Patterning the adhesive properties of amine rich polymer films

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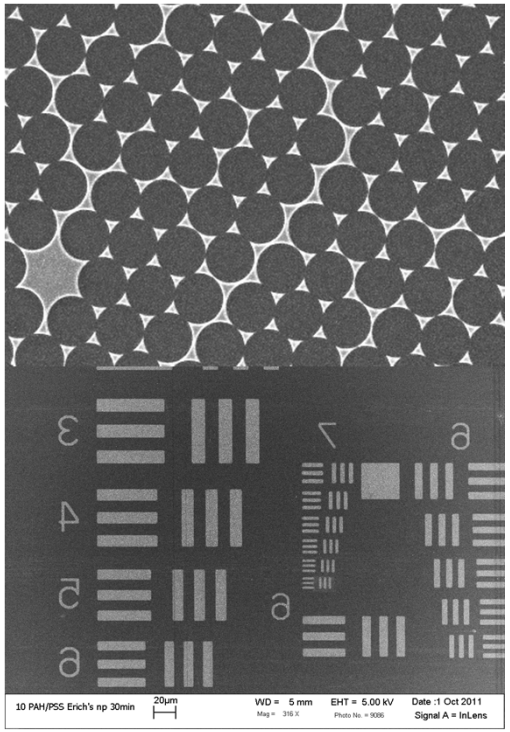
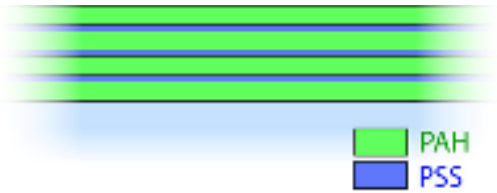
Patterned Surface Adhesion

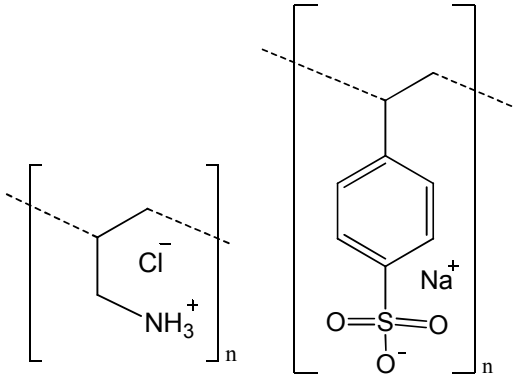
- Selective deposition of nanoparticles and structures
- Patterned adhesion is useful for plasmonic devices, nanoscale devices, biomedical and tissue engineering
- Patterning entities not compatible with lithographic processes



Amine-rich ISAM film

$(PAH/PSS)_n/PAH$ film deposited at high pH (9-9.5) contains large amounts of amine groups





PAH PSS

Pioneered by M.F. Rubner:

J. Hiller et al., Nat. Mat. **2002**,*1*,59

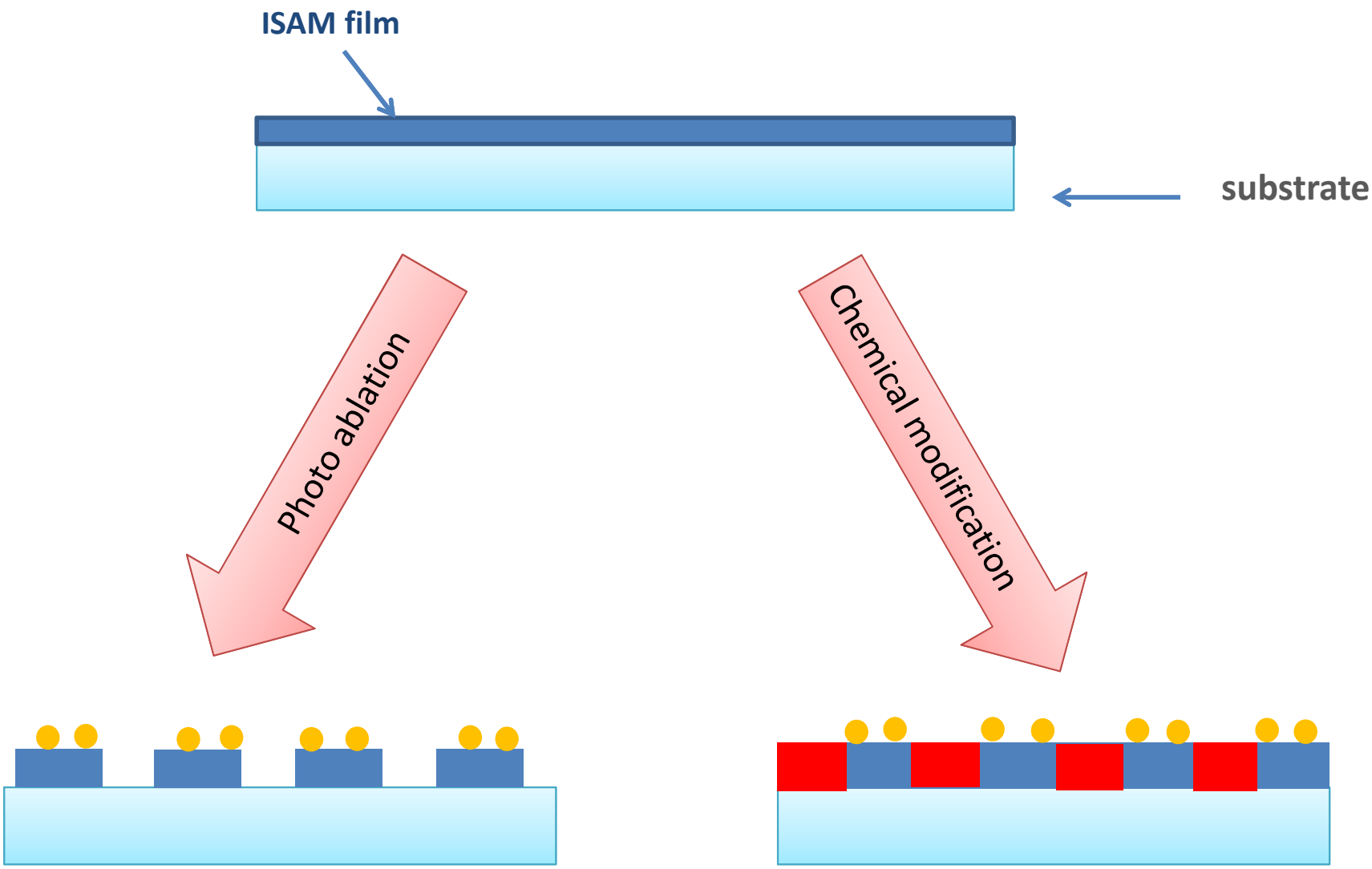
J. Hiller & M. F. Rubner, Macromol. **2003**, *36*, 4078

K.-K. Chia et al., Chem. Mater **2008**, *20*, 6756

The film undergoes hysteretic swelling and deswelling with pH

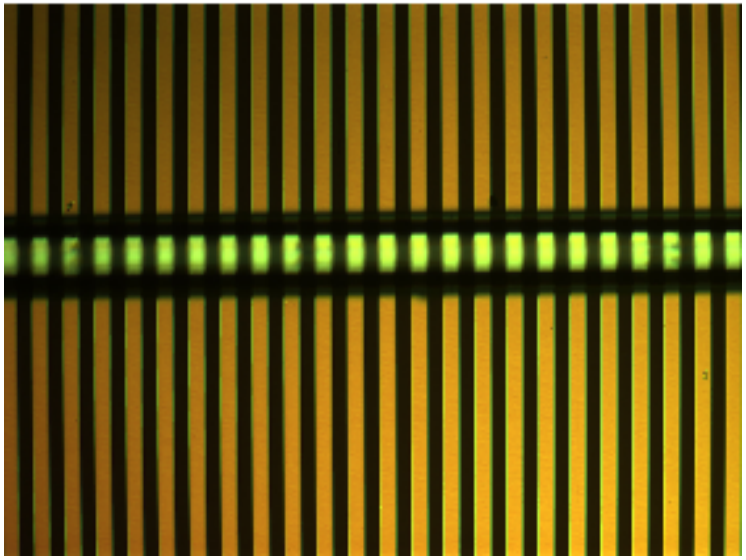
→ Creates opportunity to protect and rejuvenate the surface

Surface modification

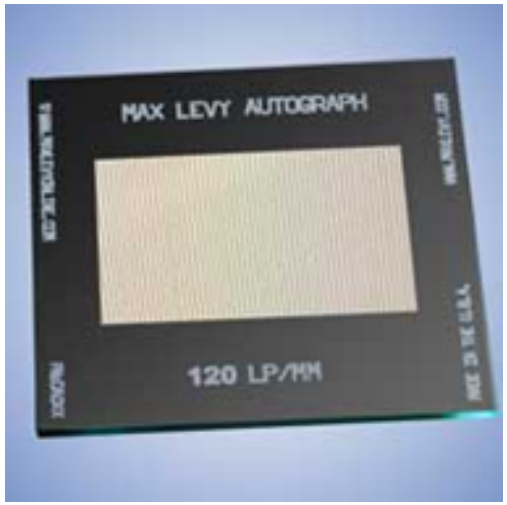


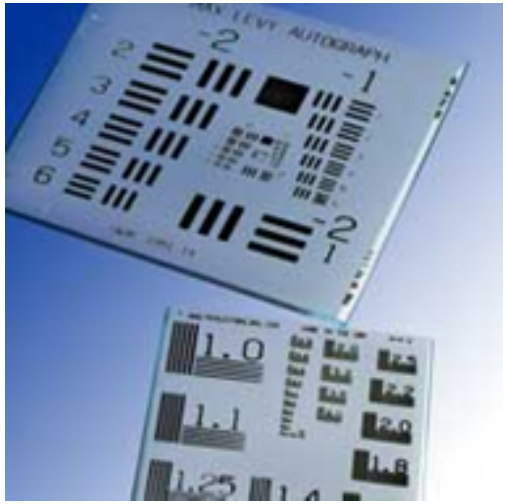
Photomasks (withstand high laser fluence)

Highly reflective metal film on fused silica substrate (high UV transmission)



Optical microscope image of a photomask with a fiber sitting on top





Laser ablation patterning

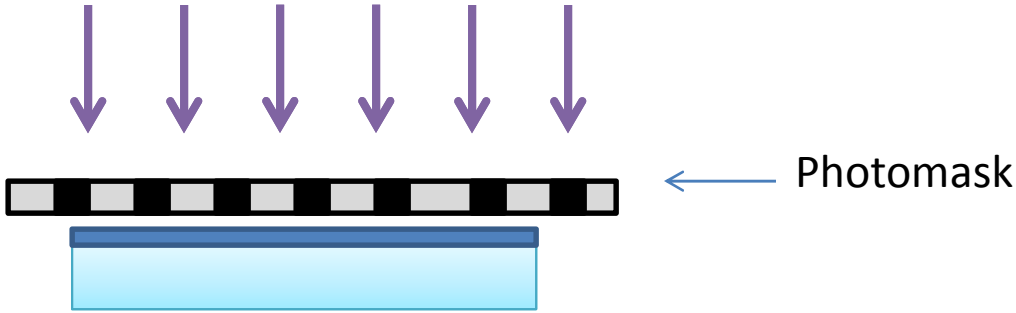
(1)

Film deposition

UV excimer laser 248 nm with pulse energy ~45 mJ/cm^2

(2)

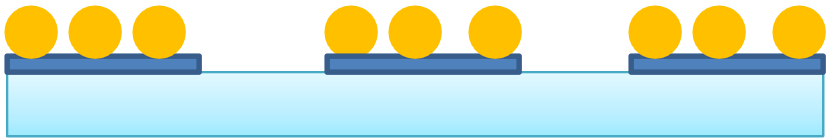
Laser ablation



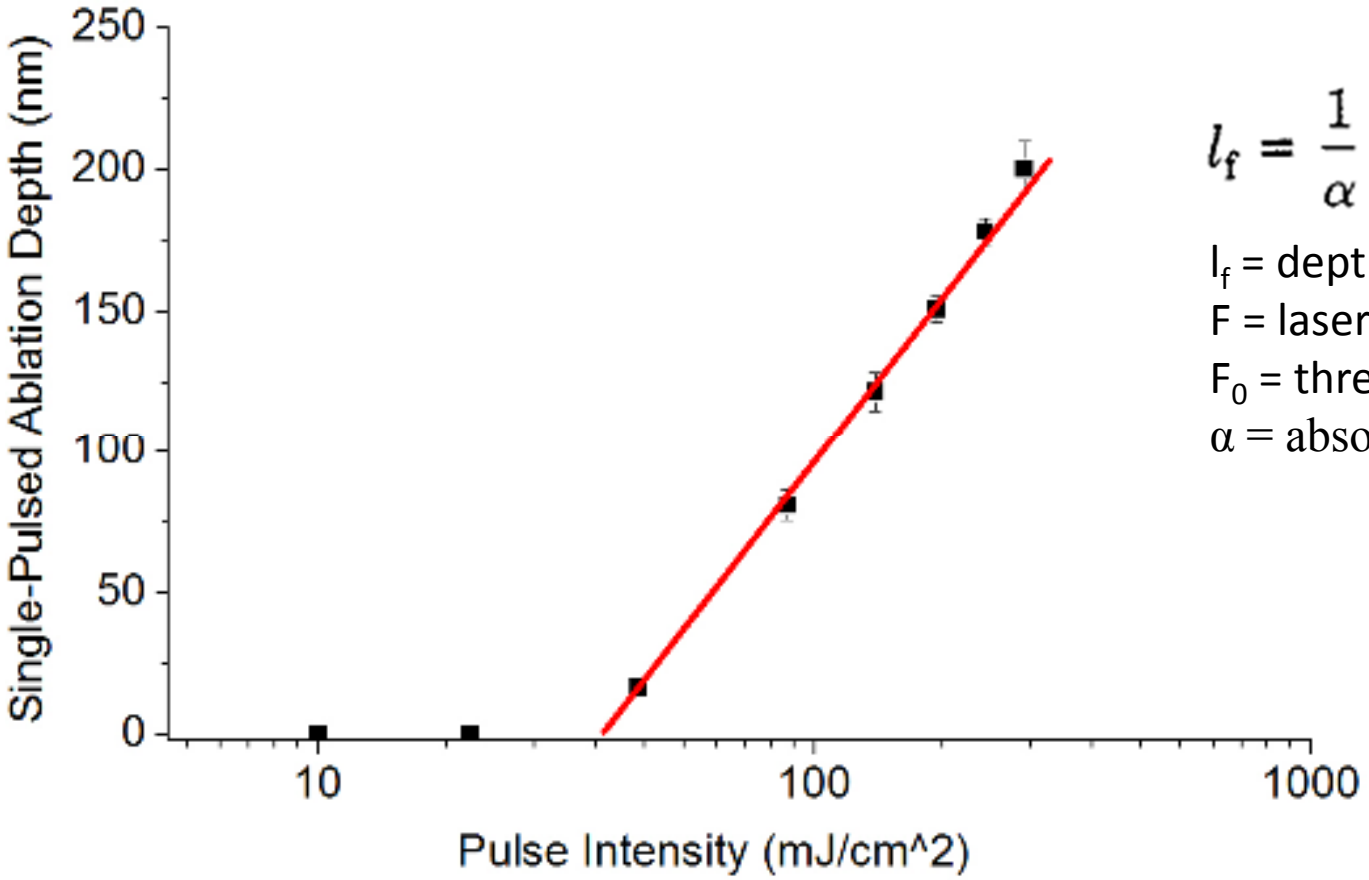
Nanoparticles selectively assemble on the patterned surface

(3)

Nanoparticle Assembly



Laser ablation threshold for polymer films



$$l_f = \frac{1}{\alpha} \log \frac{F}{F_0}$$

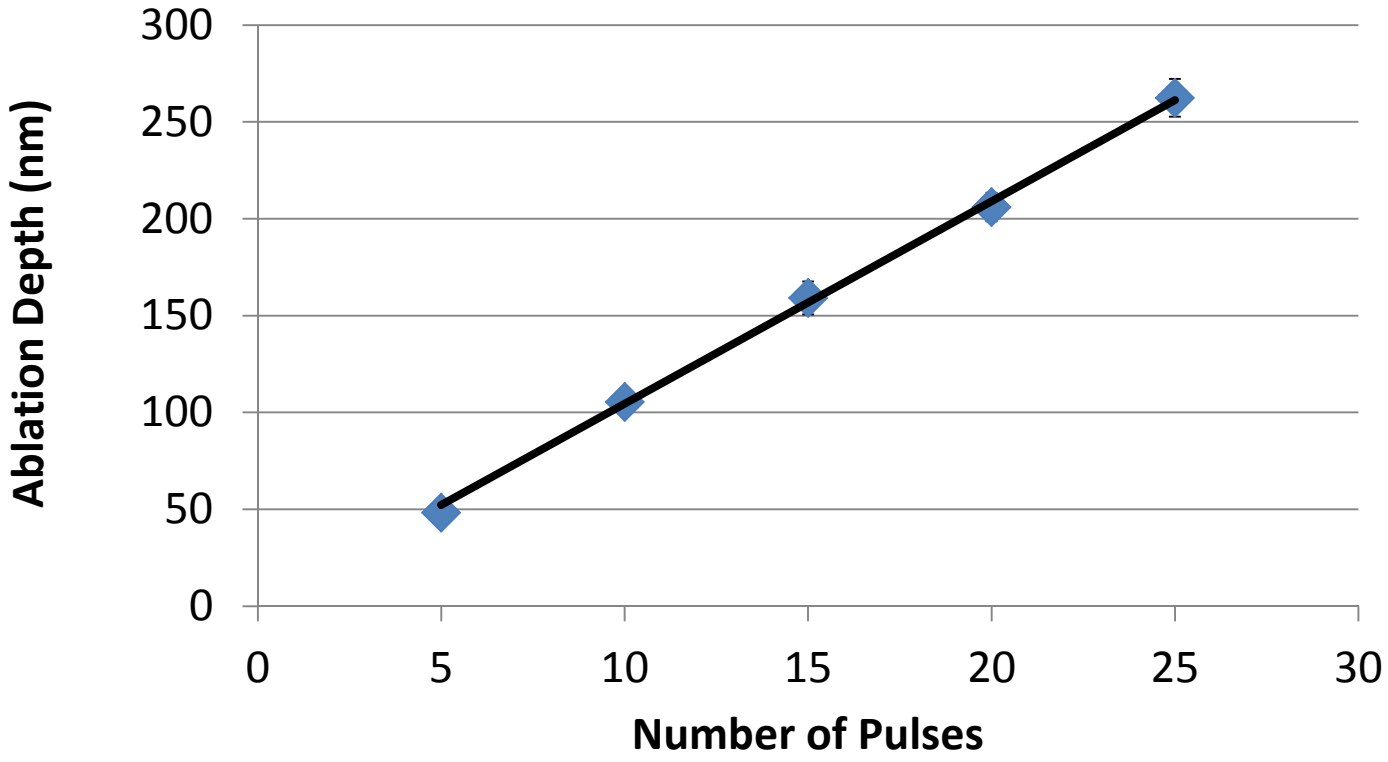
l_f = depth
F = laser fluence
F_0 = threshold fluence
α = absorptivity

Threshold fluence of PAH/PB films ~40 mJ/cm^2

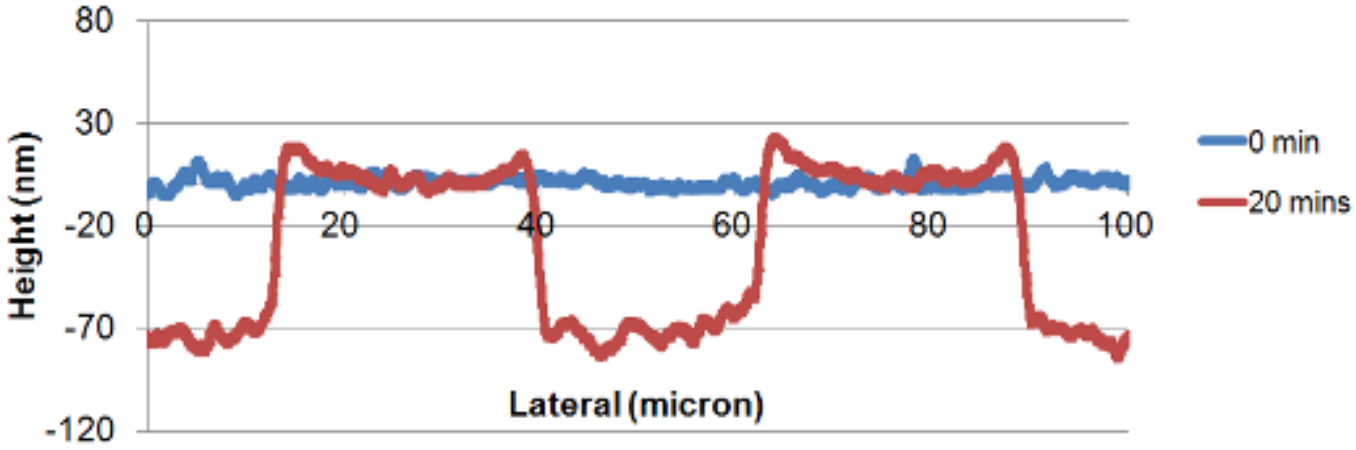
Most ablation threshold of polymer films lies in ~30-70 mJ/cm^2

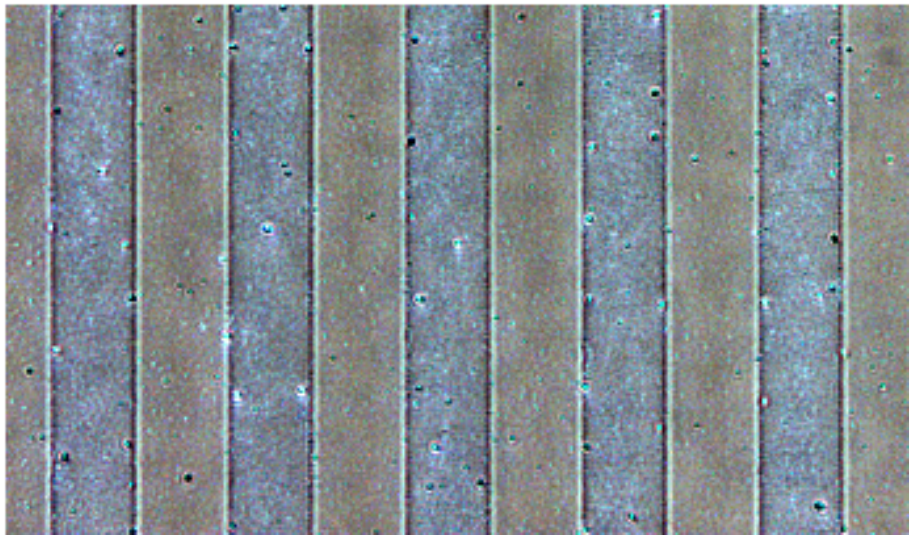
glass 1.2 J/cm^2.

Ablation depth vs number of laser pulses for polymer film (at 45 mJ/cm^2)



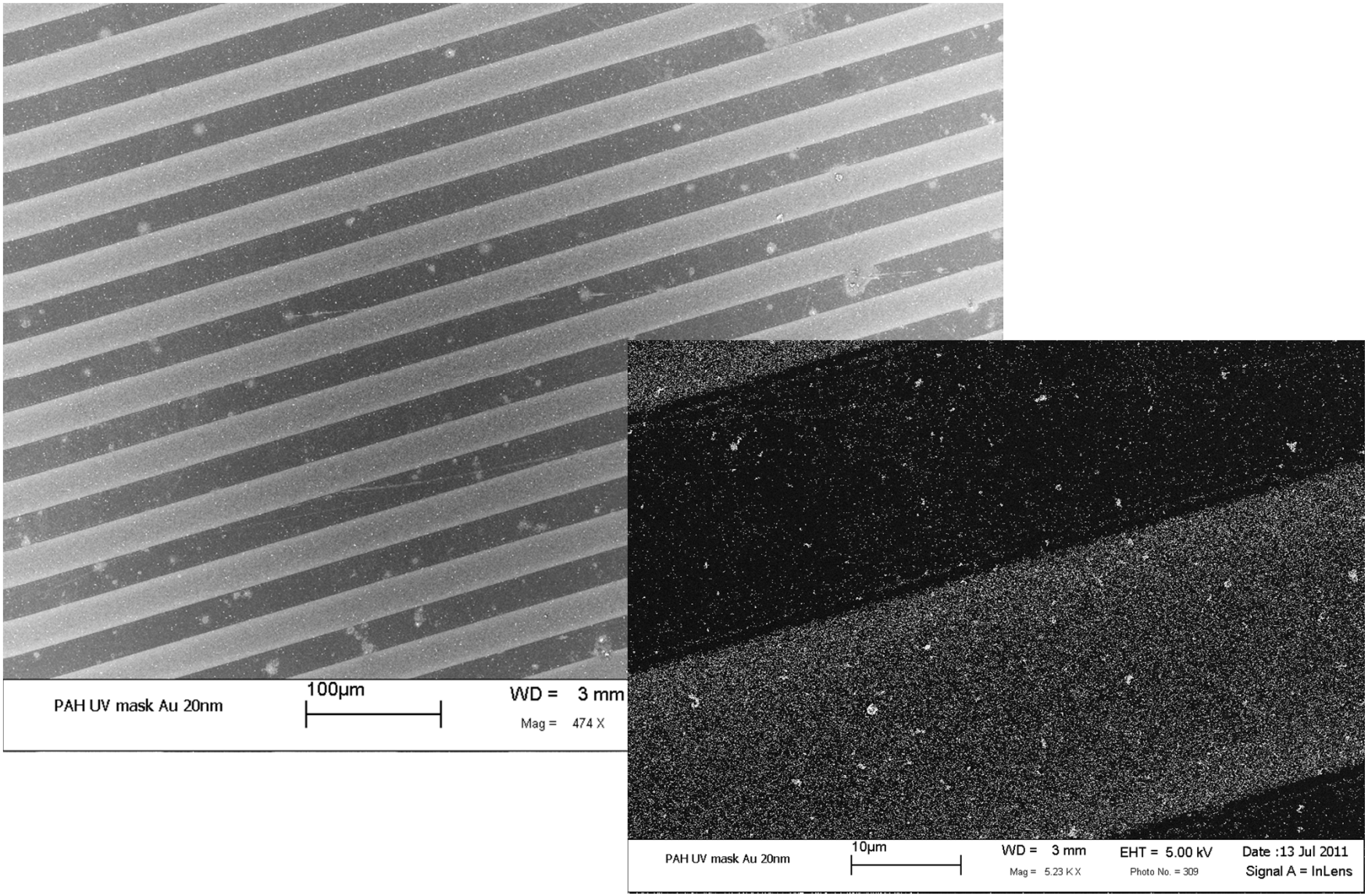
Laser Ablation profile of polymer films



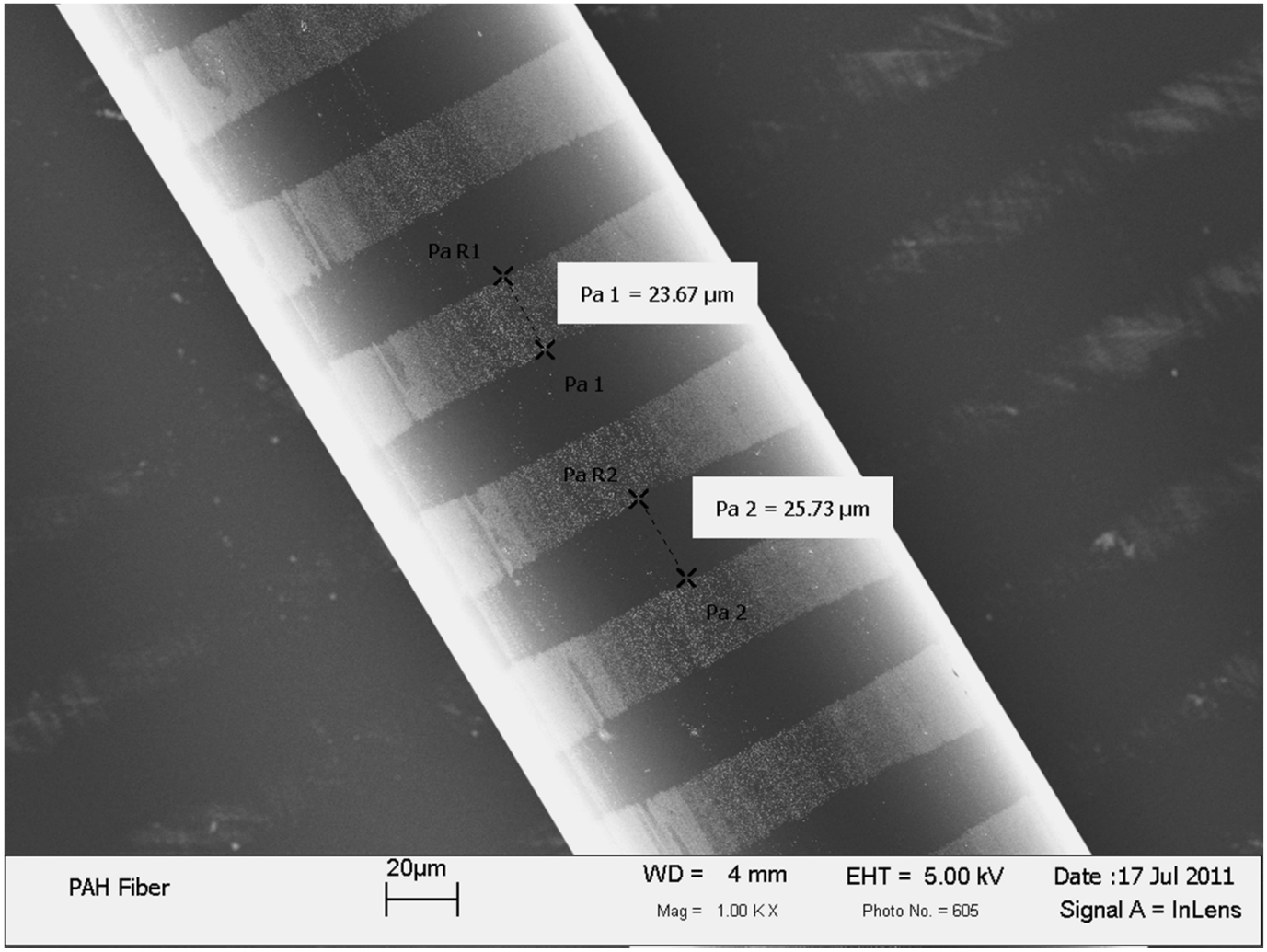


Phase-contrast optical microscope image of patterned $(PAH/PSS)_{100}$ film

Selective assembly of 20nm Au nanoparticles on 1PAH layer template



Nanoparticle pattern on one PAH layer coated fiber



Pattern of ISAM layer on planar substrate.

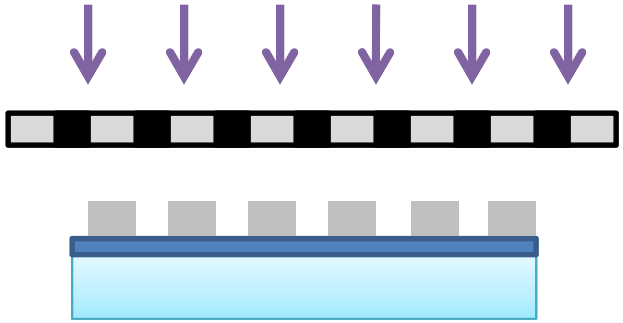
(1)

Film deposition

Al deposition

(2)

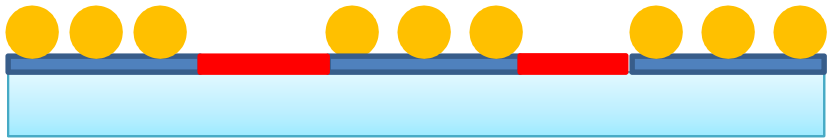
Metal evaporation



Acetic Anhydride treatment
Al etch with HCL
Au nanosphere deposition.

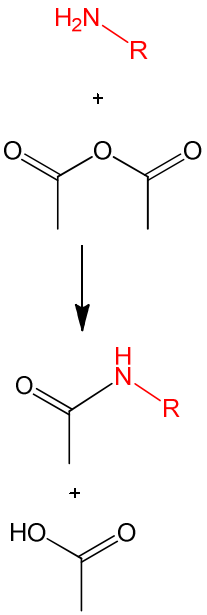
(3)

Nanoparticle Assembly



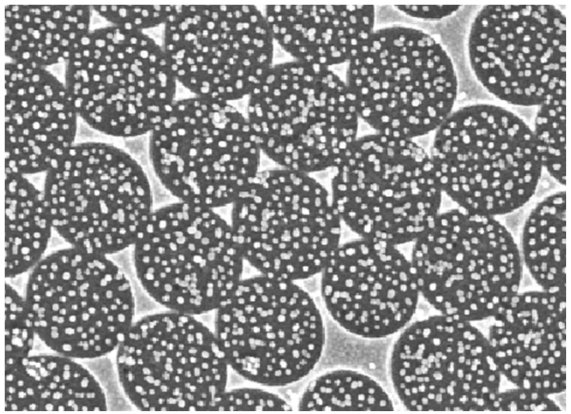
Acetic anhydride passivation

The surface amine can be passivated by acetylation with acetic anhydride

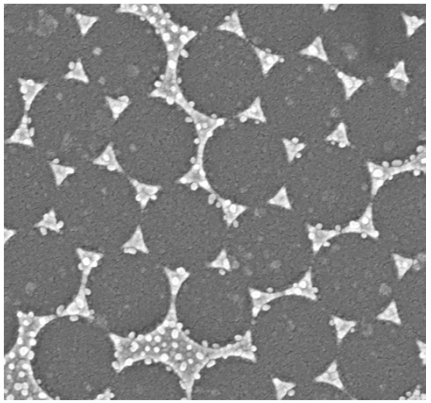


1. Expose to neat acetic anhydride for 20 min.
2. Rinse

Passivation prevents absorptions of additional particles

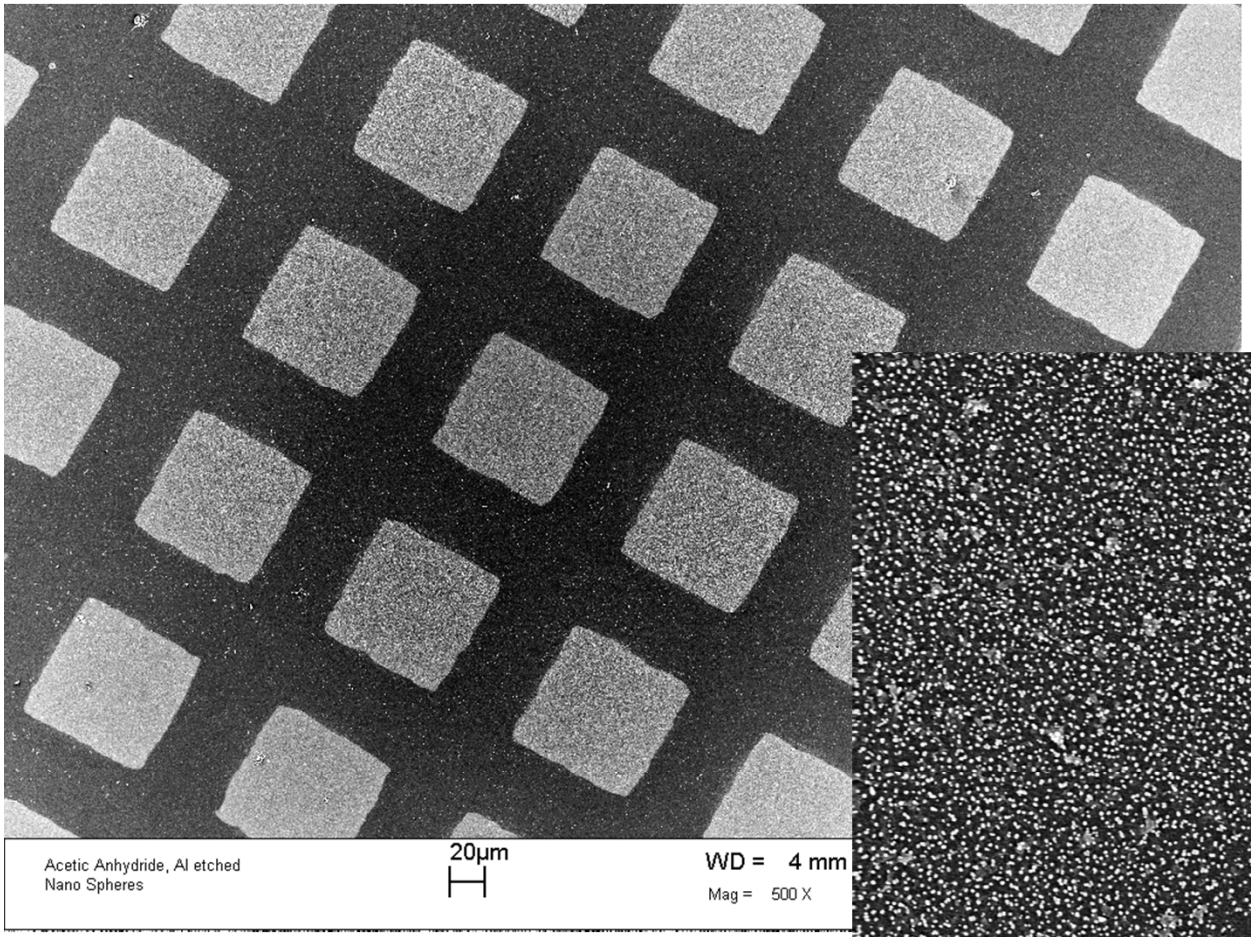


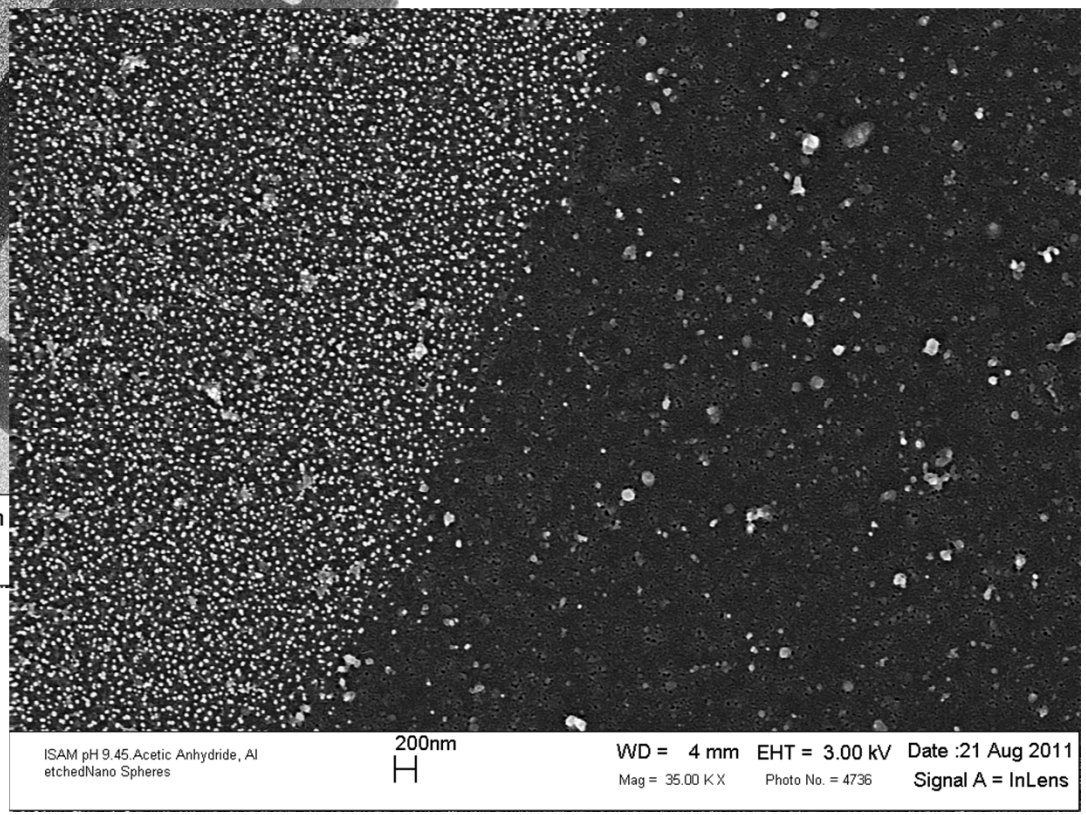
without passivation



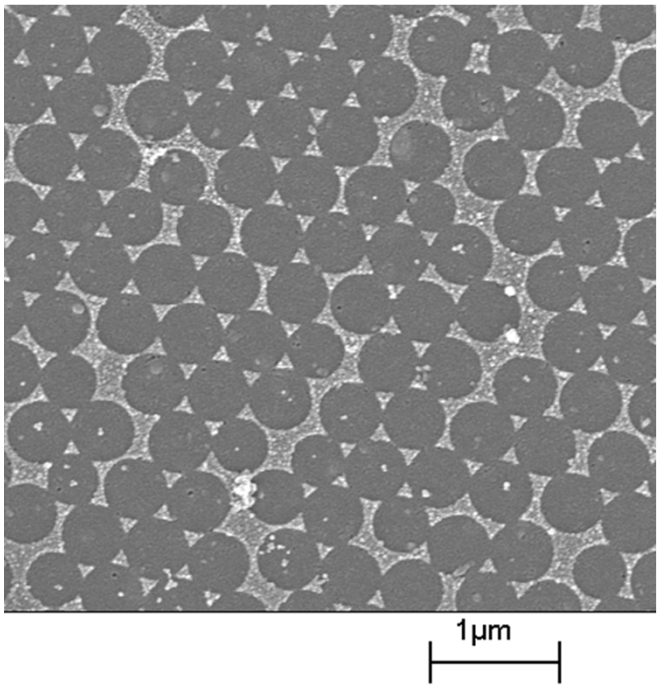
with passivation

Selective assembly of gold nanoparticles on patterned ISAM film



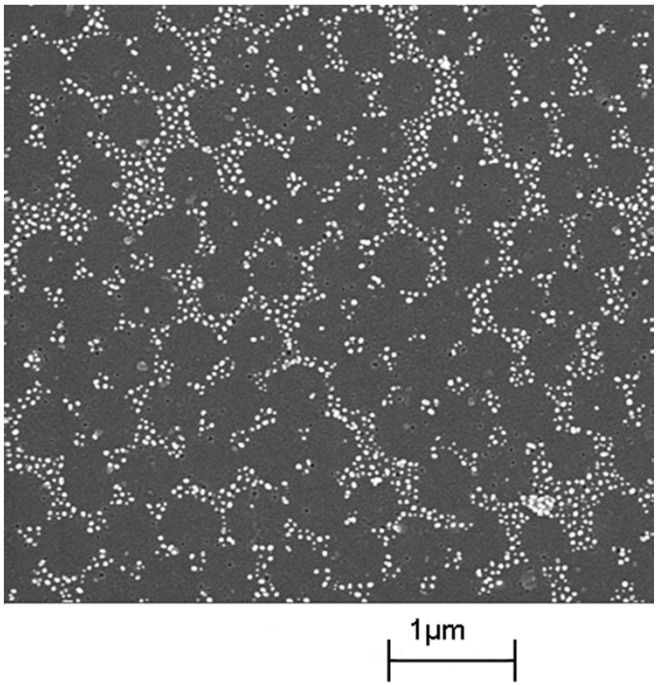


High resolution adhesion modification patterning



1. Adhere Al pattern
2. Passivate with acetic anhydride
3. Etch in 1 mM HCl
4. Deswell at pH 10.25

5. Adsorb Au nanoparticles



Adhesion-patterning “lithograhy”

Summary

- PAH terminated ISAM films provide amine rich “sticky” surfaces.
- Surface adhesion properties can be patterned by laser ablation or chemical manipulation
- Sub micron resolution can be achieved by both techniques
- Applications in nanodevice fabrication, cell biology and tissue engineering