Review* of Metallic Resists for EUV

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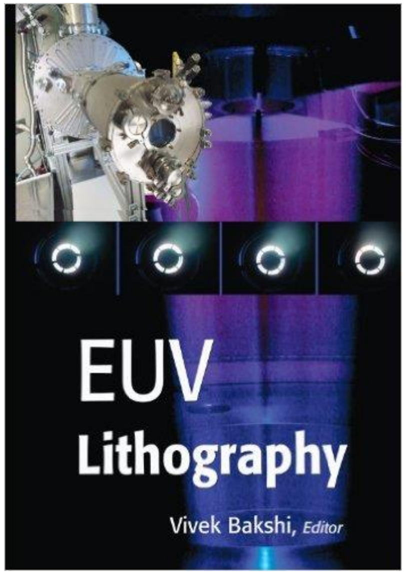
b. Sage College

I. Metal-Oxo Films (OSU/Inpria)
II. HfOx and ZrOx Nanoparticles (Cornell)
III. Molecular Organometallic Resists for EUV (MORE) (SUNY Poly and New Paltz)
    A. Tin Oxo Clusters (Cardineau)
    B. Tin Carboxylates (Del Re)
    C. Transition Metal Oxalates (Freedman)
    D. Positive-Tone Palladium (Sortland)
    E. High-Speed Main-Group Olefins (Passarelli)
IV. Acknowledgements

*For 2nd Edition:



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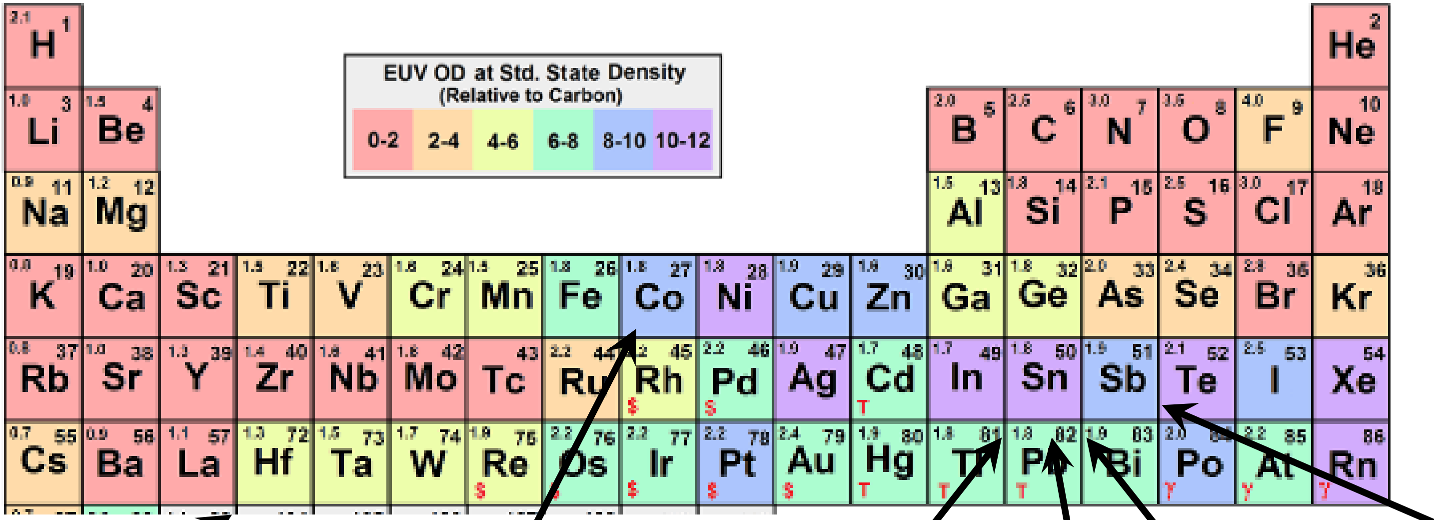
Optical Density Map of the Elements



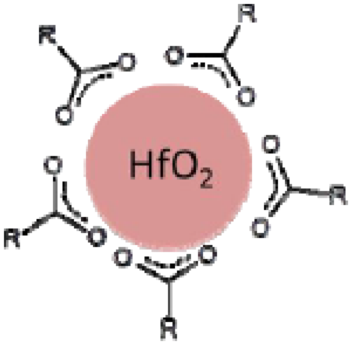
EUV OD at Std. State Density
(Relative to Carbon)

🟥	🟧	🟨	🟩	🟦	🟪
0-2	2-4	4-6	6-8	8-10	10-12

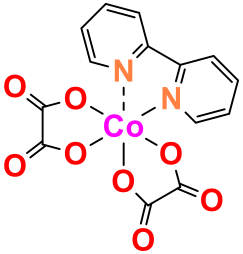
2.1 **H** 1 🟥																	**He** 2 🟥
1.0 **Li** 3 🟥	1.5 **Be** 4 🟥											2.0 **B** 5 🟥	2.5 **C** 6 🟥	3.0 **N** 7 🟥	3.5 **O** 8 🟥	4.0 **F** 9 🟧	**Ne** 10 🟥
0.9 **Na** 11 🟧	1.2 **Mg** 12 🟧											1.5 **Al** 13 🟨	1.8 **Si** 14 🟥	2.1 **P** 15 🟥	2.5 **S** 16 🟥	3.0 **Cl** 17 🟥	**Ar** 18 🟥
0.8 **K** 19 🟥	1.0 **Ca** 20 🟥	1.3 **Sc** 21 🟥	1.5 **Ti** 22 🟧	1.6 **V** 23 🟧	1.6 **Cr** 24 🟨	1.5 **Mn** 25 🟨	1.8 **Fe** 26 🟩	1.8 **Co** 27 🟦	1.8 **Ni** 28 🟪	1.9 **Cu** 29 🟦	1.6 **Zn** 30 🟦	1.6 **Ga** 31 🟨	1.8 **Ge** 32 🟨	2.0 **As** 33 🟧	2.4 **Se** 34 🟧	2.8 **Br** 35 🟥	**Kr** 36 🟧
0.8 **Rb** 37 🟥	1.0 **Sr** 38 🟥	1.2 **Y** 39 🟥	1.4 **Zr** 40 🟥	1.6 **Nb** 41 🟥	1.8 **Mo** 42 🟥	**Tc** 43 🟥	2.2 **Ru** 44 🟧	2.2 **Rh** 45 $ 🟨	2.2 **Pd** 46 $ 🟩	1.9 **Ag** 47 🟪	1.7 **Cd** 48 T 🟩	1.7 **In** 49 🟪	1.8 **Sn** 50 🟪	1.9 **Sb** 51 🟦	2.1 **Te** 52 🟪	2.5 **I** 53 🟦	**Xe** 54 🟪
0.7 **Cs** 55 🟧	0.9 **Ba** 56 🟥	1.1 **La** 57 🟥	1.3 **Hf** 72 🟨	1.5 **Ta** 73 🟨	1.7 **W** 74 🟨	1.9 **Re** 75 $ 🟨	2.2 **Os** 76 $ 🟩	2.2 **Ir** 77 $ 🟩	2.2 **Pt** 78 $ 🟦	2.4 **Au** 79 $ 🟩	1.9 **Hg** 80 T 🟩	1.8 **Tl** 81 T 🟩	1.8 **Pb** 82 T 🟩	1.9 **Bi** 83 🟩	2.0 **Po** 84 γ 🟦	2.2 **At** 85 γ 🟩	**Rn** 86 γ 🟪

Inpria HafSOx

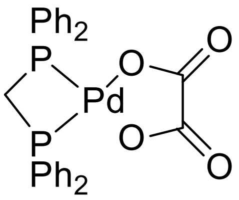
Super-Fast Nanoparticles



Negative Tone

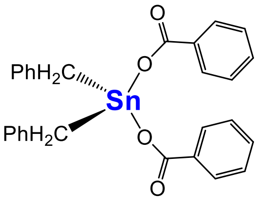


Positive Tone

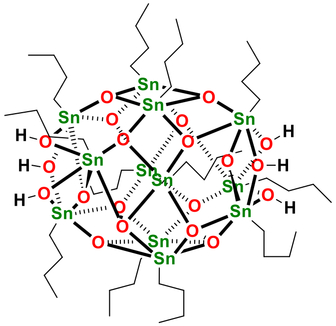


Inpria SnOx

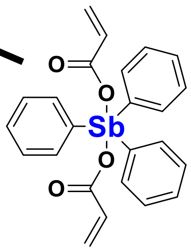
Super-Low LER



Tin-Oxo Cluster



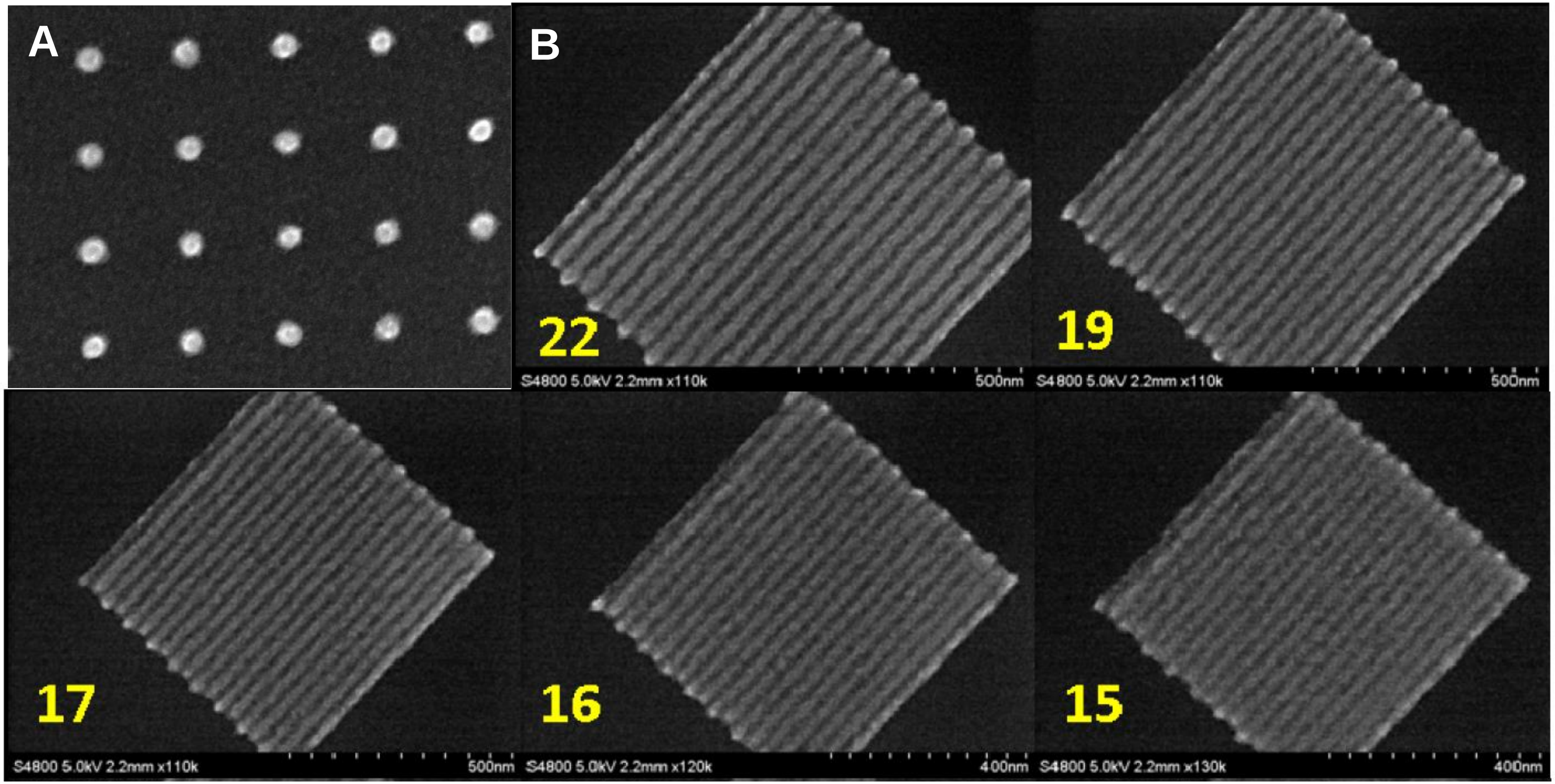
Super-Fast



Cardineau & Brainard MicElec 127 (2014) 44

I. Metal-Oxo Films (OSU/Inpria)

First Publication of EUV Results. BMET SPIE 2010



Naulleau & Anderson SPIE 2010 76361J1

I. Metal-Oxo Films (OSU/Inpria)

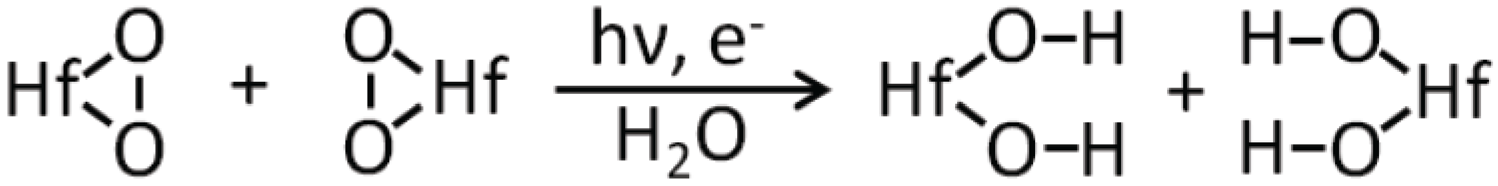
Published Photoreactivity

The key to the photoreactivity of the HafSOx resists appears to be controlling the dehydration reaction (eq 1) which crosslinks and thereby reduces the solubility of these metal oxo-films. Dehydration is prevented by binding peroxide to Hf. Fortunately, the metal peroxide decomposition can be induced by high-energy light or electrons (eq 2) thereby creating metal hydroxides that can condense and become insoluble.

In brief, the metal peroxides allow the resists to dissolve in the unexposed regions and upon photolysis the metal peroxides become metal hydroxides and condense to become insoluble features of the negative-tone resists.

$$\mathrm{Hf-OH} \;+\; \mathrm{HO-Hf} \longrightarrow \mathrm{Hf-O-Hf} + \mathrm{H_2O}$$

(1)

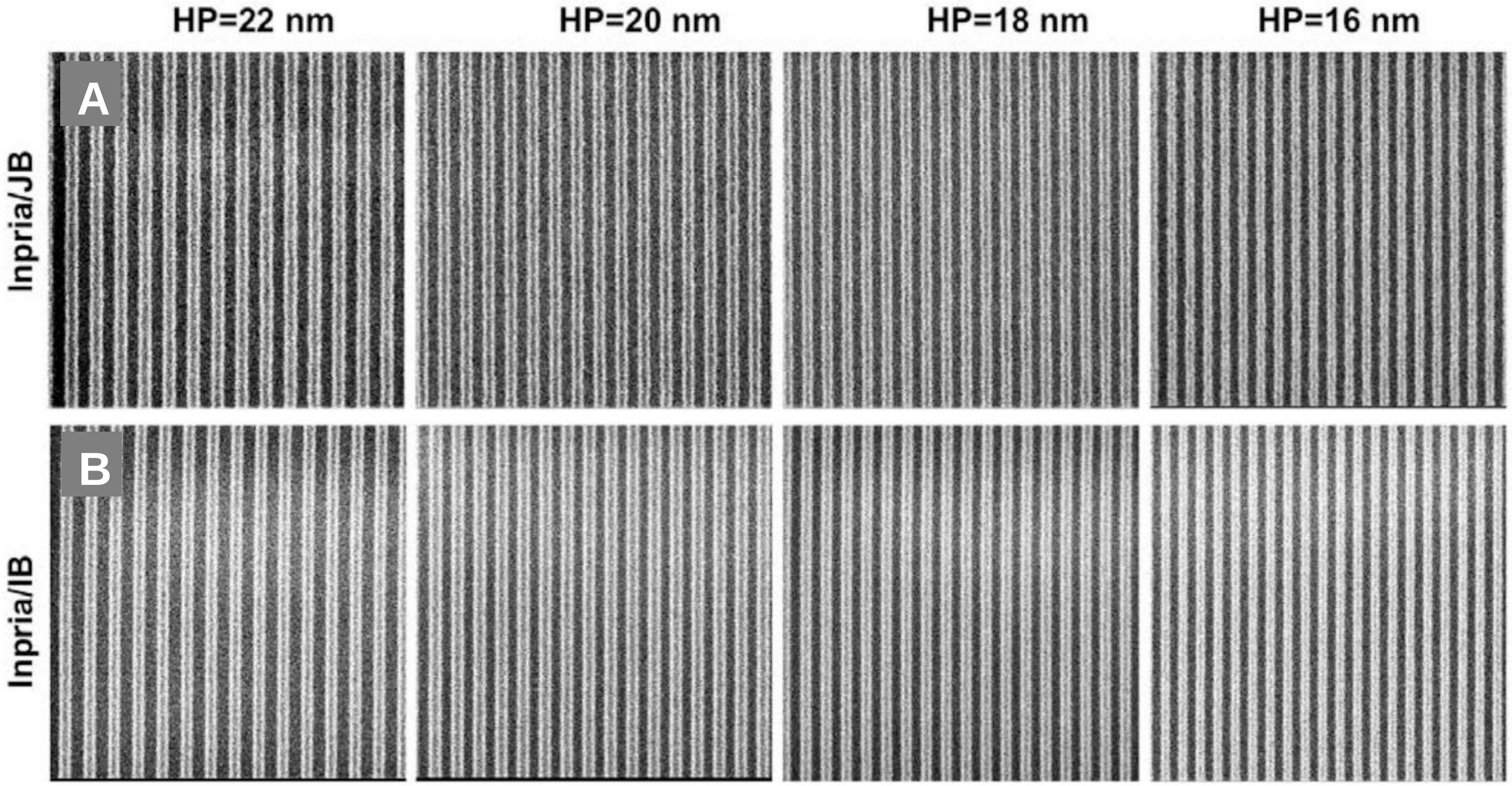


(2)

Amador & Keszler SPIE 2014 90511A

I. Metal-Oxo Films (OSU/Inpria)

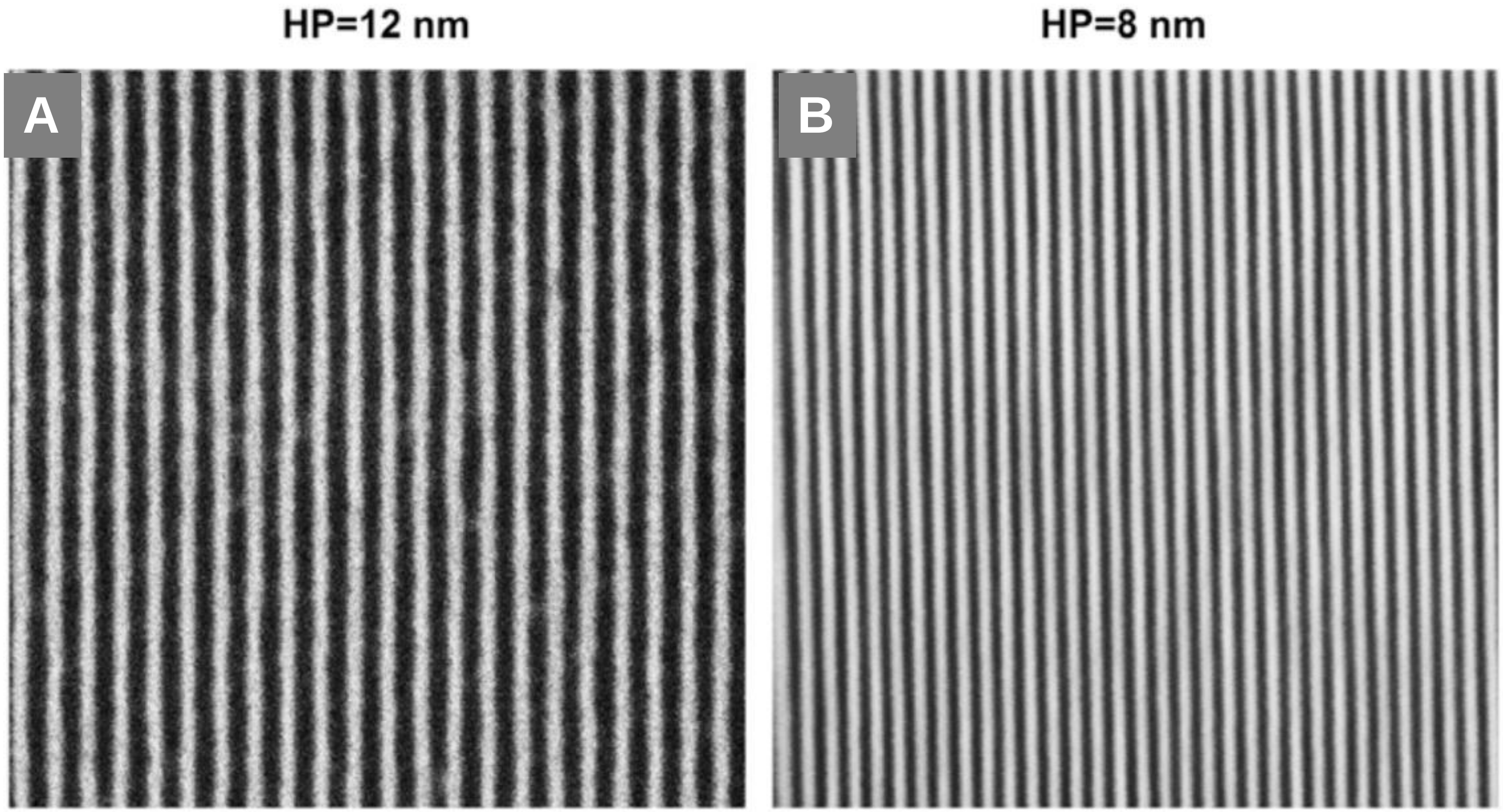
Imaging at PSI (2014)



Ekinci & Vockenhuber SPIE 2014 904804

I. Metal-Oxo Films (OSU/Inpria)

Imaging at PSI (2014)



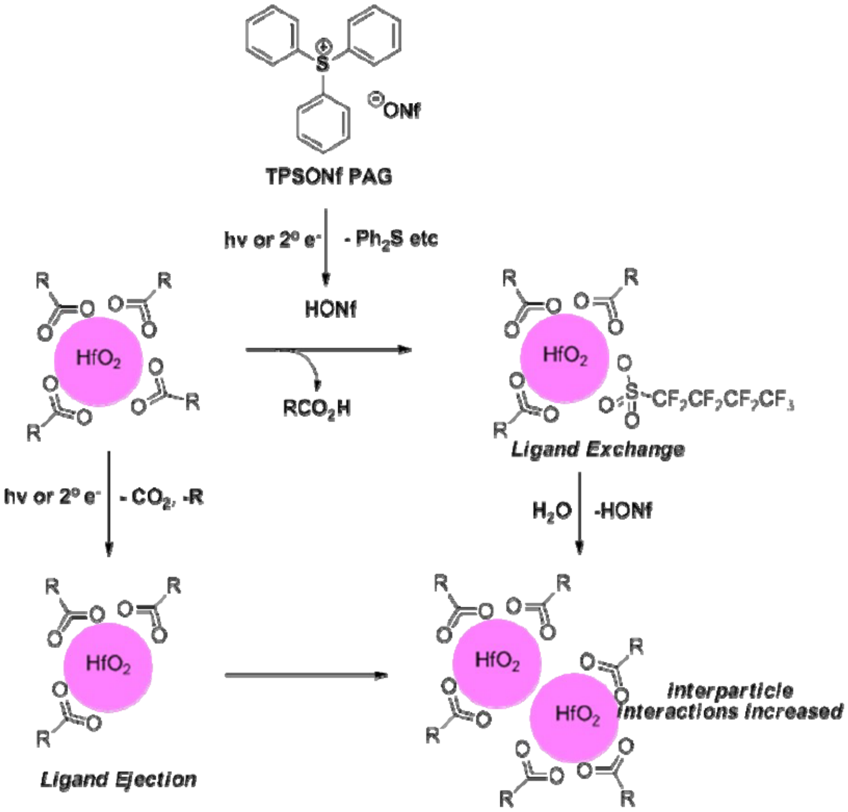
Ekinci & Vockenhuber SPIE 2014 904804

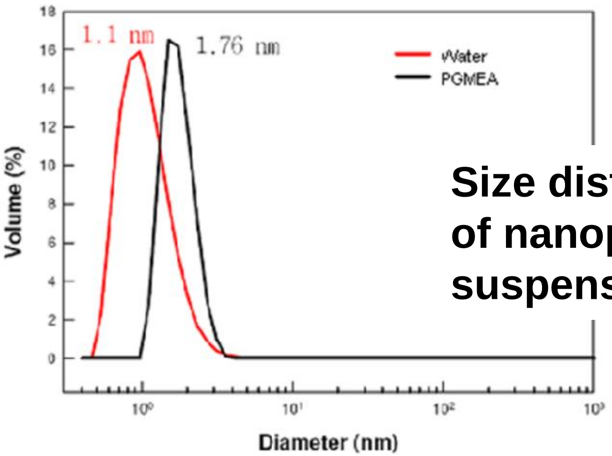
II. HfOx and ZrOx Nanoparticles

(Cornell)

Many versions of these resists were prepared using methacrylate as a ligand and formulated with either photoacid generators or free-radical initiators, suggesting that the negative-tone imaging mechanisms might involve free-radical crosslinking.

However, careful studies revealed that the negative-tone solubility switches do not involve free-radical crosslinking, but instead involves a ligand exchange mechanism that can proceed without PAGs or with the assistance of PAGs.





Size distribution of nanoparticle suspensions

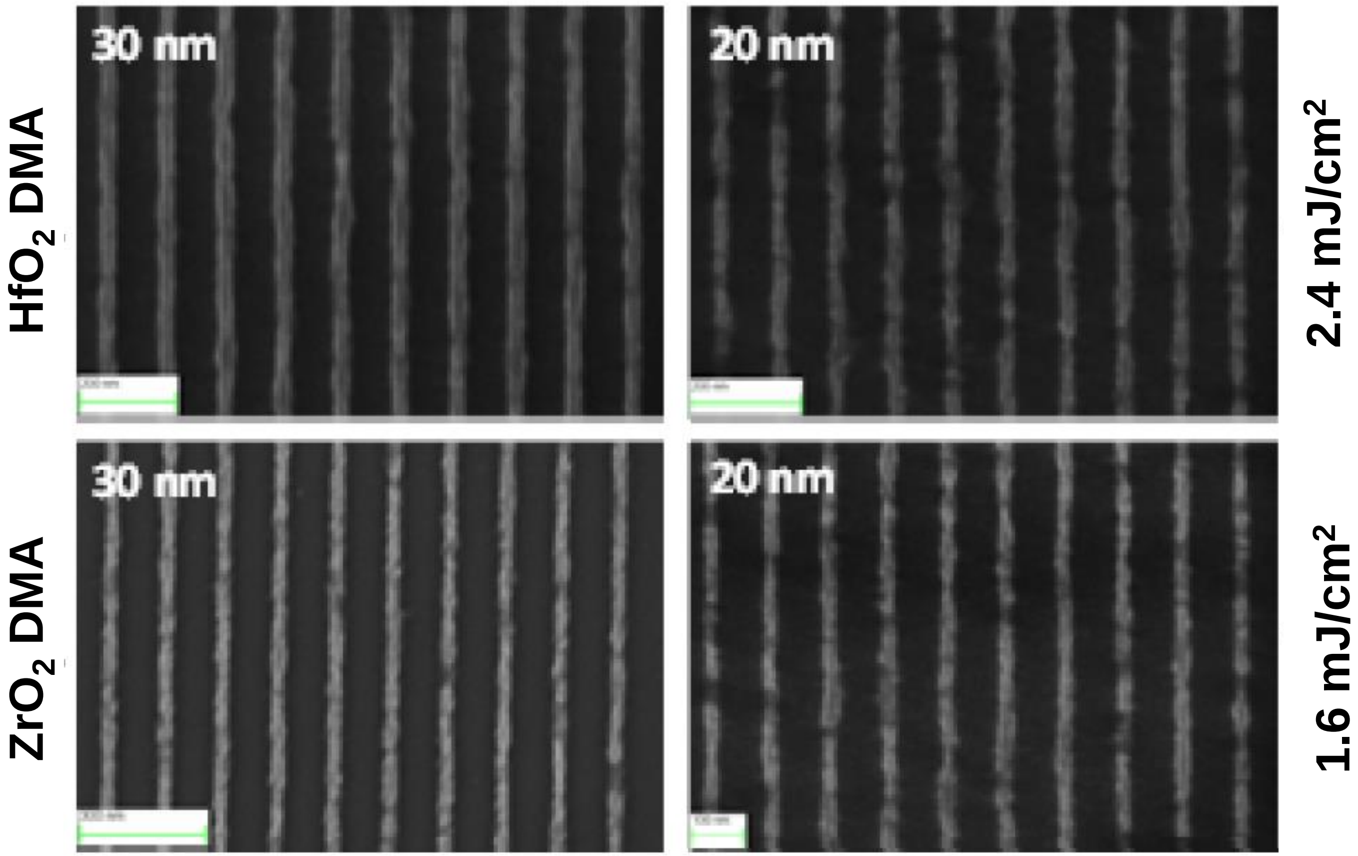
Trikeriotis SPIE 2010 76390E2

Krysak & Ober SPIE 2014 904805-5

II. HfOx and ZrOx Nanoparticles (Cornell)

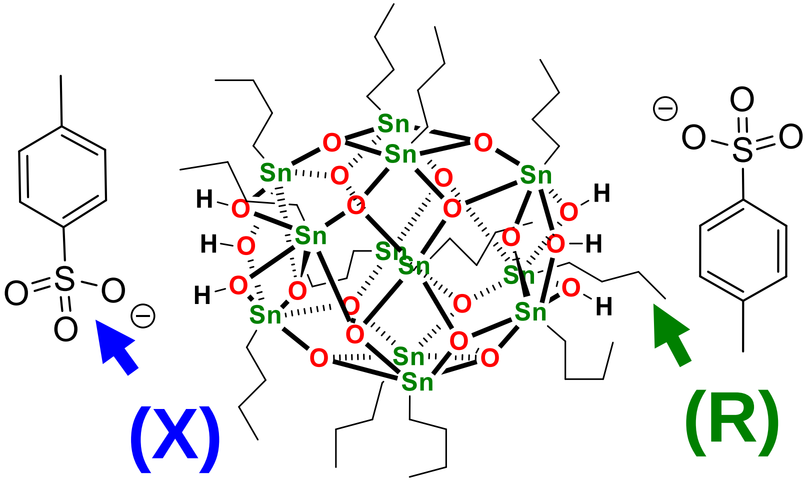
These nanoparticle resists are capable of good EUV patterning capability at extremely fast photospeeds. 20 and 30 nm isolated lines were printed using doses of 2.4 and 1.6 mJ/cm^2.

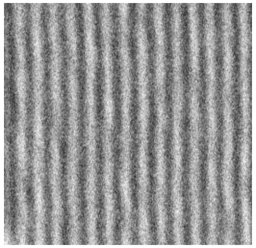
Although the LER values of these resists are modest (5-7 nm), the LER is not too poor considering that the resists are extremely sensitive and are composed of nanoparticles that are 1-2 nm in diameter.



Jiang & Ober JPST 2014 27, 663

III. MORE: A. Tin Oxo Clusters (Cardineau)

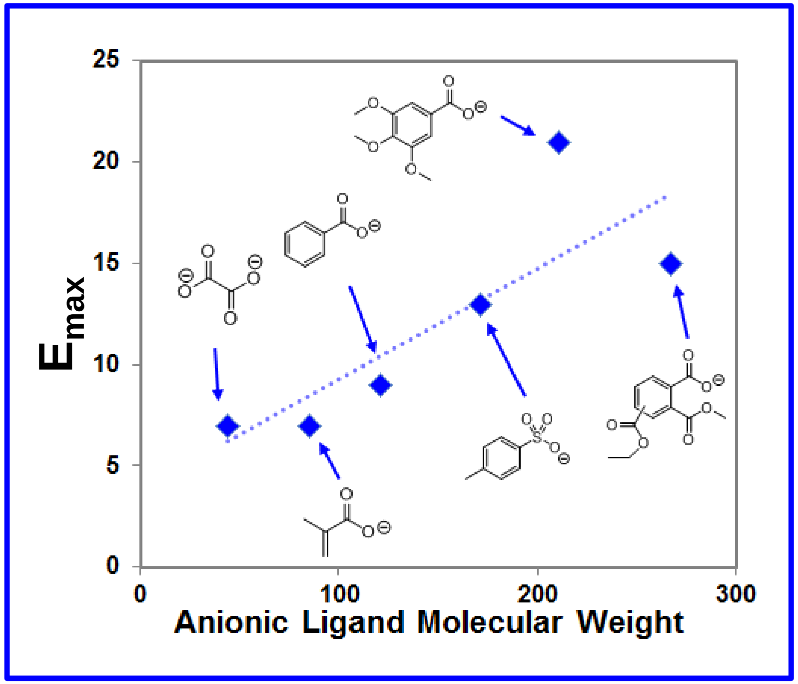




$[(PhSn)_{12}O_{14}(OH)_6]Cl_2$

Dose: 350 mJ/cm^2

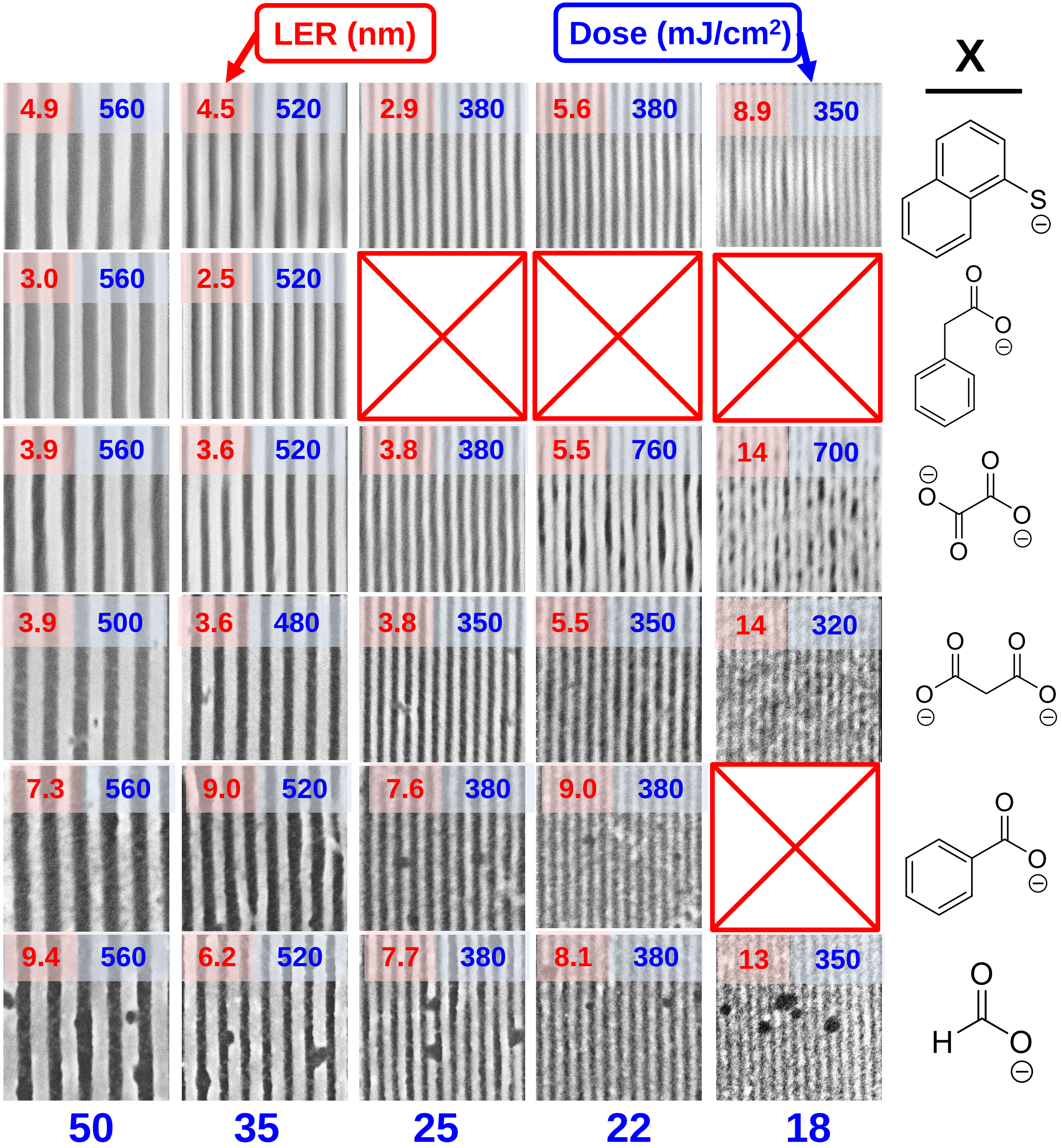
Resolution: 18 nm



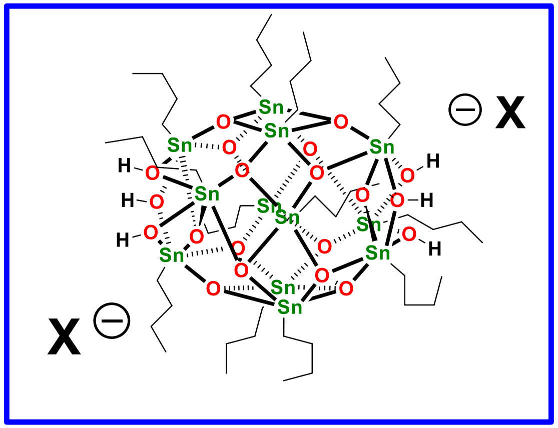
The resist sensitivity shows good correlation with anion size.

Cardineau & Brainard MicElec 127 (2014) 44

Resolution Capabilities for Various Anions.



h/p CD (nm)



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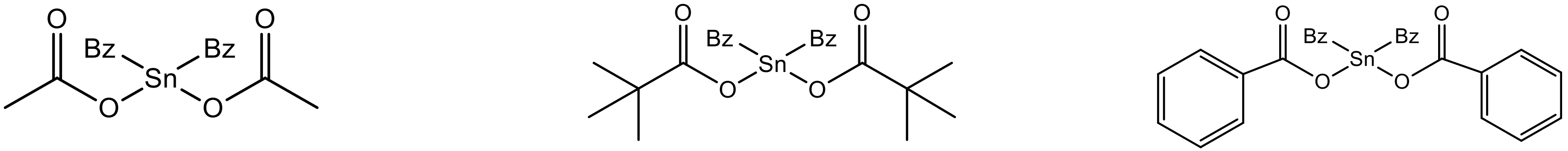
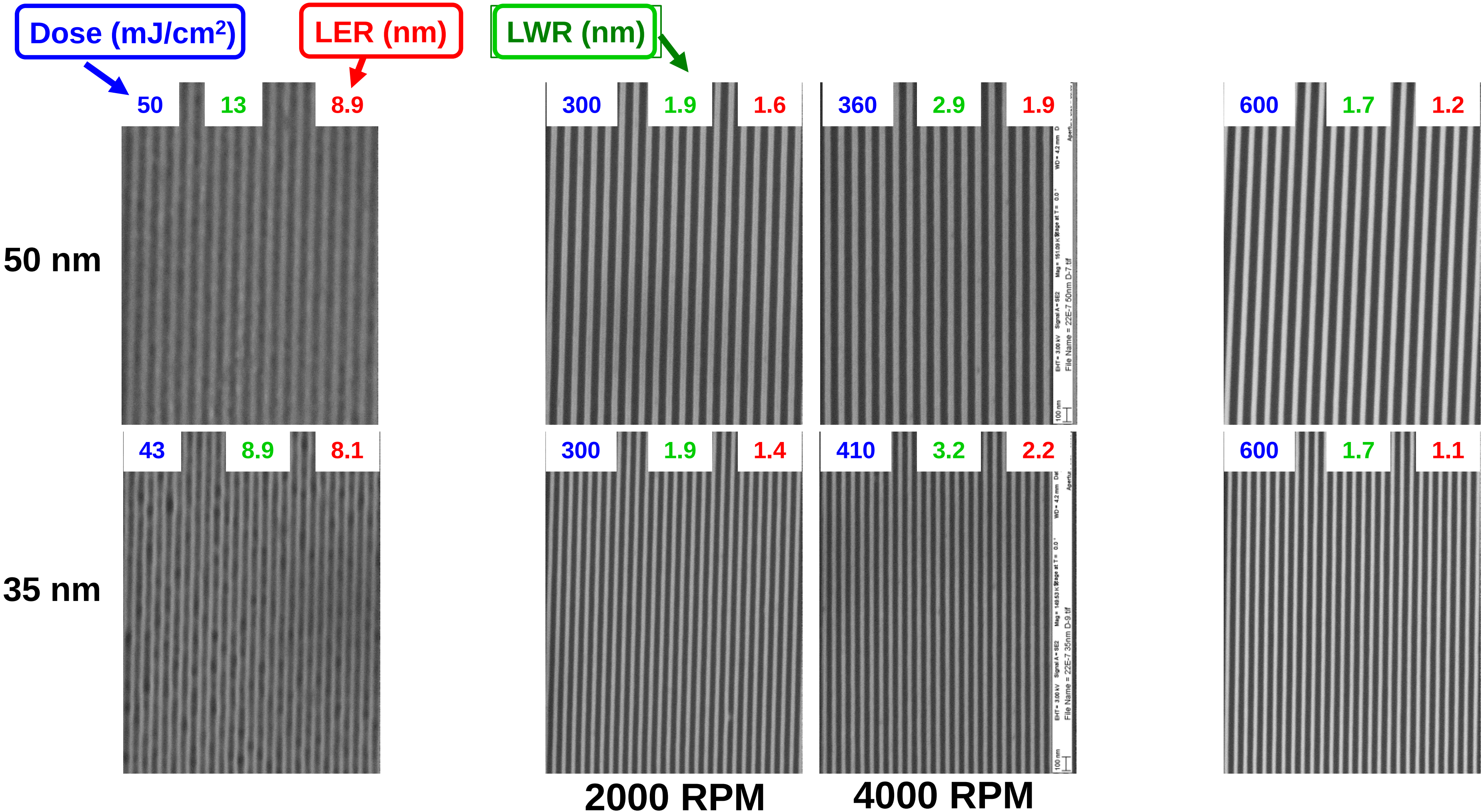
II. MORE: B. Low LER Tin Resists (Del Re)




Dose (mJ/cm²)

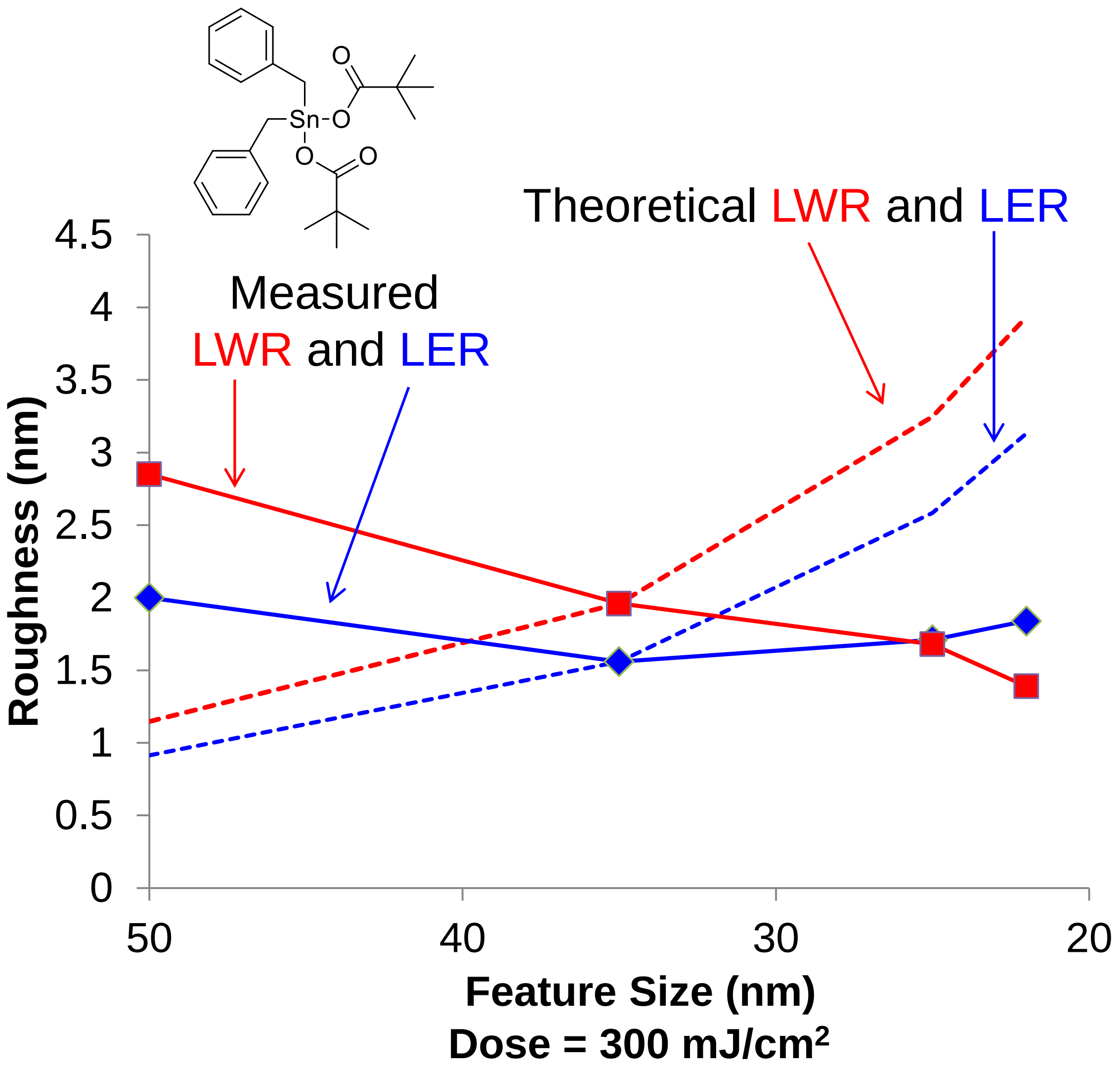
LER (nm)

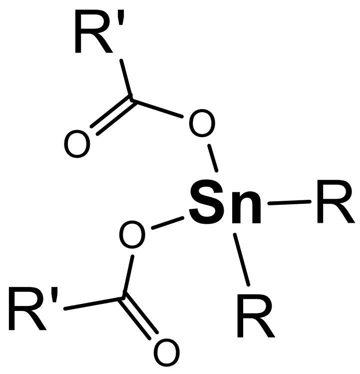
LWR (nm)

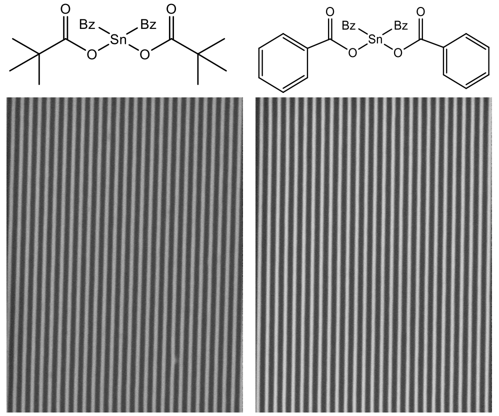
Del Re & Brainard JM3 2015 043506

II. MORE: B. Low LER Tin Resists (Del Re)

LER Does Not Follow Z Parameter



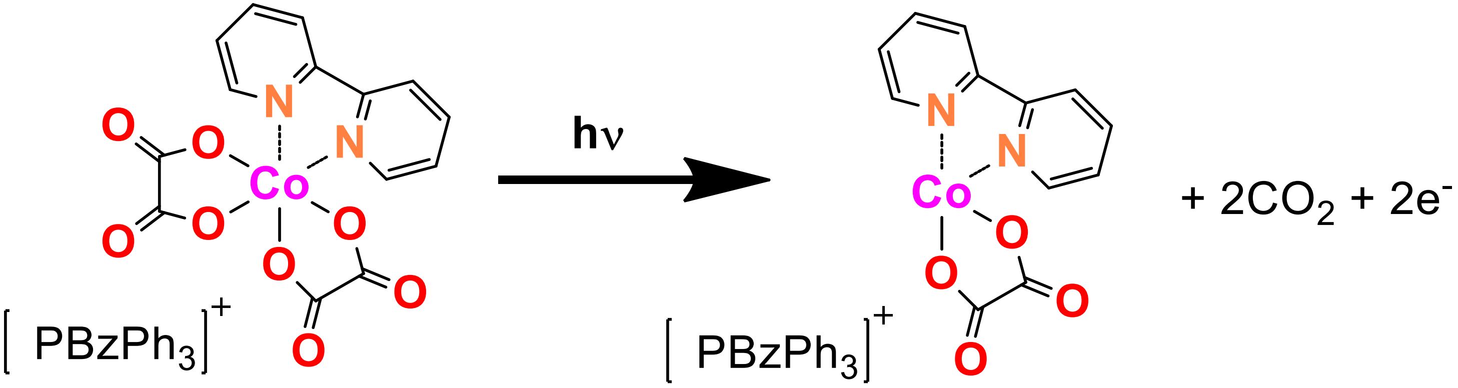




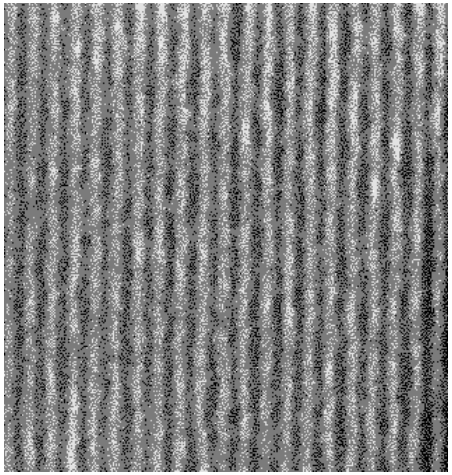
CD:	35 nm	35 nm
LER:	**1.4 nm**	**1.1 nm**
LWR:	**1.9 nm**	**1.7 nm**

Del Re & Brainard JM3 2015 043506

III. MORE: C. Transition Metal Oxalates (Freedman)

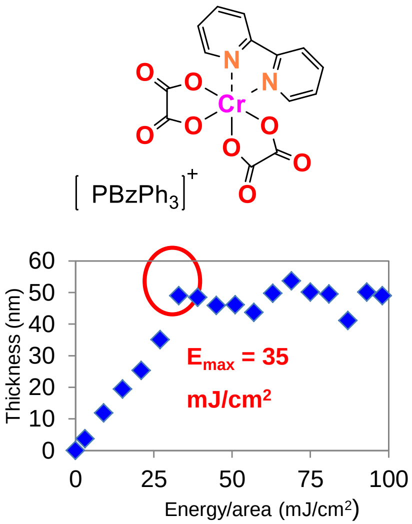


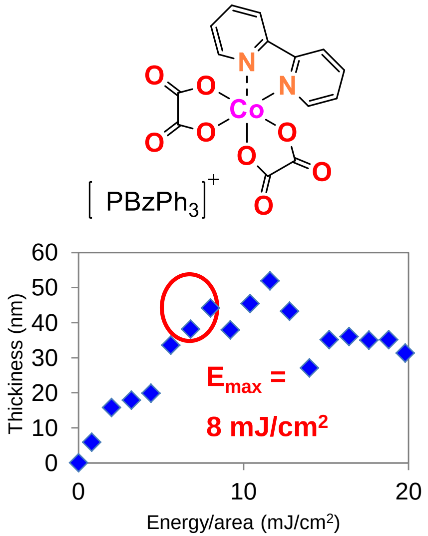
18 nm
30 mJ/cm^2

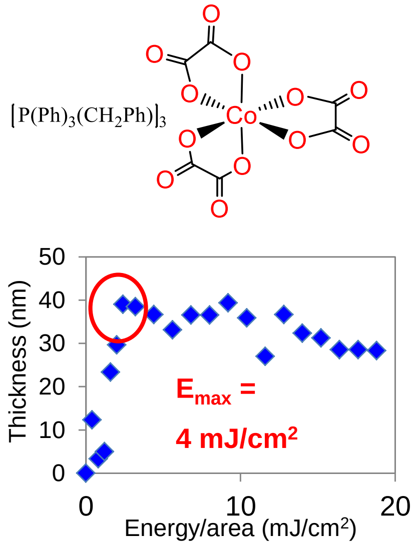


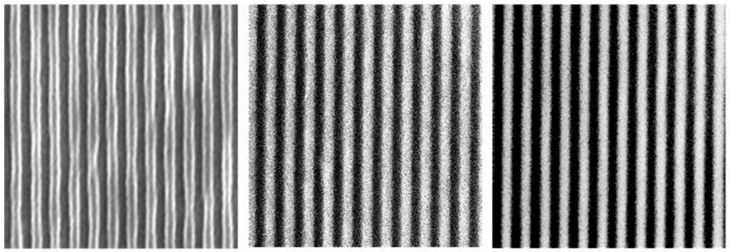
Freedman & Brainard SPIE 2014

III. MORE: C. Transition Metal Oxalates (Freedman)

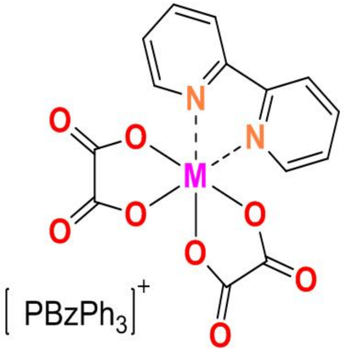






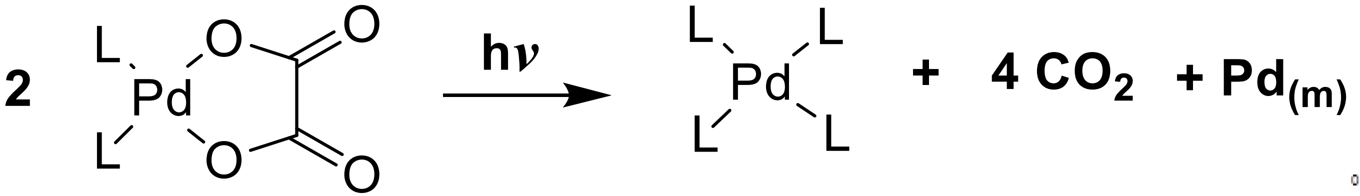


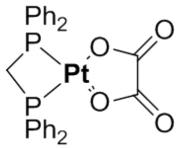
Central Metal (M):	Cr	Fe	Co
35 nm h/p lines:			
E_{size} (mJ/cm²):	70	48	27



Freedman & Brainard SPIE 2014

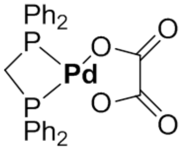
III. MORE: D. Positive-Tone Palladium Resists (Sortland)





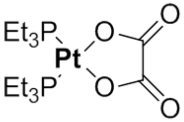
21

247 mJ/cm²



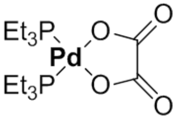
23

54 mJ/cm²



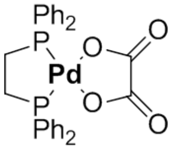
24

157 mJ/cm²



25

110 mJ/cm²



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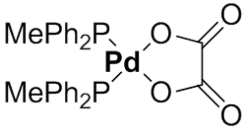
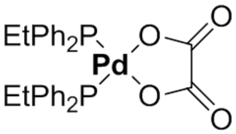
110 mJ/cm²



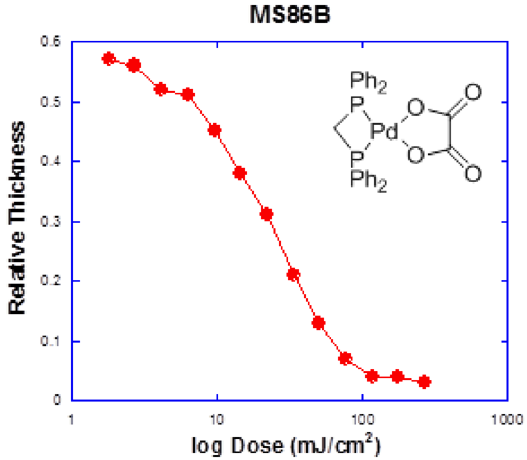
26

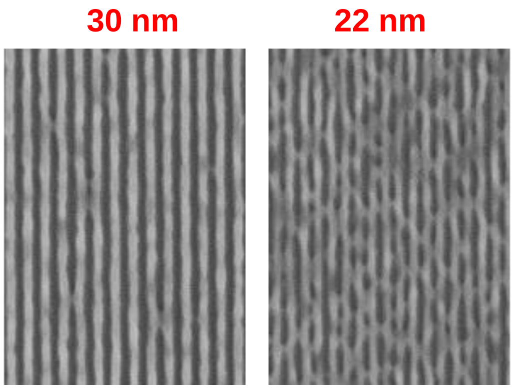
35 mJ/cm²



27

71 mJ/cm²





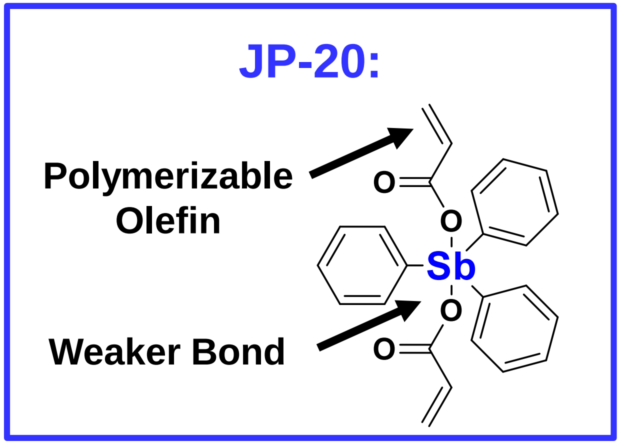
E_{size} = 50 mJ/cm²

Sortland & Brainard JM3 2015 043511

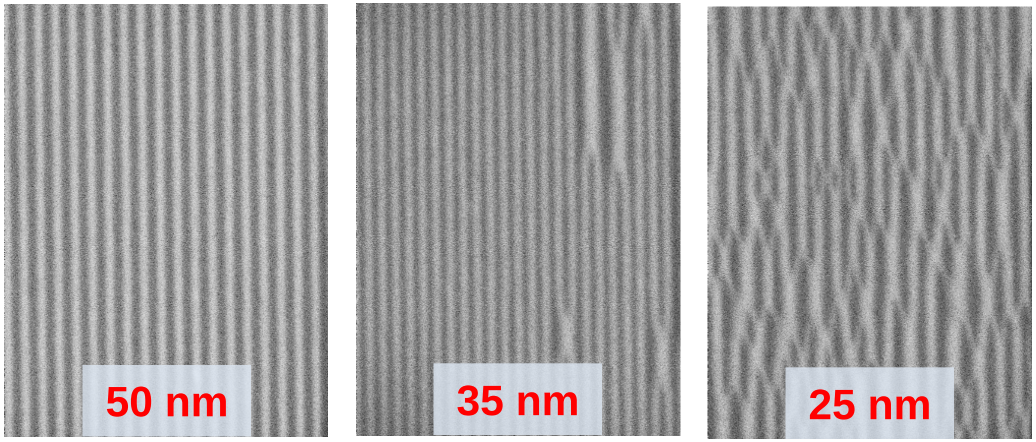
SUNY POLYTECHNIC INSTITUTE

III. MORE: E. High-Speed Main-Group Olefins (Passarelli)

Excellent sensitivity at modest resolution.



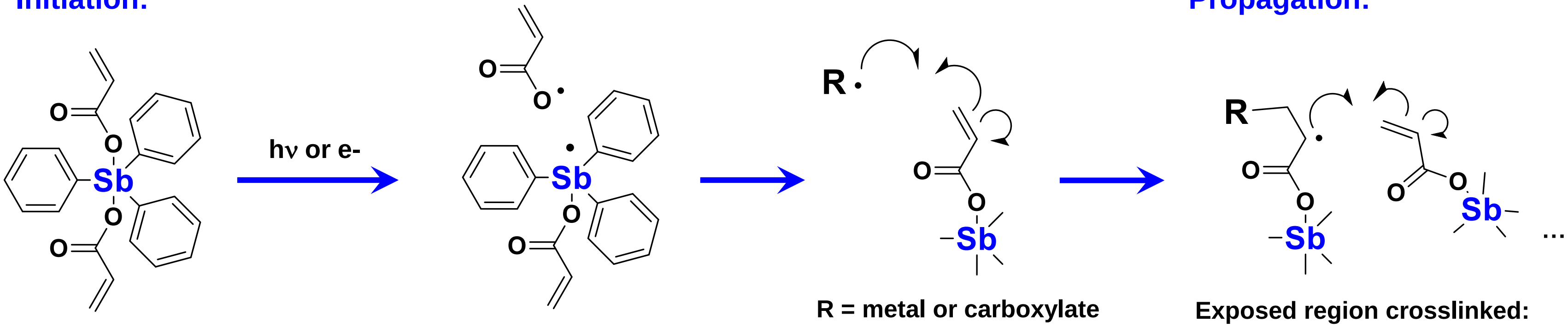
Dose = 5.6 mJ/cm^2



Proposed mechanism is based on photo-initiated free radical polymerization.

Initiation:

Propagation:



JP-20

R = metal or carboxylate centered radicals

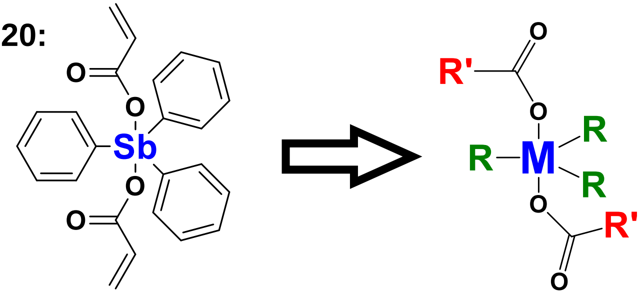
Exposed region crosslinked: less soluble in developer

EUV Symposium 6/16
Brainard and Brainard

Passarelli & Brainard JM3 2015 043503

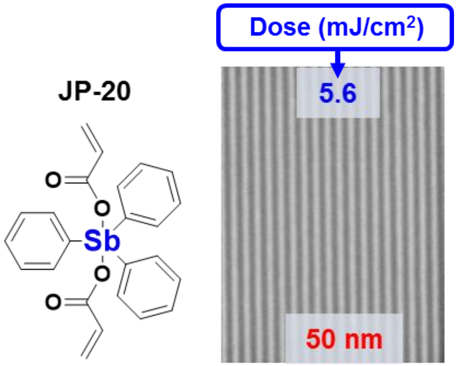
III. MORE: E. High-Speed Main-Group Olefins (Passarelli)

JP-20:

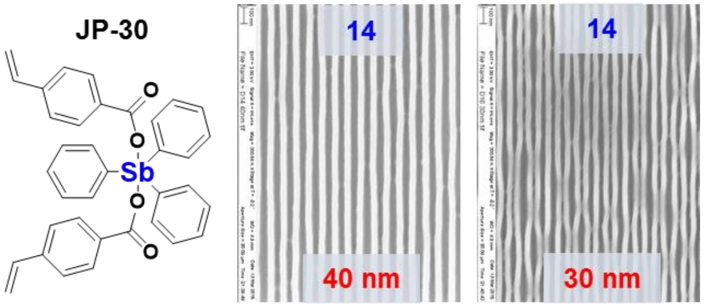


$\mathbf{M}$ = Sb, Bi, Sn or Te
R = Aliphatic or Aromatic Sb - C Group
O_2CR' = Carboxylate Group

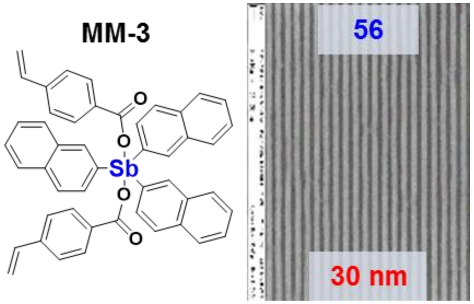
JP-20



JP-30



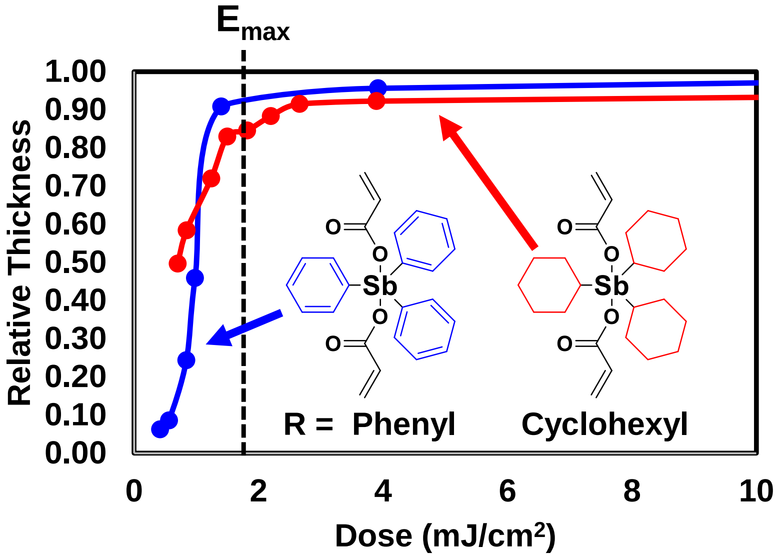
MM-3

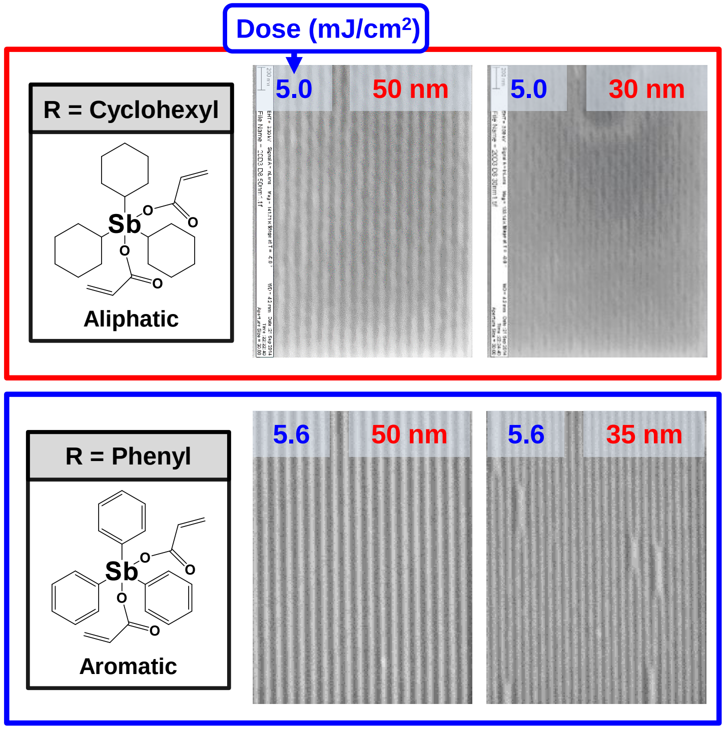


Passarelli & Brainard JM3 2015 043503

III. MORE: E. High-Speed Main-Group Olefins (Passarelli)

Unexpected Result: Changing Sb-R bond did not dramatically affect sensitivity.



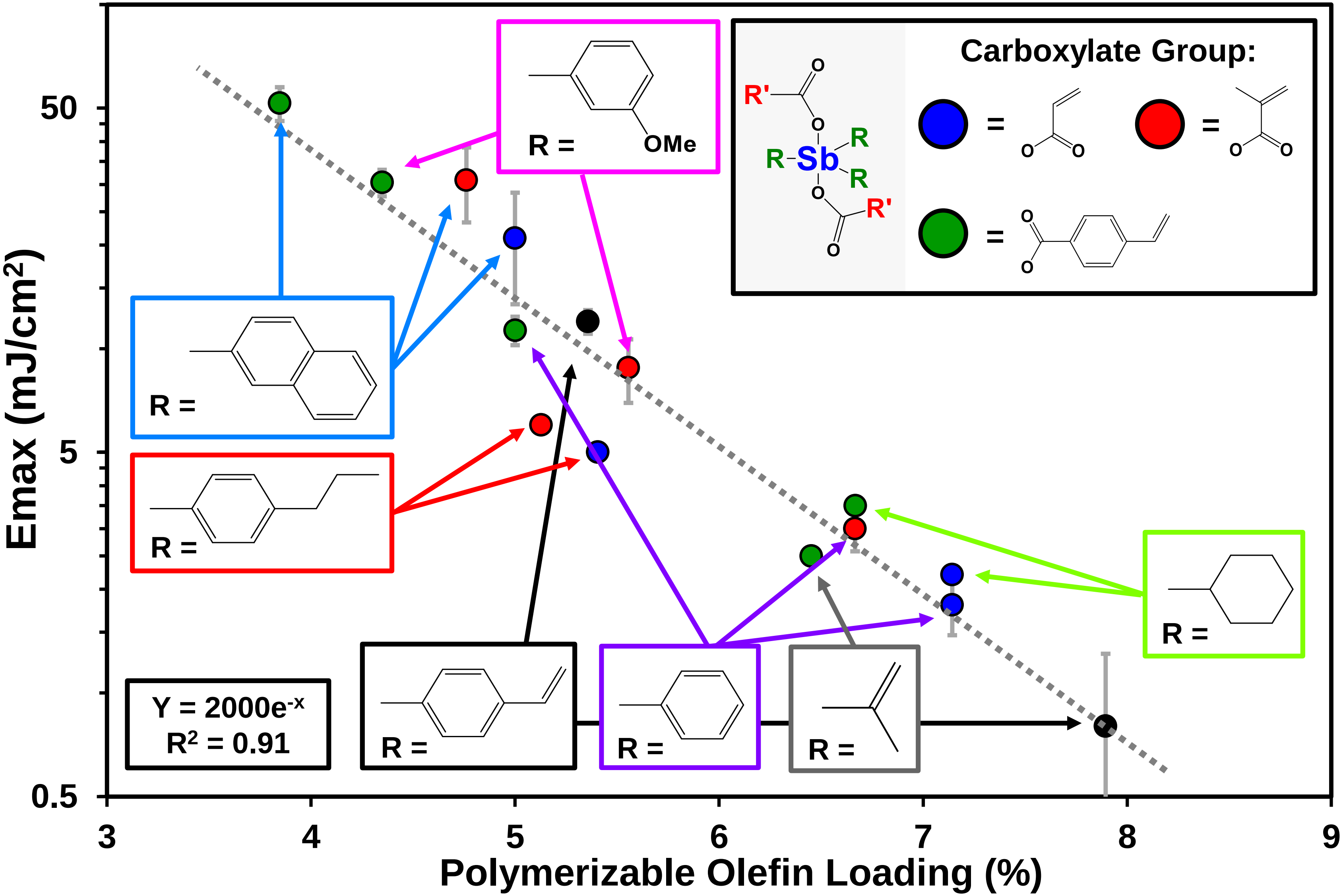


Sensitivity Hypothesis: The ratio of polymerizable olefins to space filling R groups is the largest contributor to sensitivity characteristics of antimony acrylate resists.

$$POL = \frac{\#\ of\ Polymerizable\ Olefins}{\#\ of\ Atoms\ (Excluding\ Hydrogen)} \times 100\%$$

Passarelli & Brainard JM3 2015 043503

III. MORE: E. High-Speed Main-Group Olefins (Passarelli)



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