Understanding the Patterning Mechanism of Inorganic Nanoparticle Photoresists from HfO_2 and ZrO_2

Y.-S. Chung[1], M.Krysak[1], C.Ouyang[1], M. Trikeriotis[1],

B. Cardineau[2], R. Brainard[2], E. P. Giannelis[1],

C. K. Ober[1]

(1) Materials Science & Engineering, Cornell University, Ithaca, NY

(2) College of Nanoscale Science and Engineering, University at Albany, Albany, NY

Presentation Overview

- Introduction to the inorganic photoresist platform
- Lithographic performance highlights:
  - EUV patterning
  - Etching
- Versatile resist platform:
  - Dual-tone capability
  - Alternate formulations
  - EUV absorbance optimization
- Working Hypothesis for patterning mechanism

Metal Oxide Sulfate (Inpria)

Aqueous solution-based inorganic resists (metal oxide sulfates: Hf, Zr) for **EUV** and **e-beam** lithography

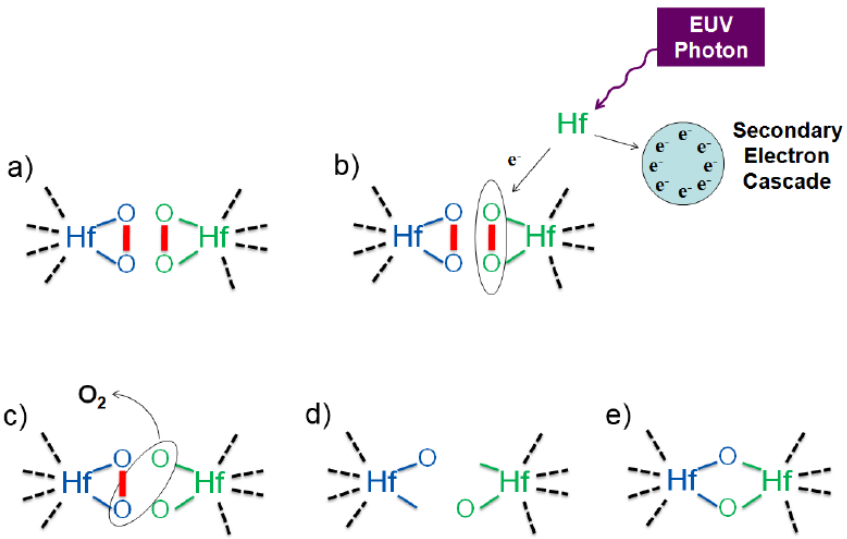
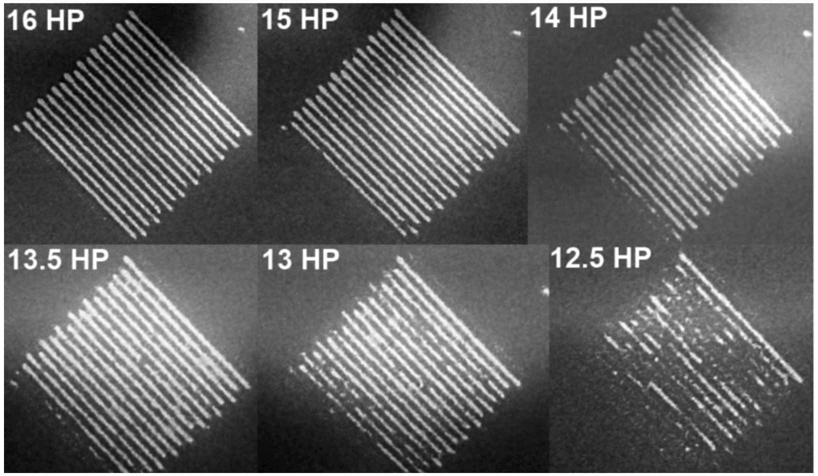
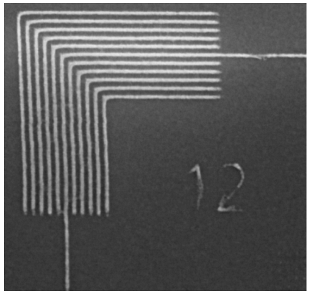


Diagram representing a simplified exposure mechanism in Inpria resist



16 nm HP – 12 nm HP lines produced by F2X mode on the SEMATECH-Berkeley MET with XE15AB resist at 70 mJ/cm2. The 16-nm HP lines printed at 13-nm CD, and they have a LER of 2.0 nm.

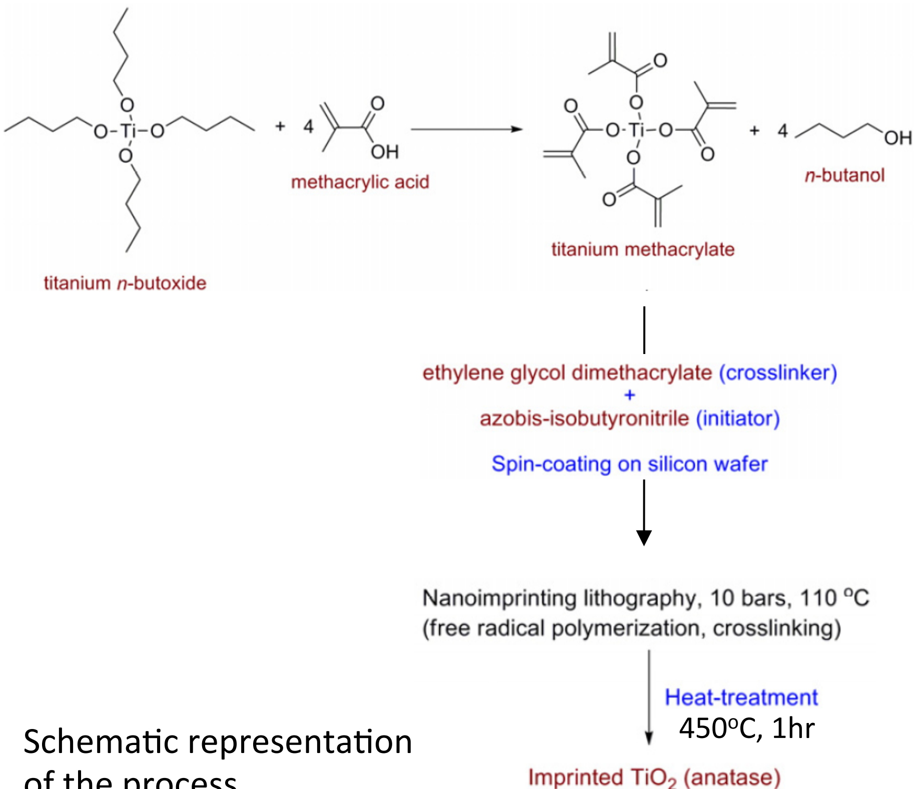


12-nm half-pitch lines patterned with e-beam lithography, XE15AB resist at 930 µC/cm2 (30 keV).

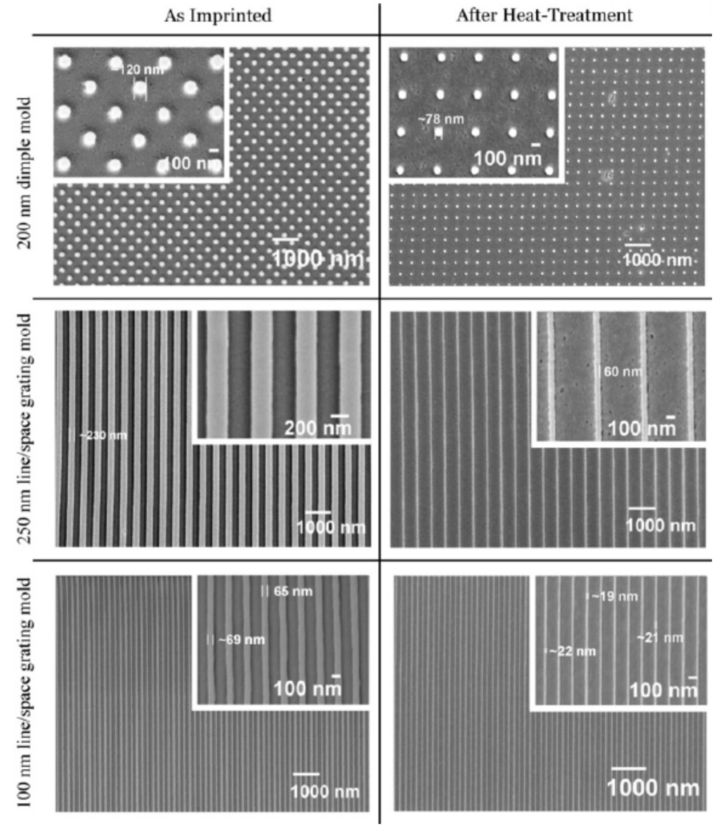
J. Stowers *et al.* 2011 Proc. of SPIE Vol. 7969 796915

Titanium Oxide Methacrylate

Organic solution-based organic/inorganic resists (metal core: Ti) for **nanoimprint** lithography



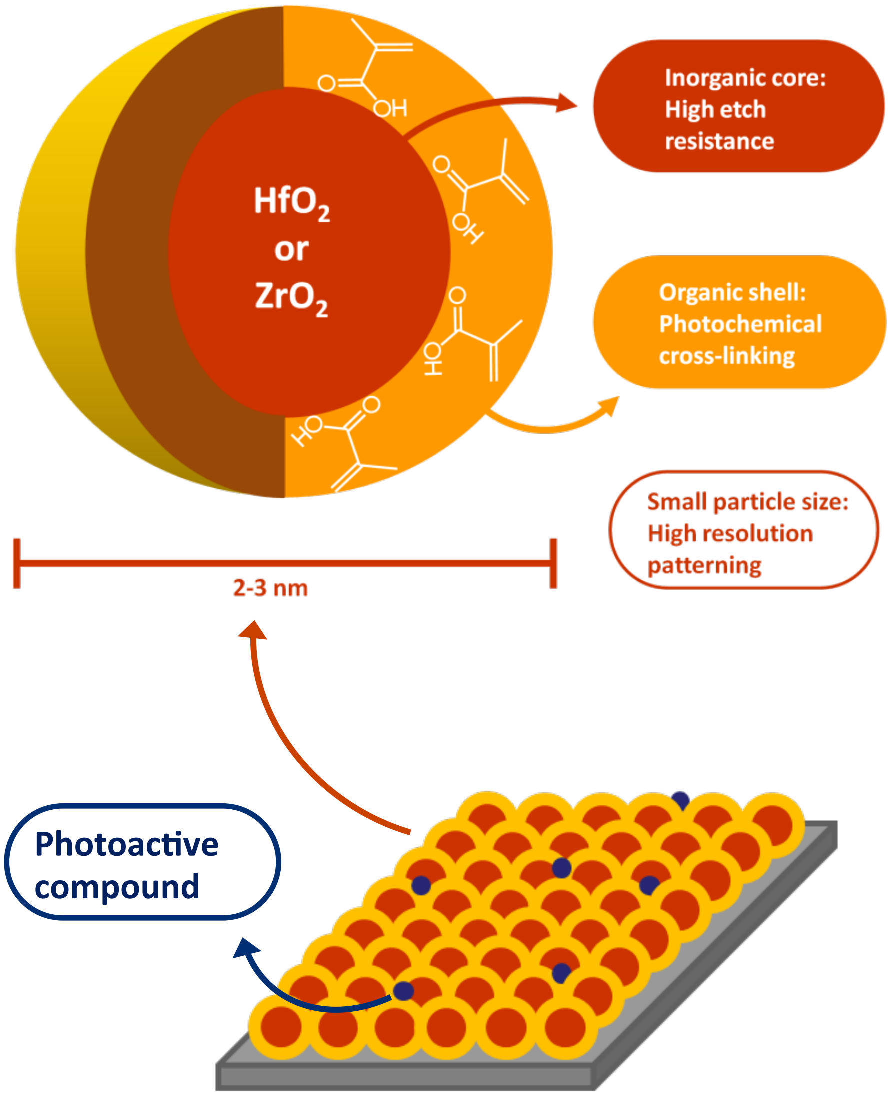
Schematic representation of the process



Composite SEM images of various as-imprinted and heat-treated structures using different molds. Heat-treatment to produce ~20 nm structures of TiO2

S. H. Lim *et al.* Nanotechnology 21 (2010) 285303

Nanoparticle Photoresist



Hybrid organic/inorganic nanoparticles:
Metal oxide with organic surface ligands

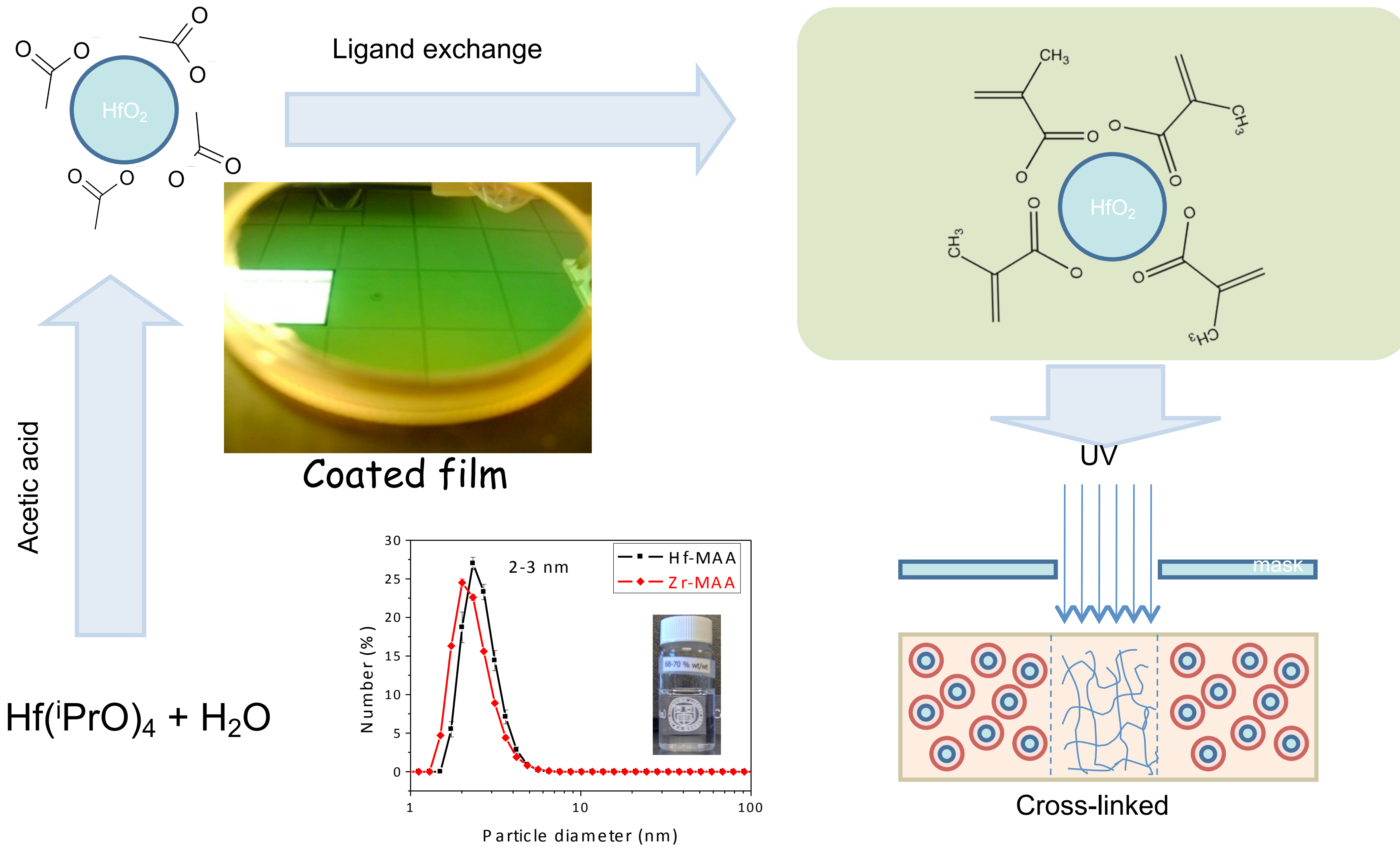
Inorganic core:
ZrO_2 or HfO_2, other metal oxides can be used.

Ligand Surface:
Carboxylate, phosphonate and sulfate studied to date

Photoactive Compounds:
Either PAG or photoradical generator

NOT CHEMICALLY AMPLIFIED

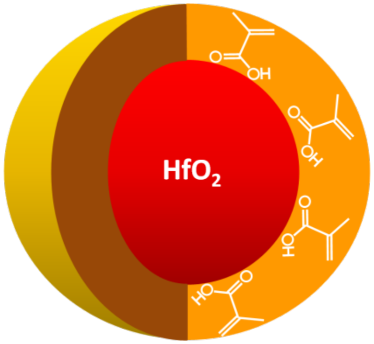
HfO_2 Nanoparticle Photoresist



CORNELL UNIVERSITY

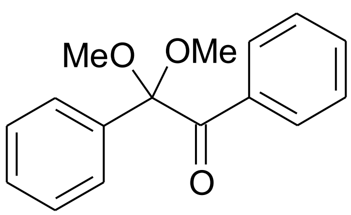
with P Zimmerman (Sematech); E Giannelis (Cornell)

HfMAA or ZrMAA: 5-10% w/v



- ✓ Spin coat from PGMEA or similar solvents
- ✓ Can plug into existing dispense process
- ✓ Aqueous base or solvent develop
- ✓ Positive or negative tone

Photoactive compound: 1-10% w/w relative to nanoparticle mass

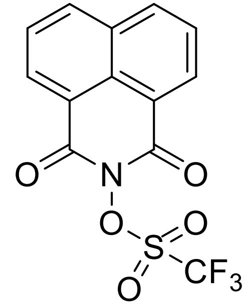


dimethoxy phenyl acetophenone

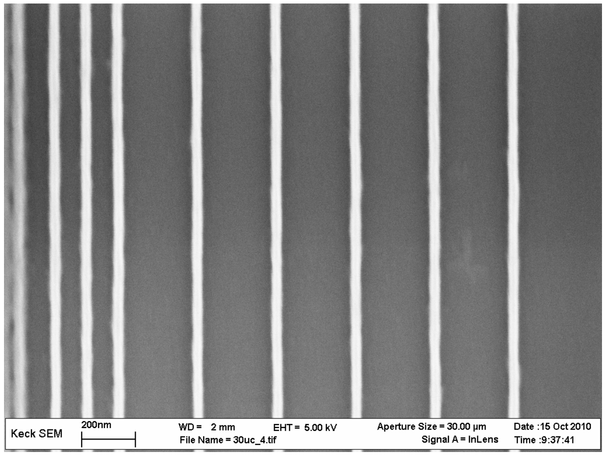
← Photoinitiator

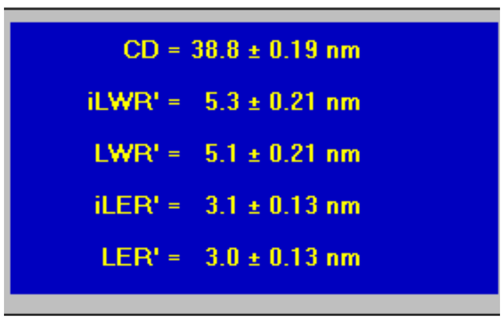
or

PAG →

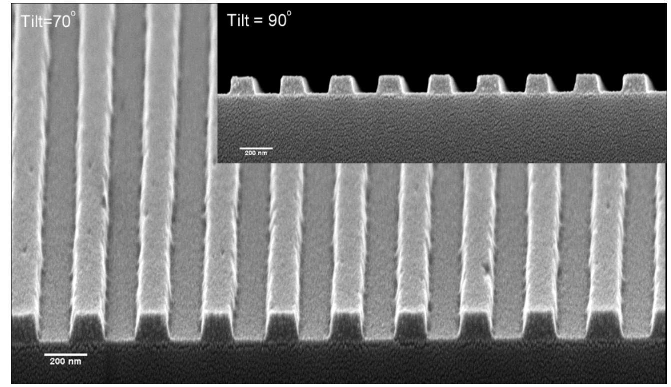


E-beam and 193i Lithography

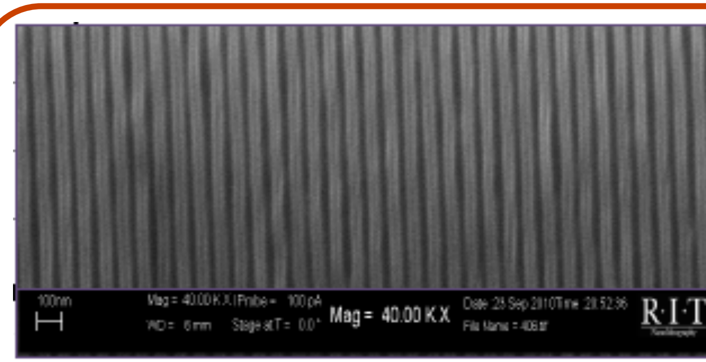




HfMAA + DPAP
E-beam, negative tone



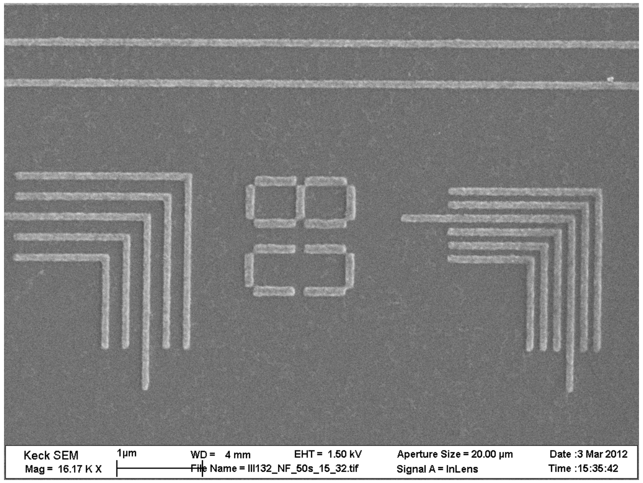
HfMAA + DPAP
193 dry, negative tone, 150nm

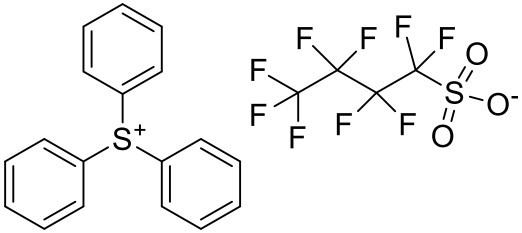


HfMAA + DPAP
193 immersion, negative tone, 40nm

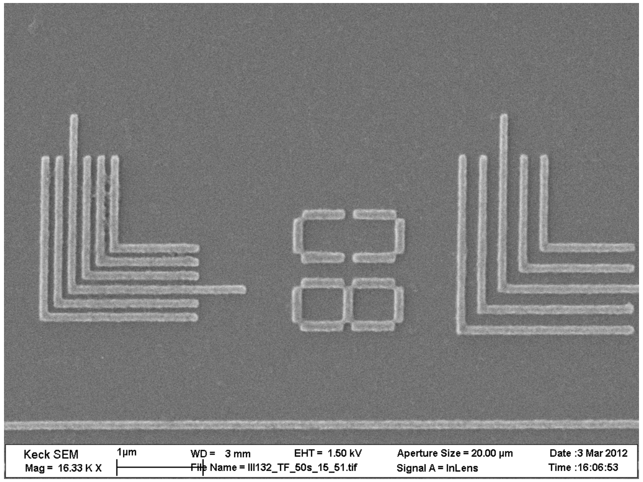
Negative-tone Patterning of ZrMAA Different PAGs

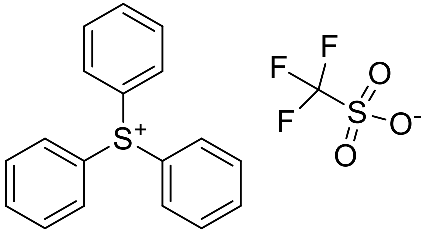
Electron beam lithography with Ionic PAGs
(Dose = 15μC/cm^2)





Triphenylsulfonium perfluoro-1-butanesulfonate

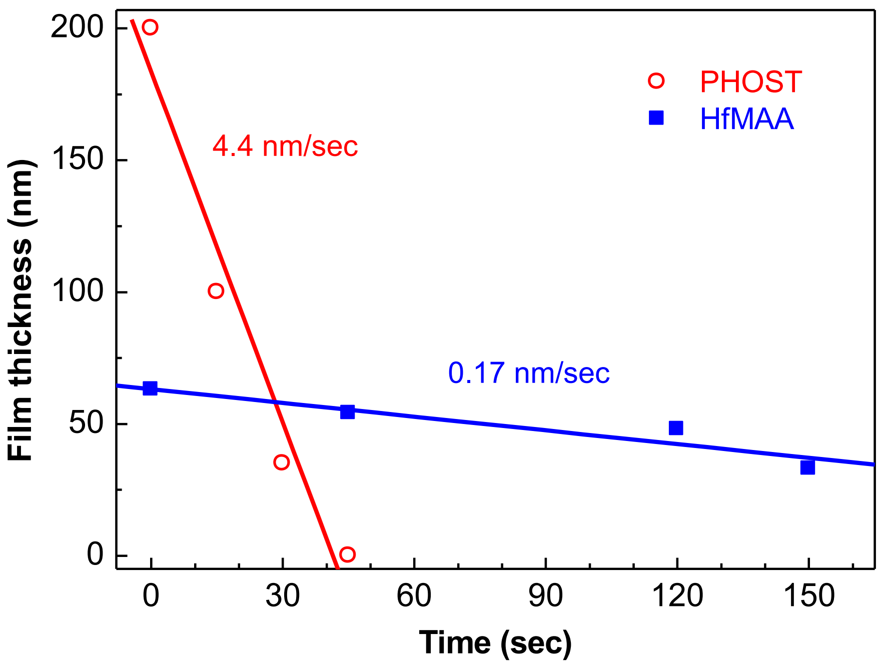




Triphenylsulfonium triflate

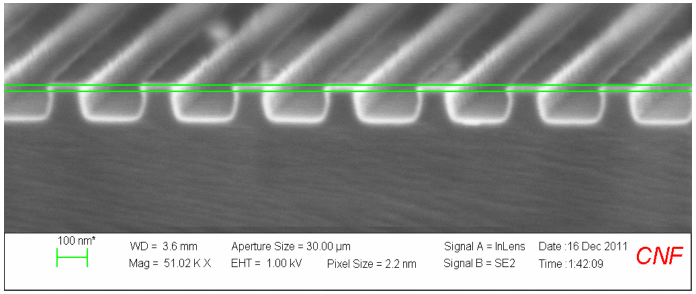
Etch Resistance / Pattern Transfer

Etch rate comparison of PHOST and Hf-MAA resist

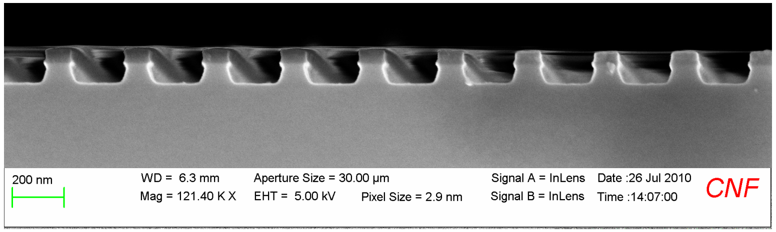


HfMAA has 25 times better etch resistance than PHOST

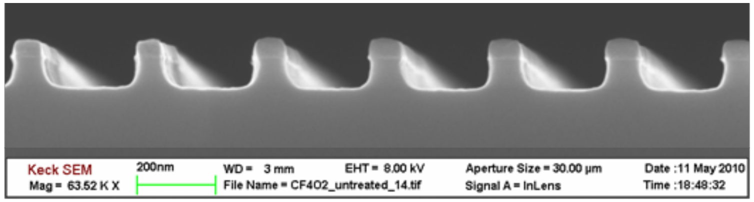
O_2 plasma treatment has no detrimental effect on pattern transfer



SF_6/O_2 pattern transfer

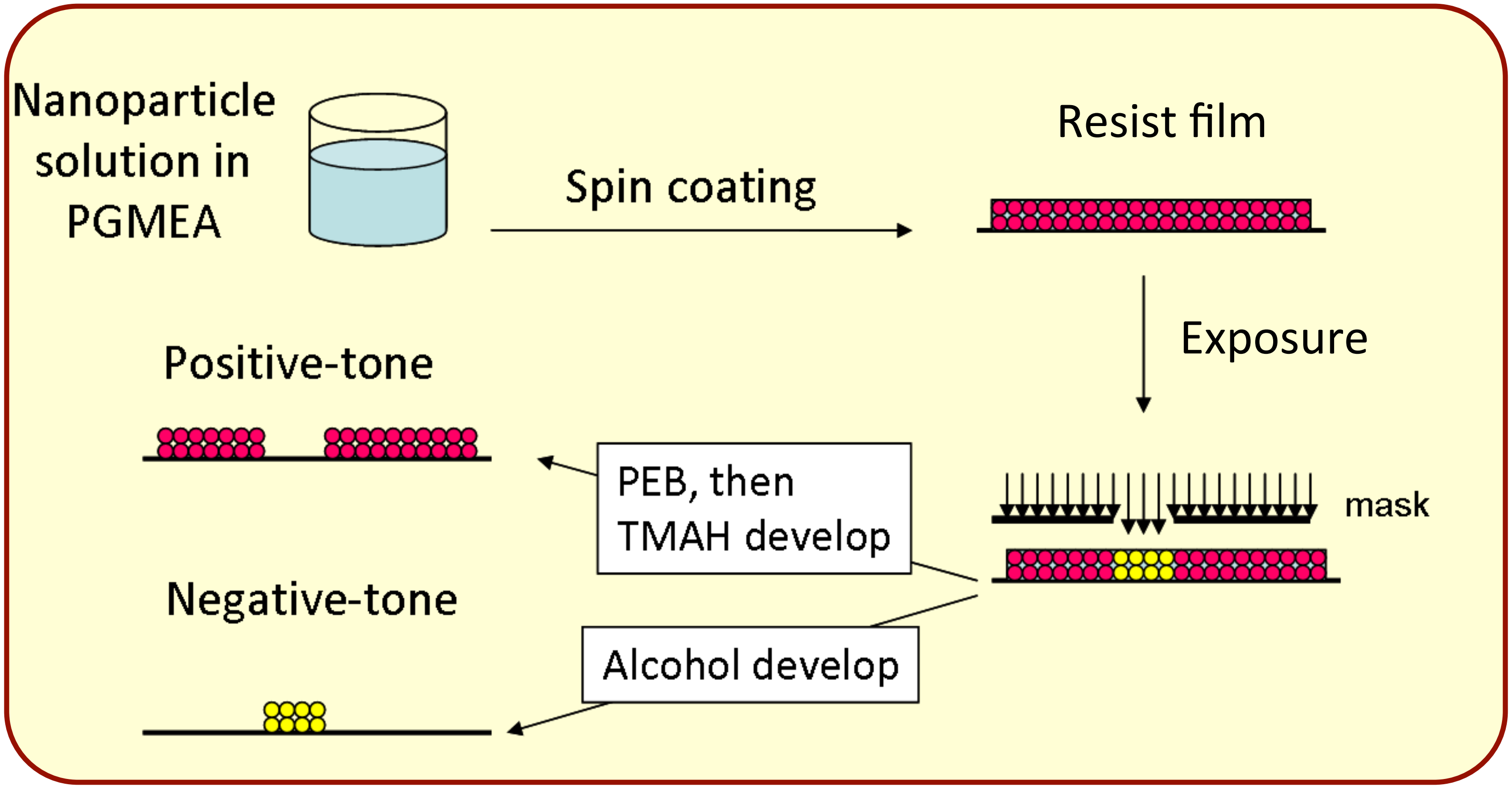


CF_4 pattern transfer



Resist Process Flow Schematic

Dual tone photoresist



Absorption optimization

Film absorption depends on atomic composition and density

$$\mu = \frac{N_A \rho}{MW} \sum_i x_i \sigma_{\alpha i}$$

Organic/inorganic hybrid

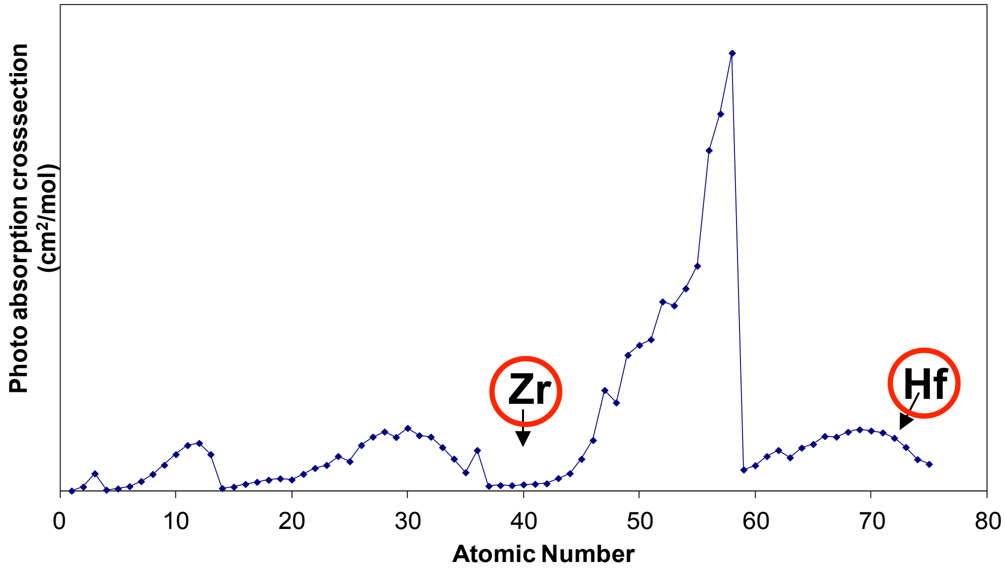
Inorganic:

$HfO_2 - ZrO_2$ high density materials

Hf has higher absorbance than Zr at 13.5 nm

Organic:

Lower density



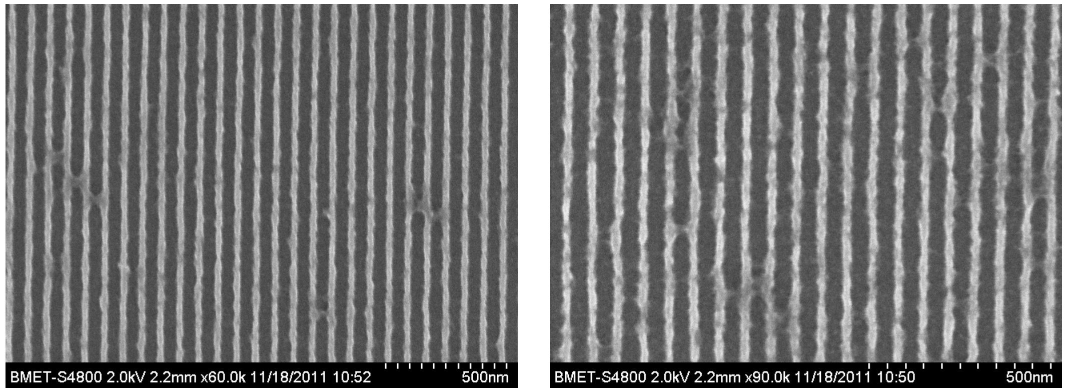
Absorption optimization:

- Hf:Zr ratio
- Organic content – film density

EUV Lithography

High EUV sensitivity

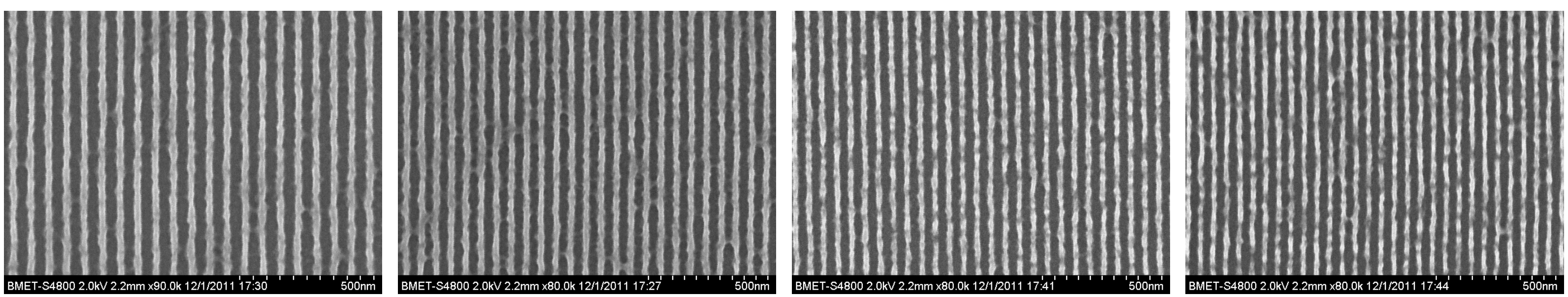
SuMMIT analysis:
CD = 26.1 ± 0.11 nm
LWR = 6.0 ± 0.10 nm
LER = 3.8 ± 0.07 nm



SuMMIT analysis:
CD = 21.5 ± 0.58 nm
LWR = 9.0 ± 0.18 nm
LER = 5.6 ± 0.18 nm

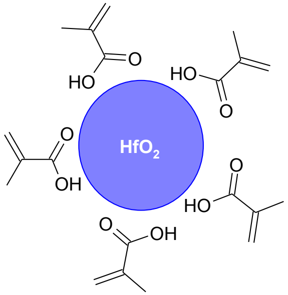
Zr-MAA + PAG **Dose: 4.2 mJ/cm^2**

Half pitch 34nm 32nm 30nm 28nm

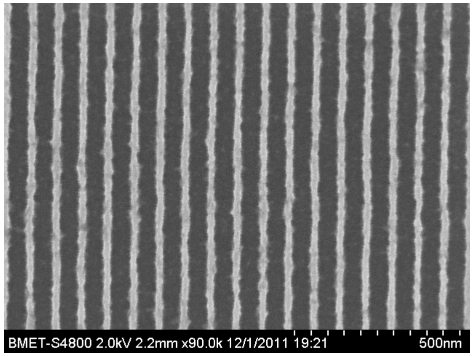


Zr-MAA + PAG Dose: 16.5 mJ/cm^2

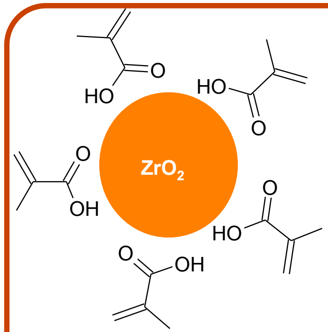
Alternative Cores and Ligands



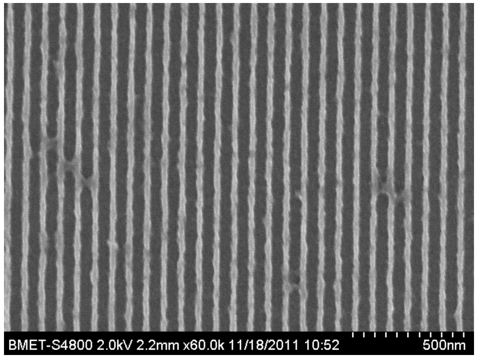
HfMAA



- ✓ Dual-tone
- ✓ EUV
- ✓ E-beam, 193, DUV

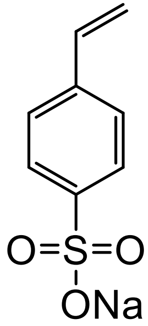


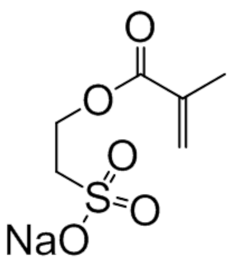
ZrMAA

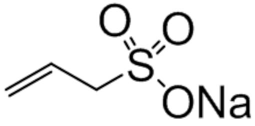


- ✓ Dual-tone
- ✓ EUV
- ✓ E-beam, DUV

Alternative ligands:







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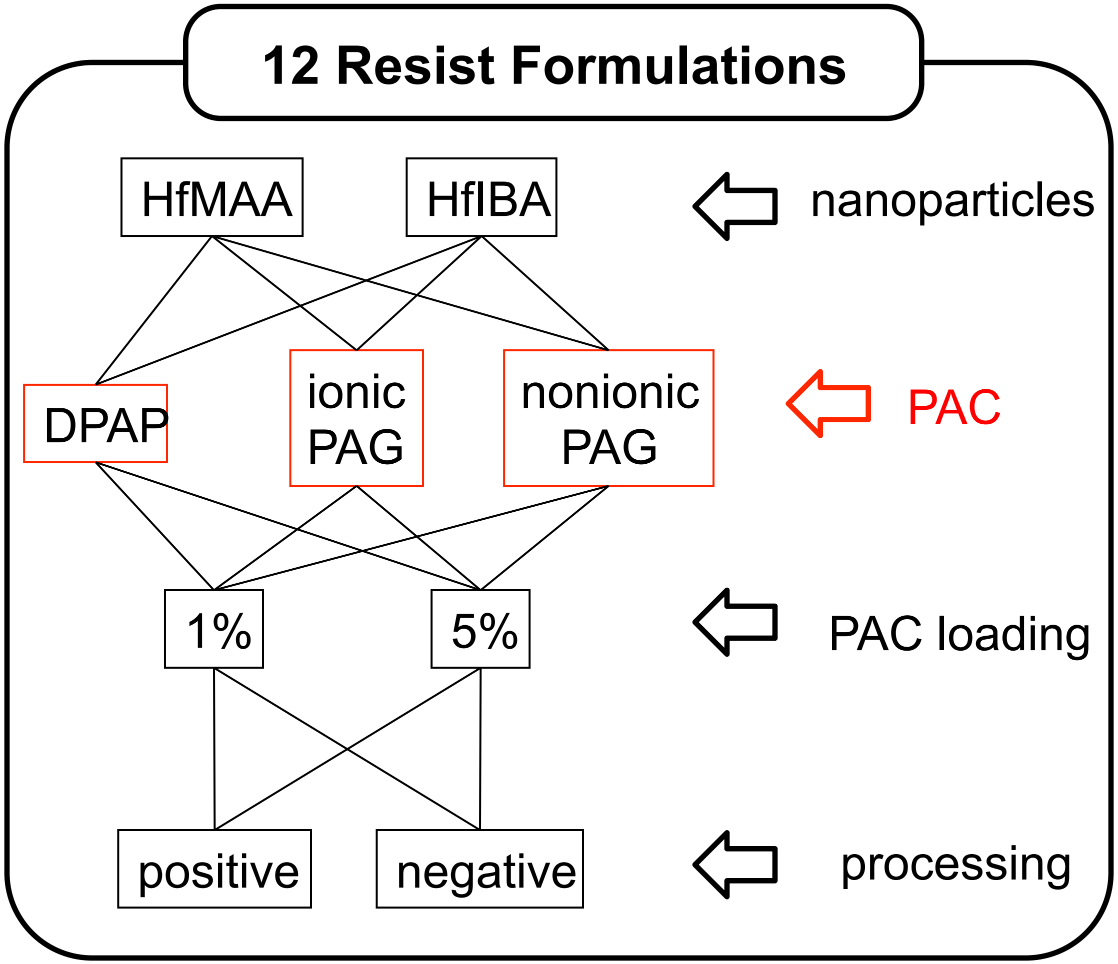
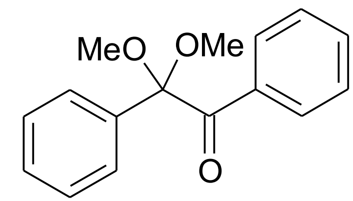
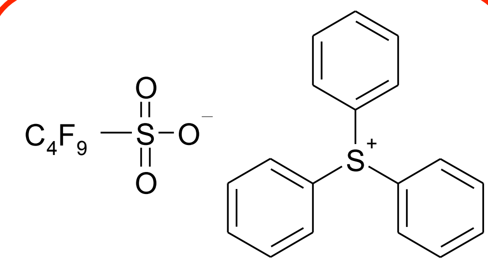
Understanding Patterning



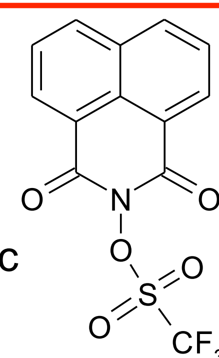


DPAP



ionic PAG

nonionic PAG



To Explain in Proposed Mechanism

- Negative tone
  - Organic alcohol developer, no PEB
  - Photoinitiator or photoacid generator aids ligand crosslinking
  - IR also suggests a change in the bonds corresponding to the binding ligands
- Positive tone
  - Aq. base developer, PEB needed
  - Solubility of unexposed regions is changed with PEB
- Patterning with no double bonds

Negative Tone Process

Spin coating
On bare Si, unprimed, no underlayer. Film thickness 30-120 nm

PAB
110°C / 60s

Exposure

Development
Negative: 4-methyl-2-pentanol (or mixture with PGMEA) (organic alcohol)

NO post exposure bake, organic alcohol developer

Positive Tone Process

Spin coating
On bare Si, unprimed, no underlayer. Film thickness 30-120 nm

PAB
110^{o}C / 60s

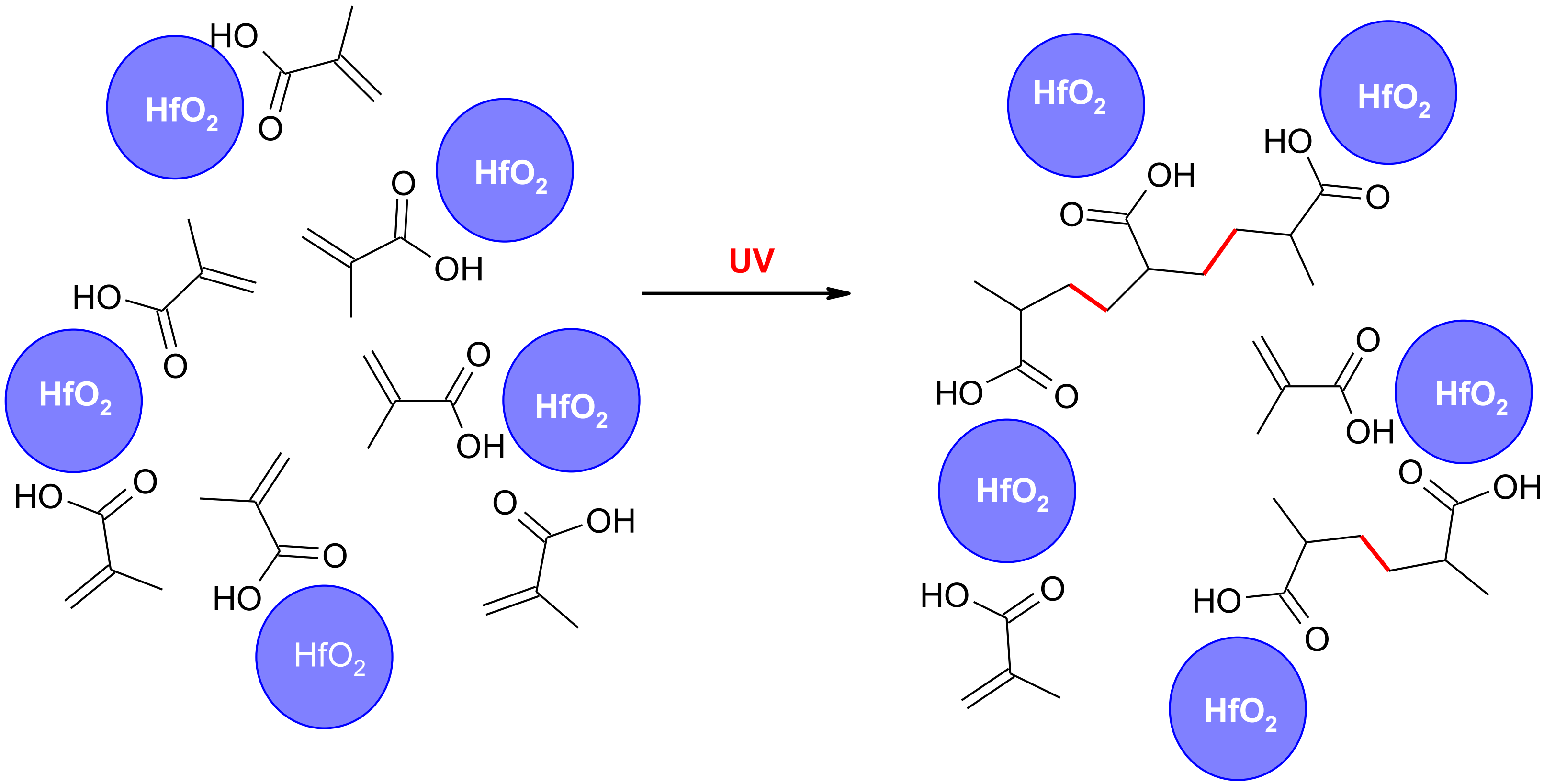
Exposure

PEB
130^{o}C / 3-5 min

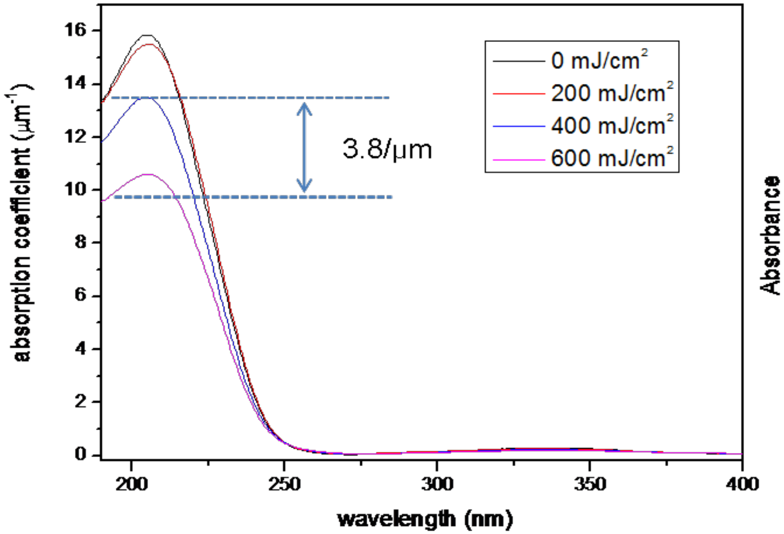
Development
Positive: TMAH (0.1 – 1.0M)
(aqueous base)

post exposure bake, aqueous base developer

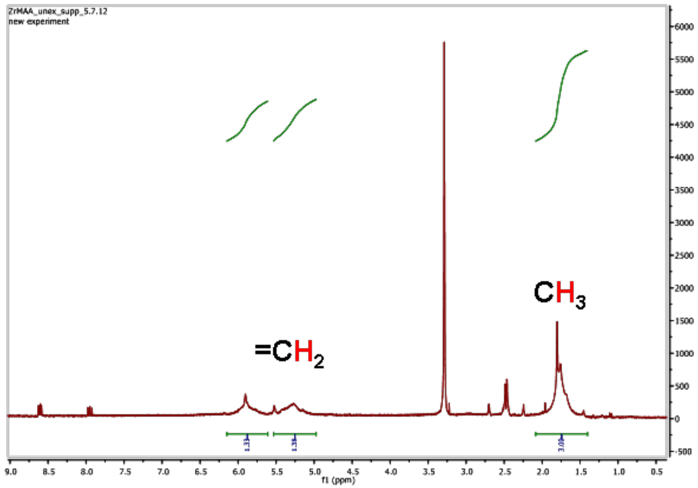
Original Hypothesis – Negative tone cross-linking

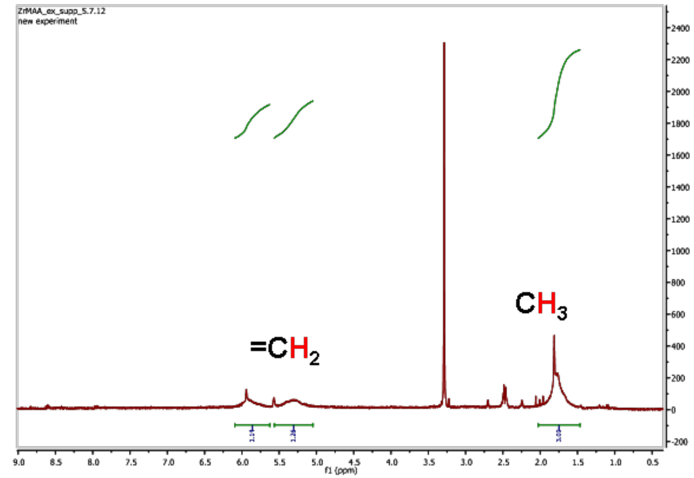


Investigation of cross-linking hypothesis



No change in absorbance with exposure up to 200 mJ/cm^2 - typical exposure doses for patterning



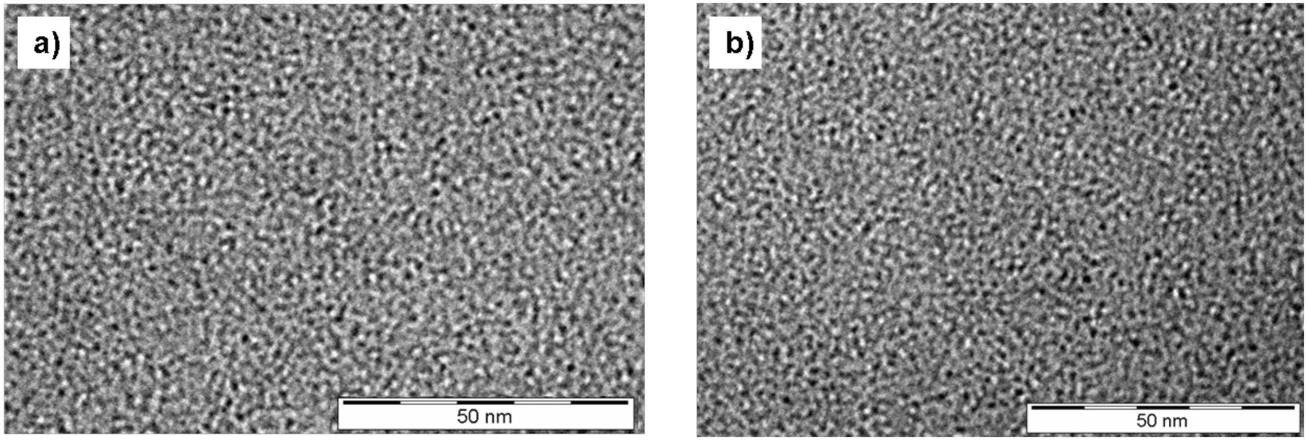


Peak Integrations:	1.29	1.36	3.00	1.17	1.11	3.00

No significant change in the number of double bonds upon exposure

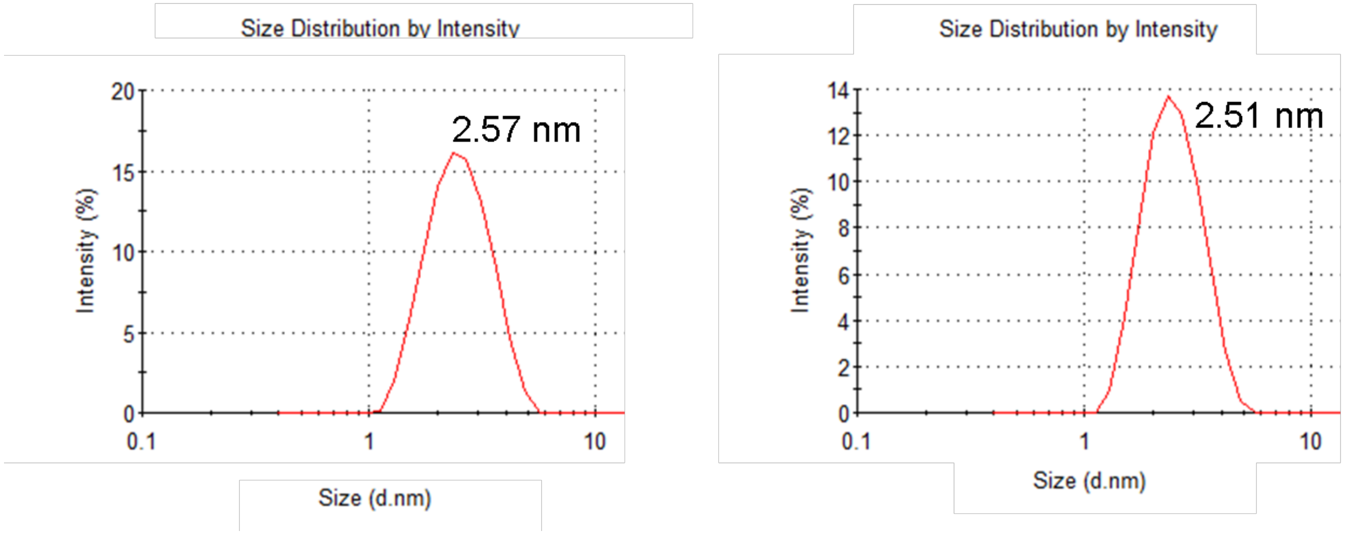
Investigation of Metal Oxide Formation

TEM Analysis – No size change after exposure



Unexposed No PEB

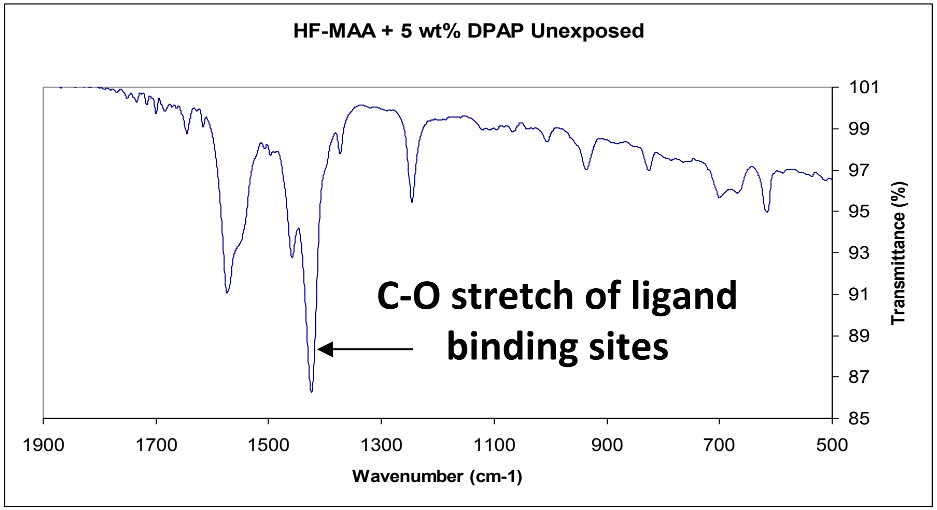
Exposed No PEB

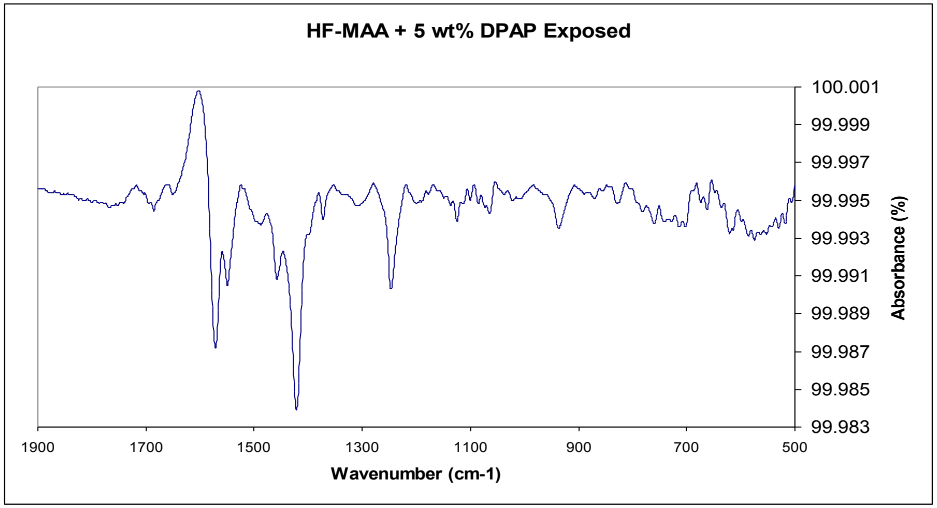


DLS – No size change after exposure

Evidence of Ligand Displacement After Exposure

In-film IR analysis





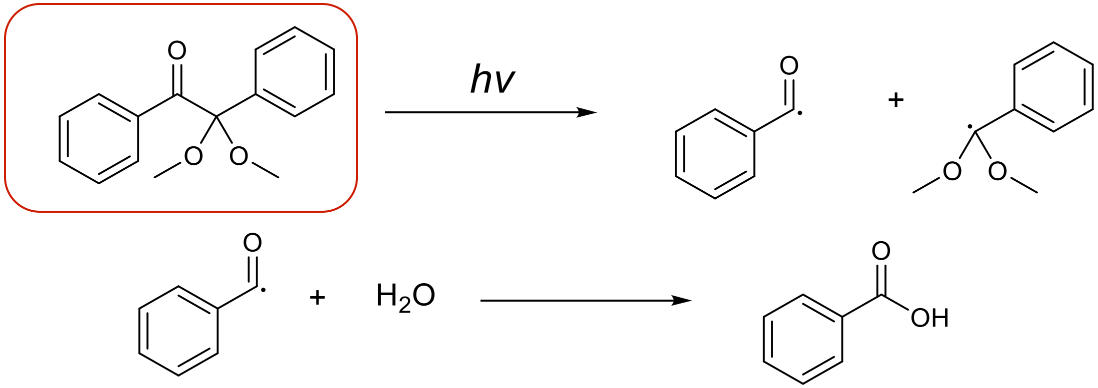
HfO_2-MAA Unexposed Reference Spectrum

HfO_2-MAA Exposed

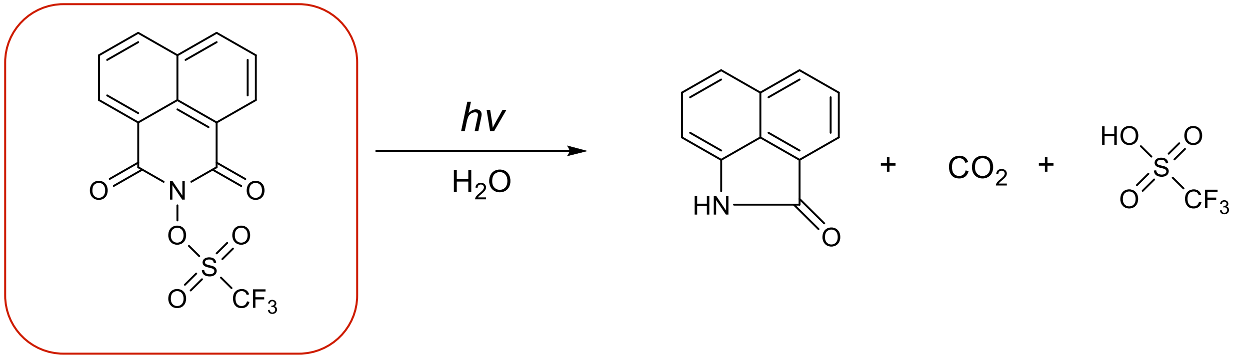
Loss of ligand binding site peaks indicate a change at the ligand/nanoparticle interface

Photoactive Compound Mechanism

Radical Initiator : DPAP (2,2-Dimethoxy-2-phenyl acetophenone)

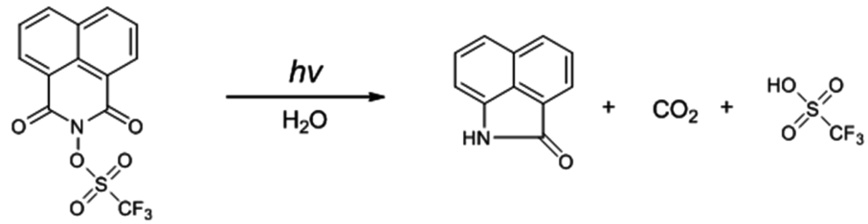


Photoacid Generator (PAG): (N-Hydroxy-naphthalimide triflate)

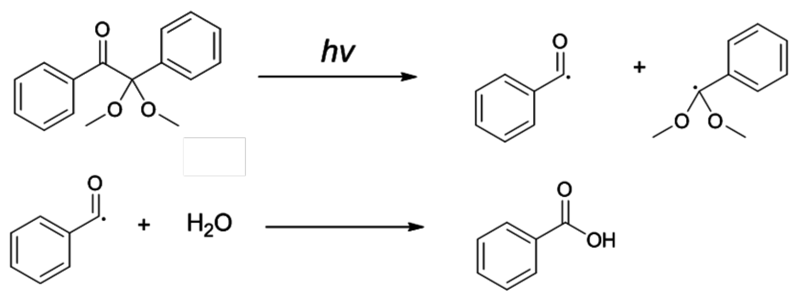


Negative Tone Mechanism Hypothesis

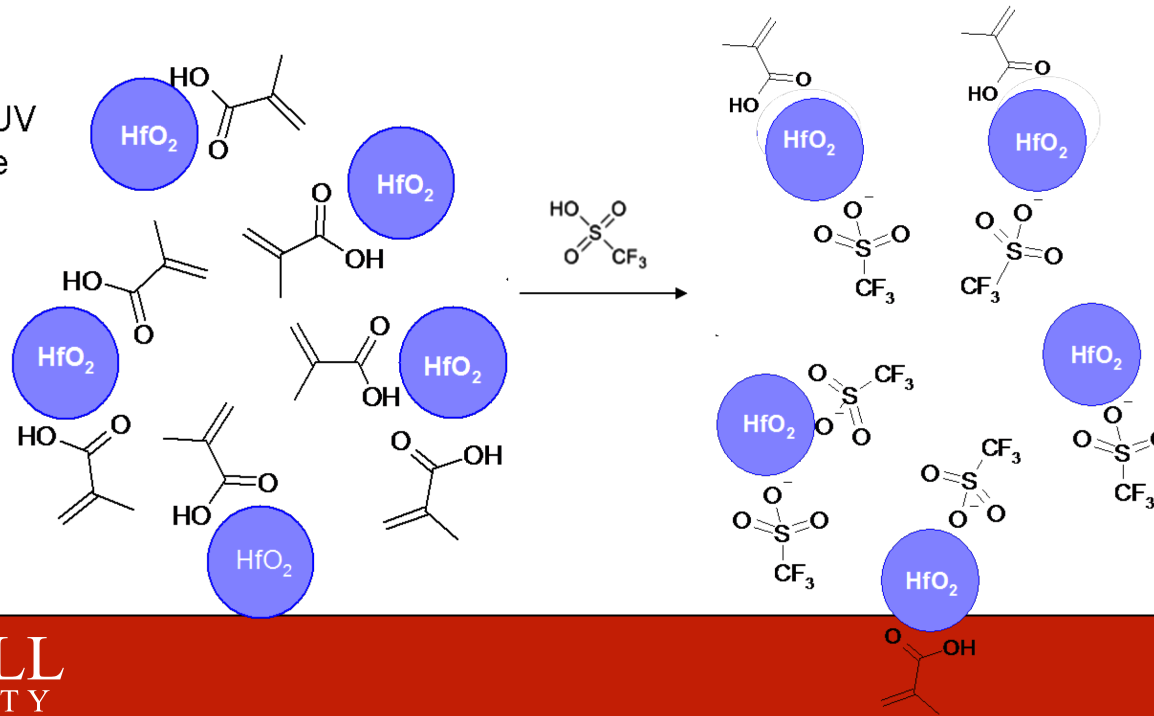
photoacid generator mechanism



photoradical initiator mechanism



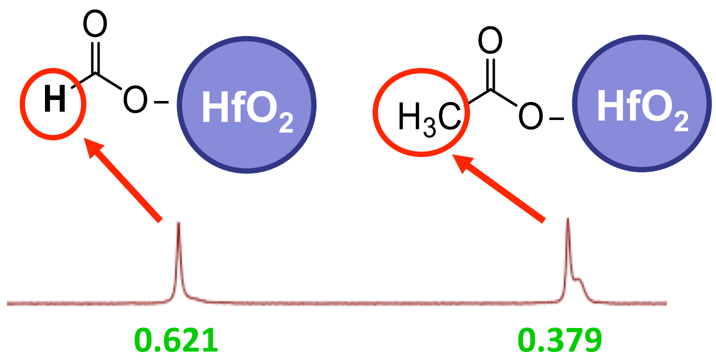
film upon UV exposure



Triflic and benzoic acid can exchange with carboxylic acid, changing the solubility of the nanoparticles

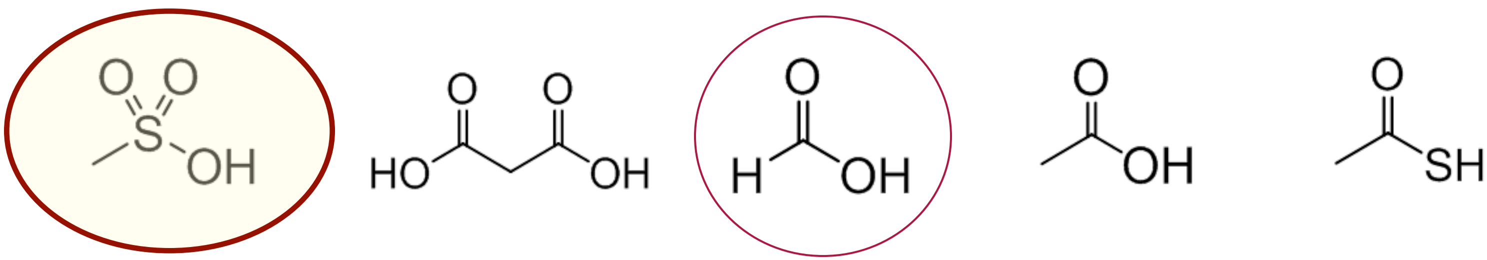
Binding Energies of Various Ligands

Collaboration with Prof. R. Brainard's group at CNSE



Ligand binding studies using ^{1}H NMR

Relative Binding Energies (Kcal/mol) (Relative to Acetic Acid):

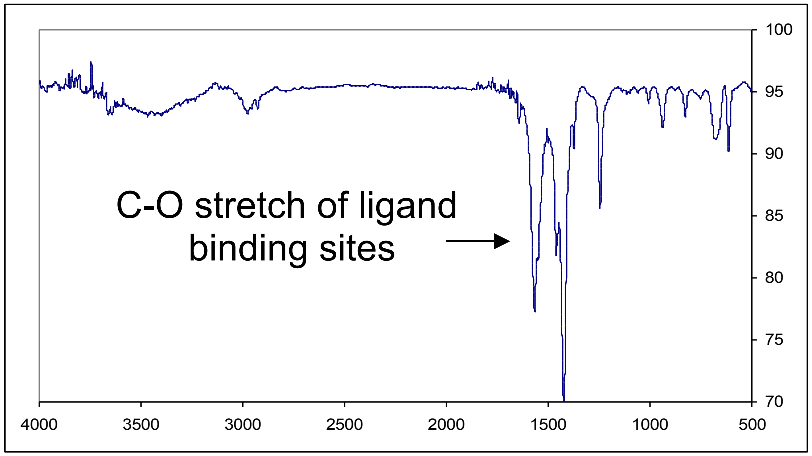


Stronger Binding Ligands

Sulfonic acid binds more strongly than carboxylic acid

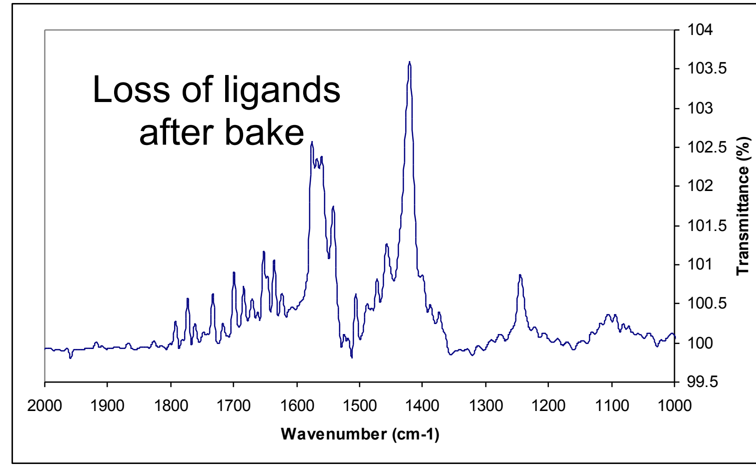
FT-IR Studies Before and After PEB

In-film IR analysis

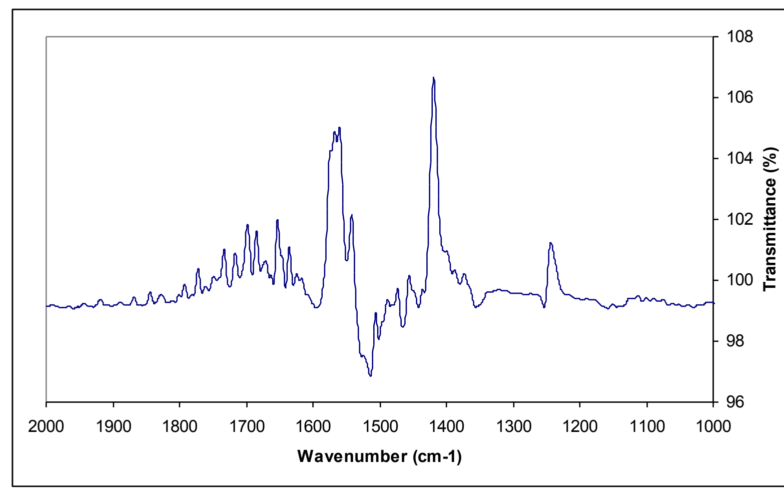


ZrO_2-MAA Unexposed

Higher intensity of ligand loss in unexposed vs. exposed film after PEB

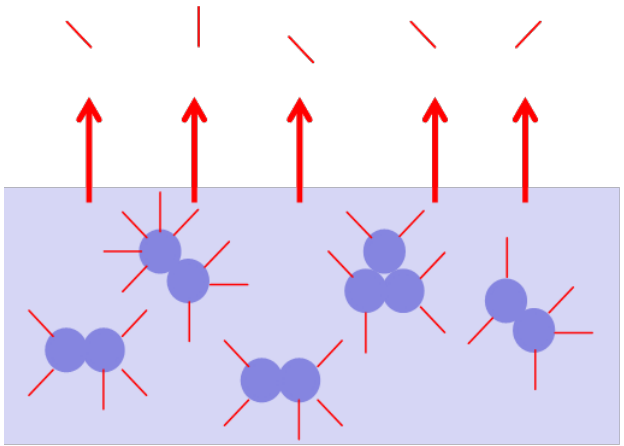


ZrO_2-MAA Exposed + PEB

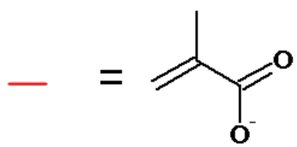


ZrO_2-MAA Unexposed + PEB

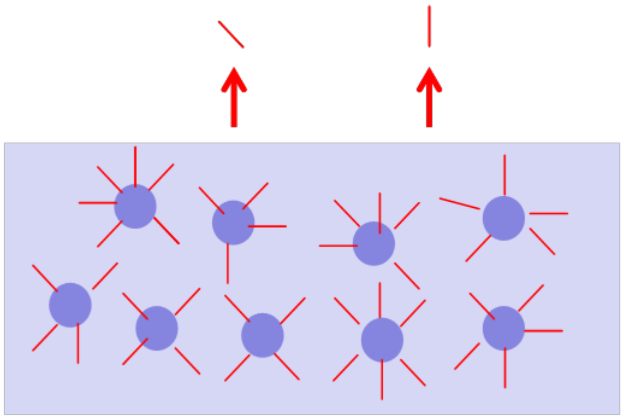
Positive Tone Mechanism Hypothesis



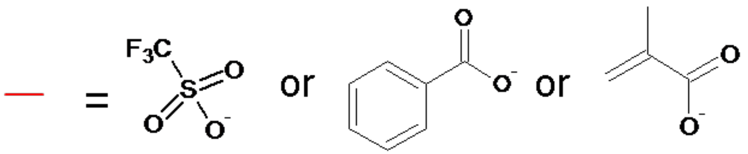
Unexposed



Carboxylic acid ligands leave film during PEB



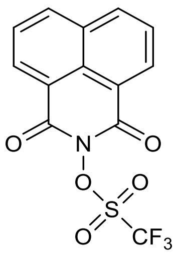
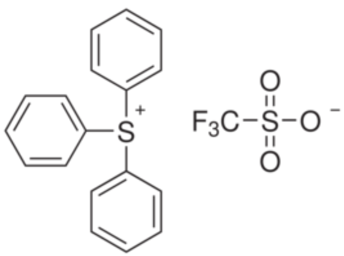
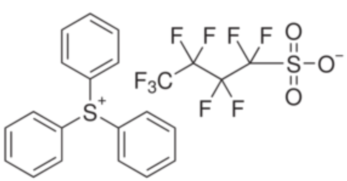
Exposed



Sulfonic acid ligands, which bind more strongly to the metal oxide, do not leave during PEB

Triflic acid and benzoic acid-substituted particles are more soluble in aqueous base than particles in unexposed areas

Effect of PAG on Patterning Ability

PAG	Negative Tone Process	Positive Tone Process
	Negative Tone Patterns	Positive Tone Patterns
	Negative Tone Patterns	**Negative Tone Patterns**
	Negative Tone Patterns	**Negative Tone Patterns**

Ionic PAGs do not produce positive tone patterns

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