induced re-polymerization on the surface

Plasma-Assisted Vapor Phase Deposition of PE

5W plasma

The AFM height images (5x5 μm) of the films prepared by PVD of PE on Si with activation by the 5 W plasma in dependence on deposition time

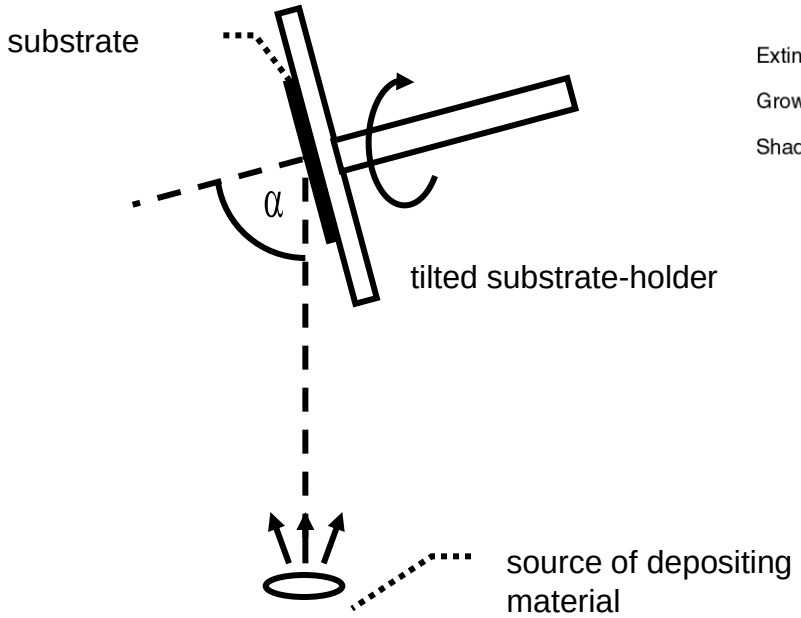


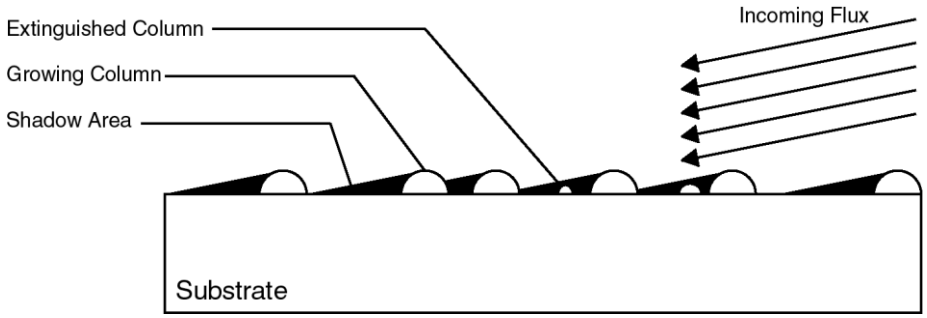
θ - coverage

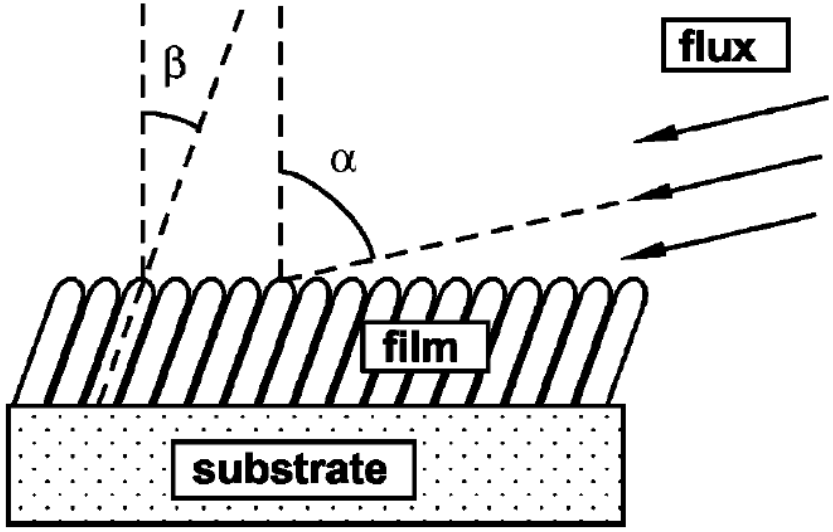
GLAD

Nanostructured thin films by Glancing Angle Deposition (GLAD)

GLAD







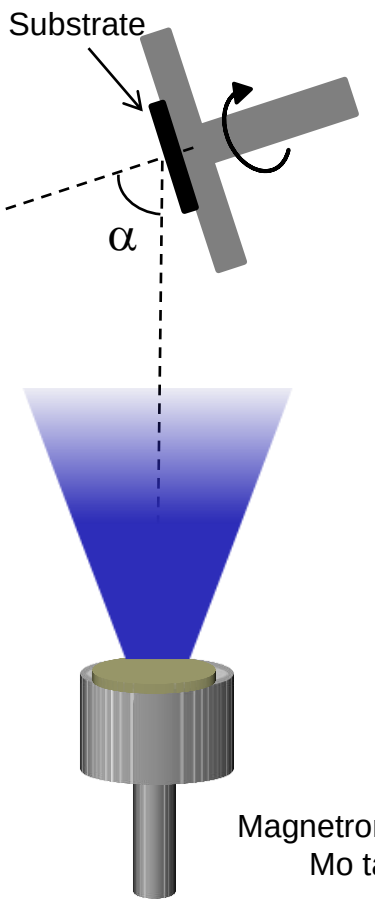
Originated in 1995.

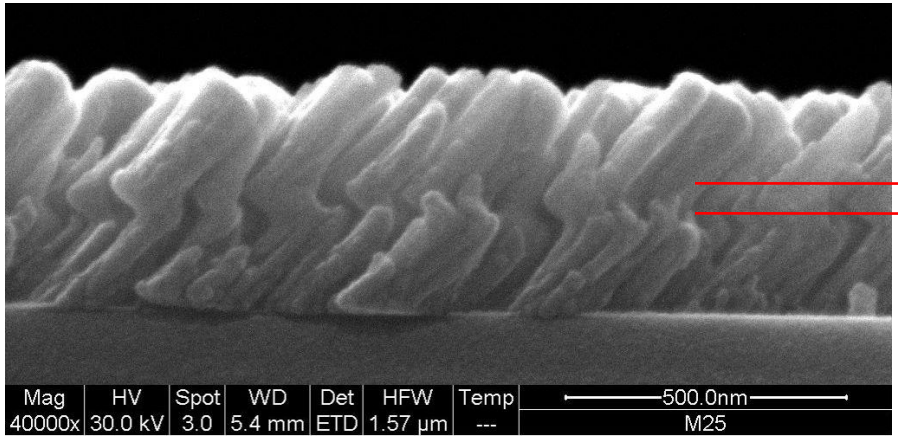
Glancing angle deposition employs oblique angle deposition and substrate motion to engineer thin film microstructures on a nanometer scale in three dimensions.

K. Robbie, L. J. Friedrich, S. K. Dew, T. Smy, M. J. Brett, J. Vac. Sci. Technol. A13 (1995) 1032.

K. Robbie, J. C. Sit, M. J. Brett, J. Vac. Sci. Technol. B16 (1998) 1115.

GLAD



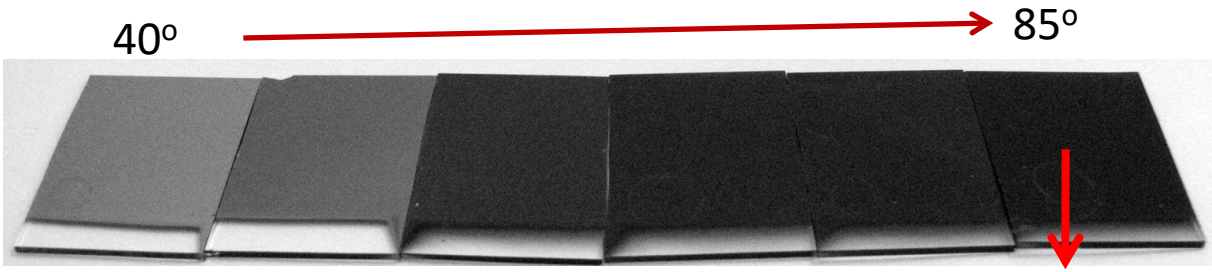


$\alpha = 75^{o}$

$\alpha = -75^{o}$

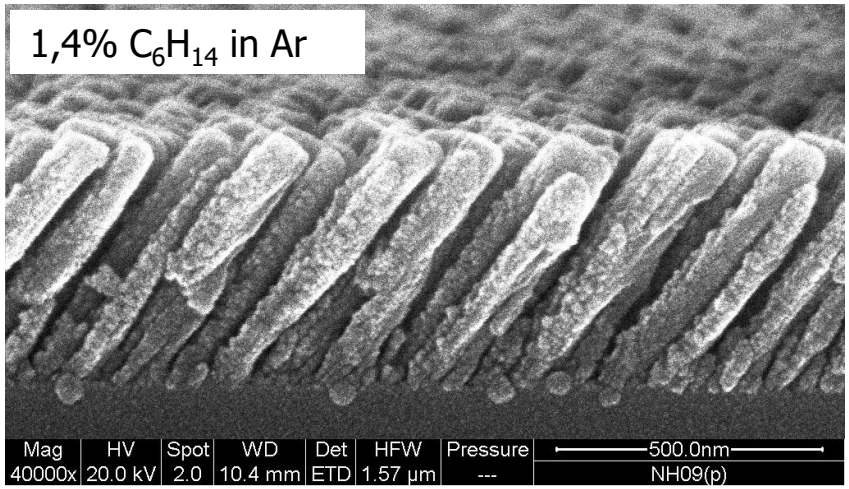
$\alpha = 75^{o}$

Molybdenum columns with zig-zag structure

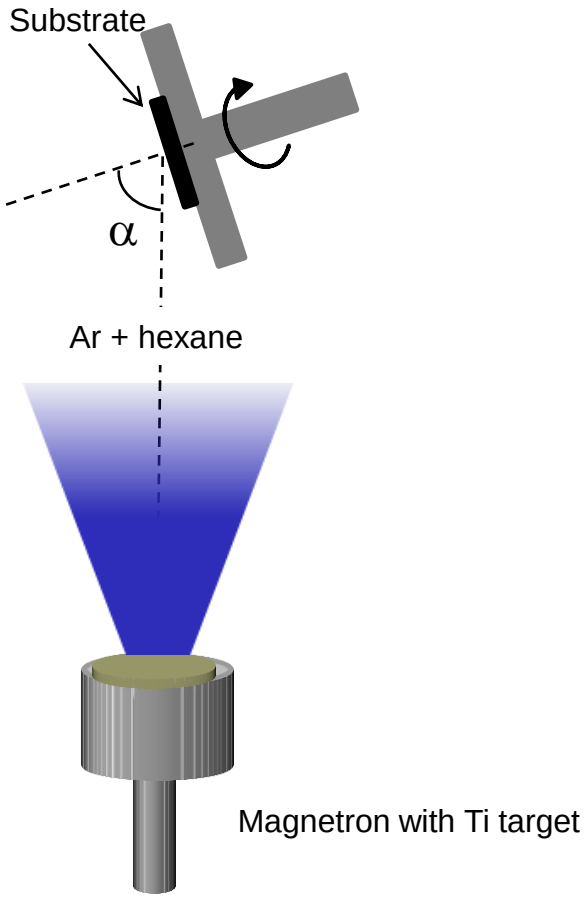


Ar, pressure 0.06 Pa, DC 0.45 A, 30 min

GLAD



Nanocomposite Ti/ hydrocarbon plasma polymer films deposited by magnetron sputtering in GLAD configuration
(75°, total pressure 0.16 Pa, DC 0.3 A)



*A. Choukourov, et al, Plasma Proc. Polym., **7**, 25-32, 2010*

Conclusions

- **fully vacuum-based process**
  - •scalable
  - •limited use of toxic substances – environmentally friendly
  - •relatively fast and cheap
  - • possibility to coat virtually any substrate material