Fundamental resist exposure mechanisms:
A preliminary study based on mass spectrometer measurements

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Content

- **Reactions impacting selected outgassed components**
    - PAG decomposition reactions to generate catalytic acids
    - Acid-catalyzed deprotection reactions
- **Resist materials and experimental facilities**
- **Discussion of mass spectrometer results and comparison to hot plate sensitivity measurements**
- **Summary**

Chemical changes in typical EUV photoresists

Acid generation

Expose resist sample

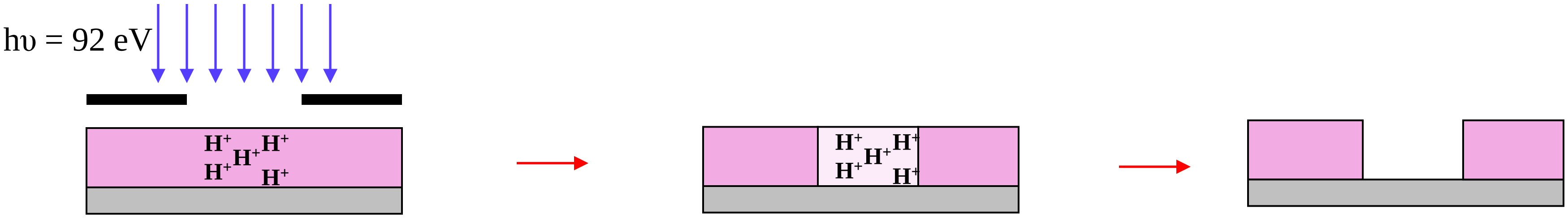
(vacuum conditions)

Acid-catalyzed deprotection

Post Exposure Bake (PEB)

(atmospheric conditions)

Develop in Aqueous Base to reveal pattern



Hot plate

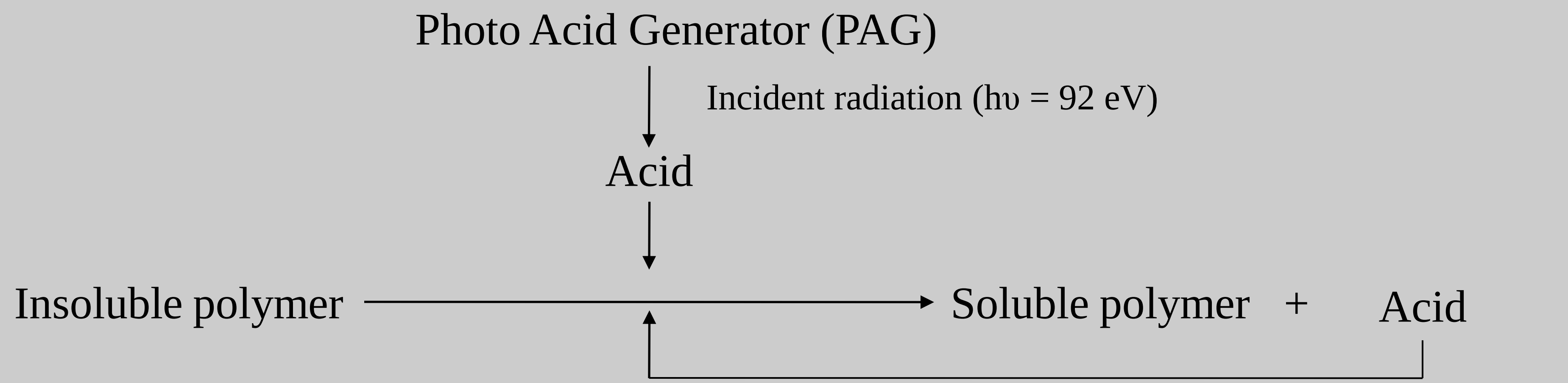


Photo Acid Generator (PAG)

Incident radiation (hυ = 92 eV)

Acid

Insoluble polymer → Soluble polymer + Acid

Grant, W. *Chemically Amplified Resists* (SPIE 2008)

Resist components are released based on the extent of chemical reactions in film

Acid generation

Expose resist sample

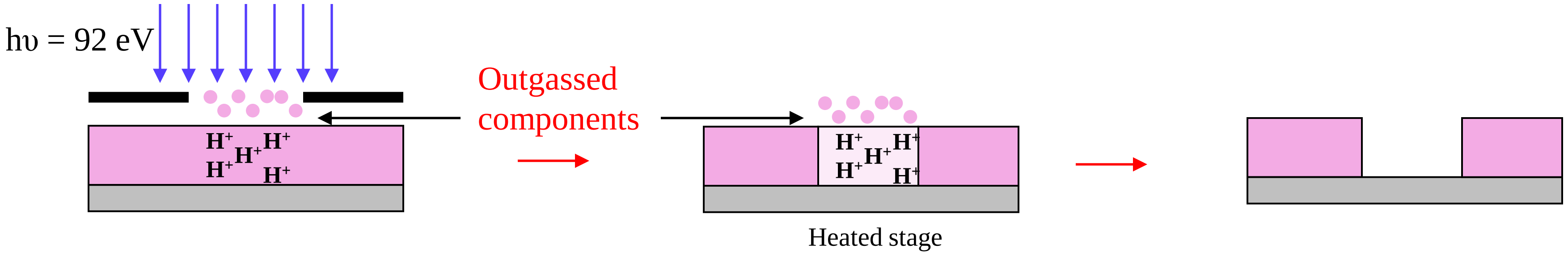
(vacuum conditions)

Acid-catalyzed deprotection

Post Exposure Bake (PEB)

(vacuum conditions)

Develop in Aqueous Base to reveal pattern



Outgassed components

Heated stage

Reaction products outgas as chemistry progresses

Decomposed PAG components

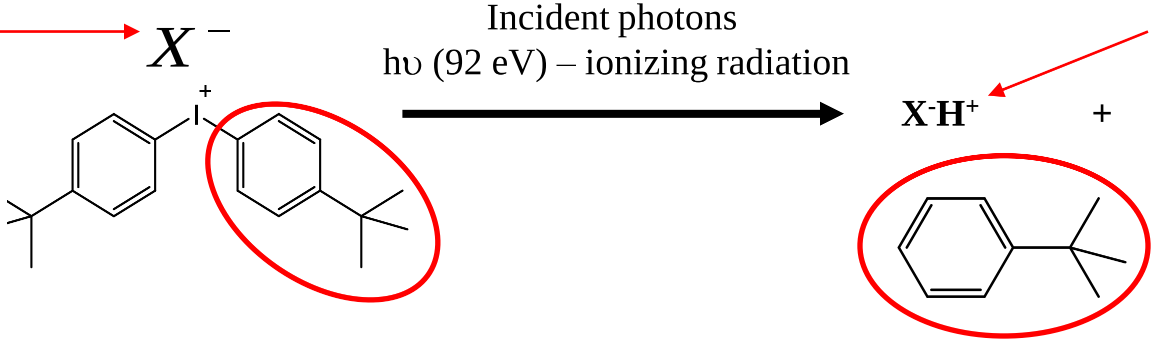
- outgas at time of exposure
- can be used to understand acid generation efficiencies

Deprotected species

- outgas as acid diffuses
- can be used to understand acid diffusion and acid-catalyzed deprotection

Reaction products from EUV resist platforms used for experimentation

PAG decomposition to generate acid



PAG Anion

X^-

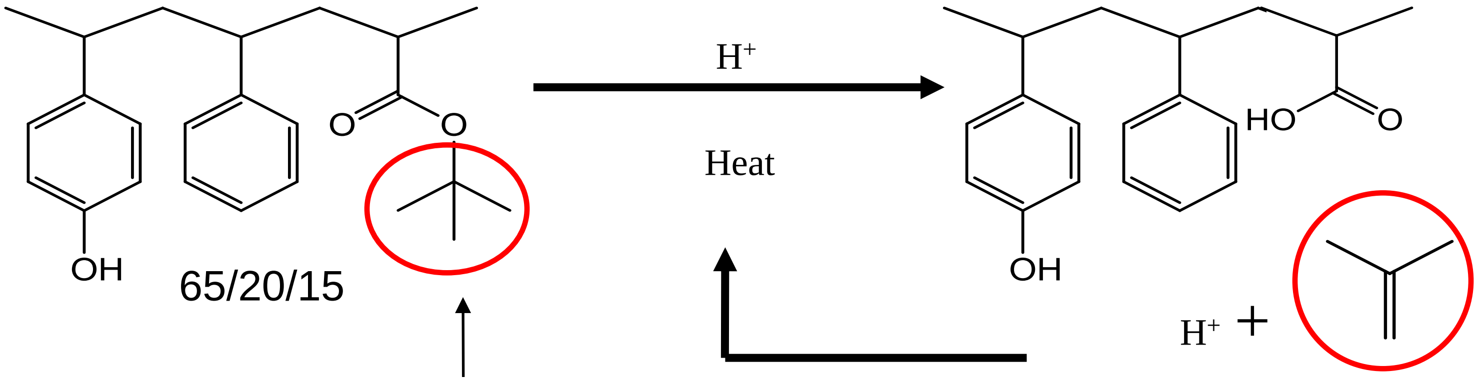
Incident photons
hυ (92 eV) – ionizing radiation

Photoacid

X^-H^+ + **Side products**

tert-Butylbenzene is detectable with mass spectrometer

Acid- catalyzed deprotection of the polymer



Protected ESCAP polymer (Insoluble in aqueous base)

Deprotected polymer (soluble in aqueous base)

H^+

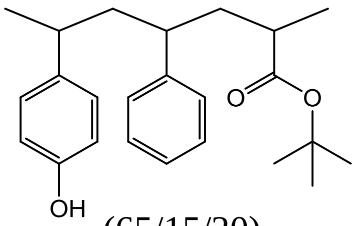
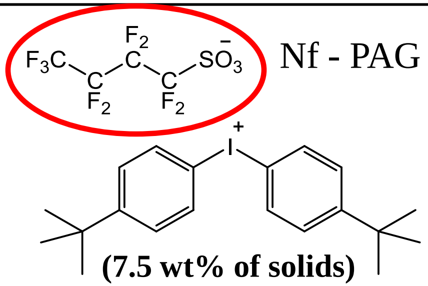
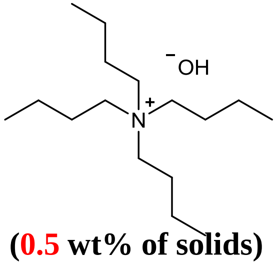
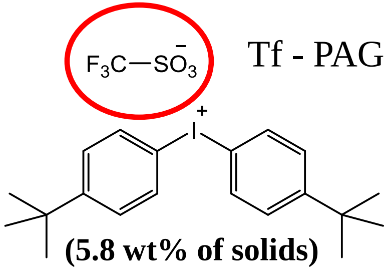
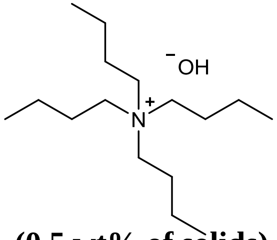
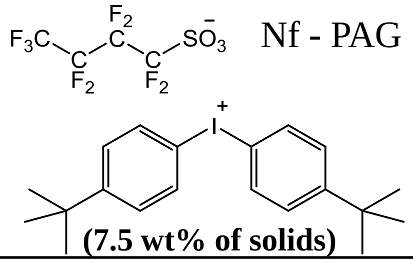
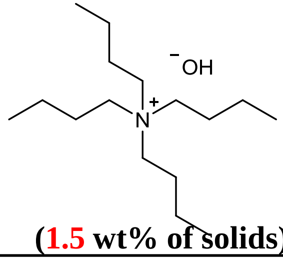
Heat

Protection group

H^+ +

Isobutene is detectable with mass spectrometer

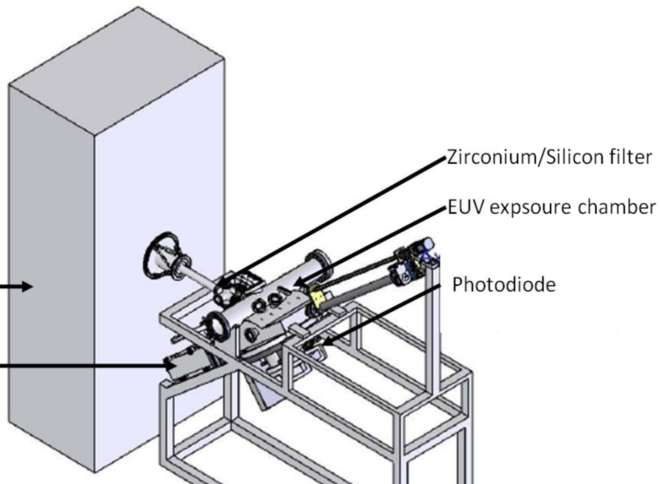
Chemical formulation of resists used for the experiments

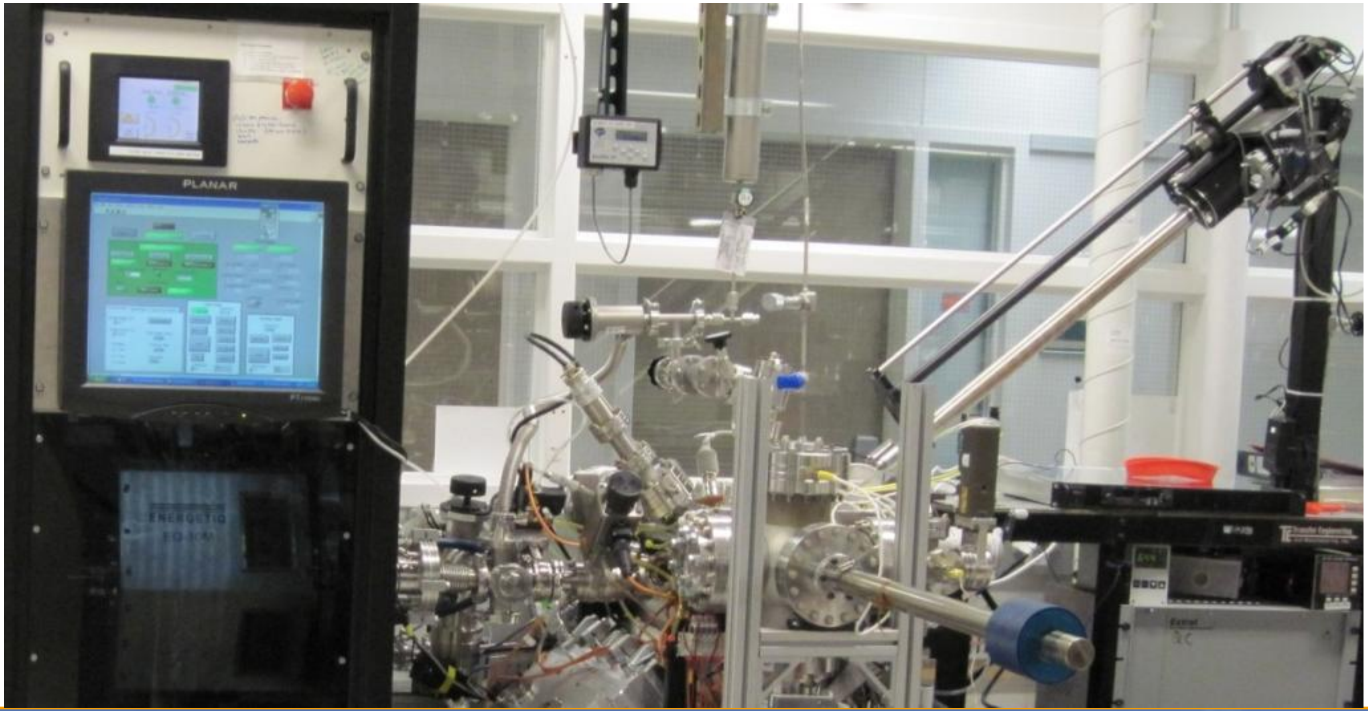
Resist name	Polymer (ESCAP)	Photo Acid Generator	Base quencher (TBAH)
Resist A	 (65/15/20)	 Nf - PAG **(7.5 wt% of solids)**	 **(0.5 wt% of solids)**
Resist B		 Tf - PAG **(5.8 wt% of solids)**	 **(0.5 wt% of solids)**
Resist C		 Nf - PAG **(7.5 wt% of solids)**	 **(1.5 wt% of solids)**

Comparative wt% for the two types of PAG's used were based on the equivalent number of **moles** in each formulation.

Facilities for experiments

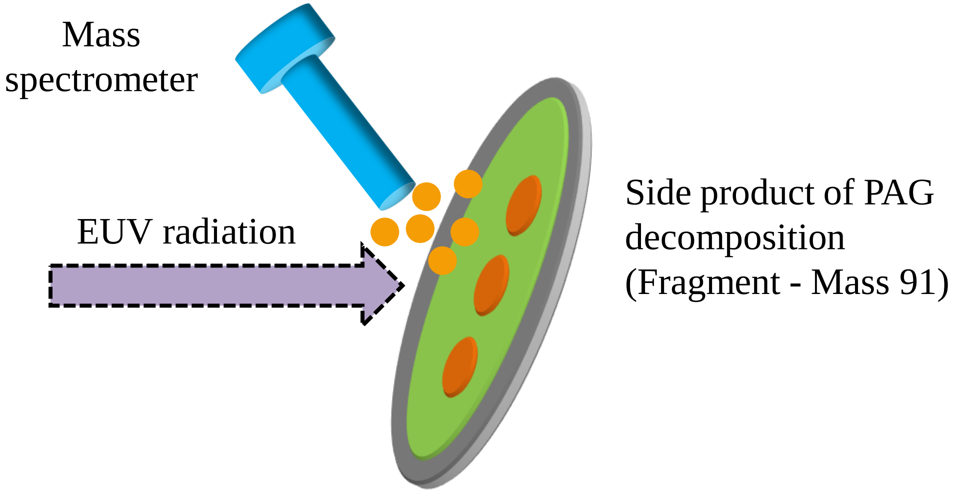
- Xenon pulsed discharge produced plasma source (Energetiq EQ-10M)
- Extrel quadruple mass spectrometer
- AXUV photodiode for EUV power calibration
- Vacuum chamber with 300 mm wafer capability





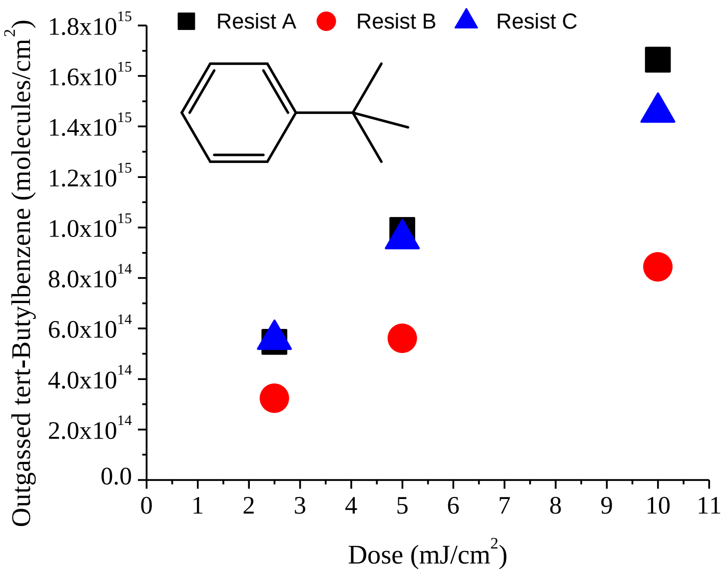
Results and Discussion

PAG decomposition at different EUV exposure doses

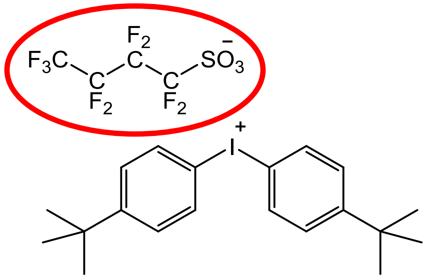


- More PAG decomposition in Resist A and Resist C compared to Resist B
  - Higher acid generation with Nf – anion than Tf- anion present (same number of moles of PAG) - Average of 1.8X
  - Same acid generation for resists with Nf – anion present despite difference in base quencher content

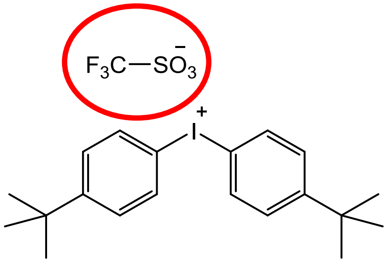
Side product of PAG decomposition (Fragment - mass 91)



Resist A and Resist C

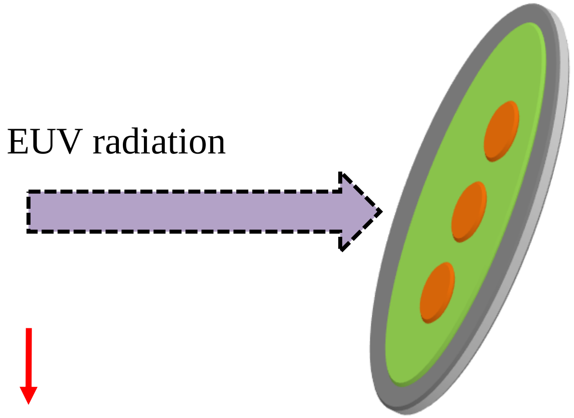


Resist B



Resist A (0.5 TBAH) and Resist C (1.5 TBAH)

Hot plate sensitivity measurements procedure for resists



Resist coated wafers were mounted on a position adjustable sample stage for multiple exposure doses at different spots on sample

110 C
Post Exposure Baking (PEB) on hot plate
(Brewer Science CEE Model 1300 (60 seconds)

→

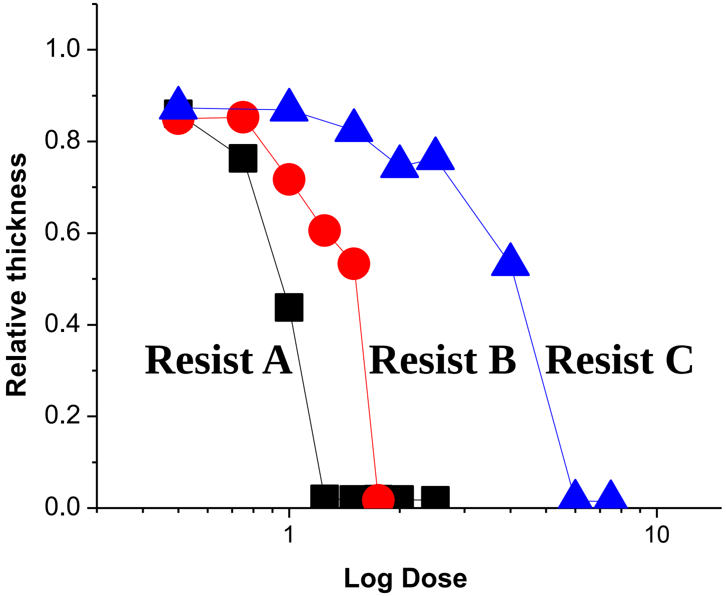
Development in MF-26A (TMAH) 45 seconds

→

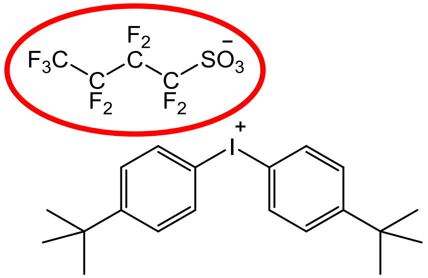
Thickness measurements with a Woollam ellipsometer

Sensitivity measurements at different EUV exposure doses

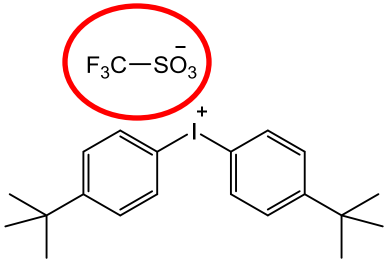
- Higher sensitivity in Resist A compared to Resist B
  - Higher acid generation with Nf – anion than Tf- anion present (From outgassing data)
  - However E_o measurements show less than a factor of 1.8X difference in sensitivity (1.3X)
  - This is most likely an indication of more reactions involving generated photoacid
  - Photoacid diffuses as an H^+ and an anion (X^-)*
- Higher sensitivity in Resist A compared to Resist C
  - Even though same number of acids are generated, deprotection is inhibited by higher base quencher content



Resist A and Resist C



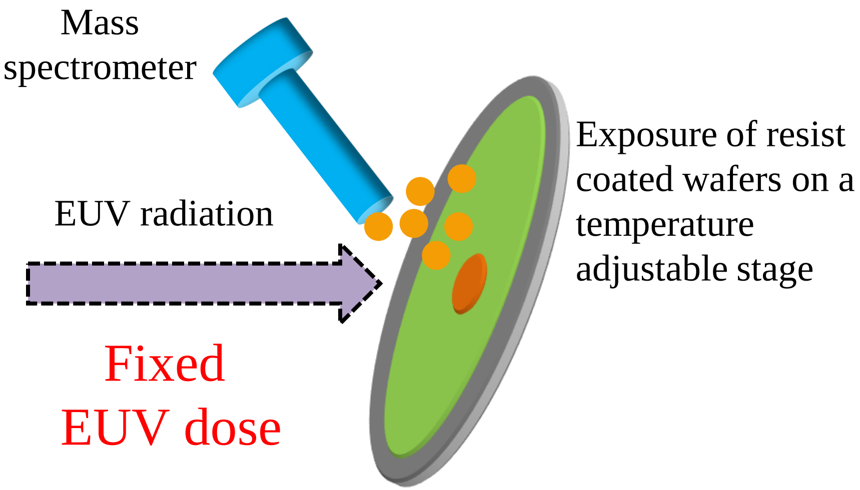
Resist B



Resist A (0.5 TBAH) and Resist C (1.5 TBAH)

*Kang et al, "Characterization of the photacid diffusion length and reaction kinetics in EUV photresists with IR spectroscopy" Macromolecules 43, 4275-4286 (2010)

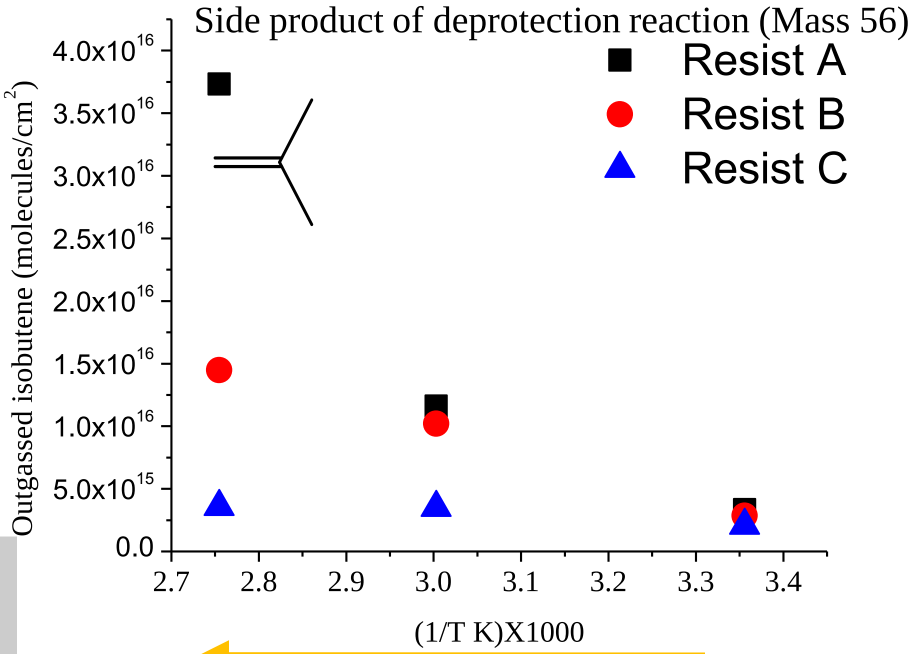
Deprotection reaction at different sample temperatures in vacuum



Exposure of resist coated wafers on a temperature adjustable stage

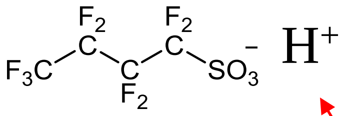
Fixed EUV dose

- Deprotection reaction cleaves protection sites to release isobutene
- For the same number of acids generated, more deprotection at higher temperatures – higher reaction rates and diffusivity of acids
- Extent of deprotection is inhibited by higher base quencher content (Resist A vs. Resist C)



Increasing temperature

Resist A and Resist C

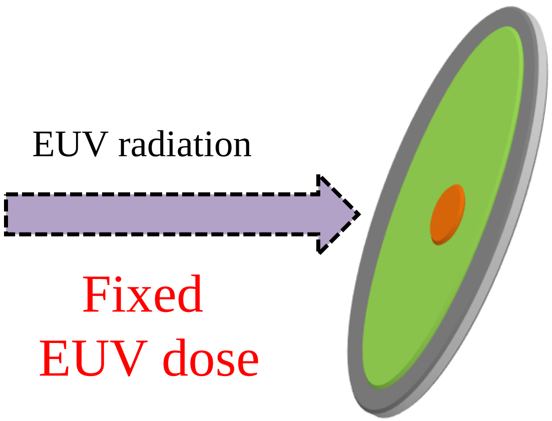


Resist B

$F_3C-SO_3^-$ H^+

Photoacid

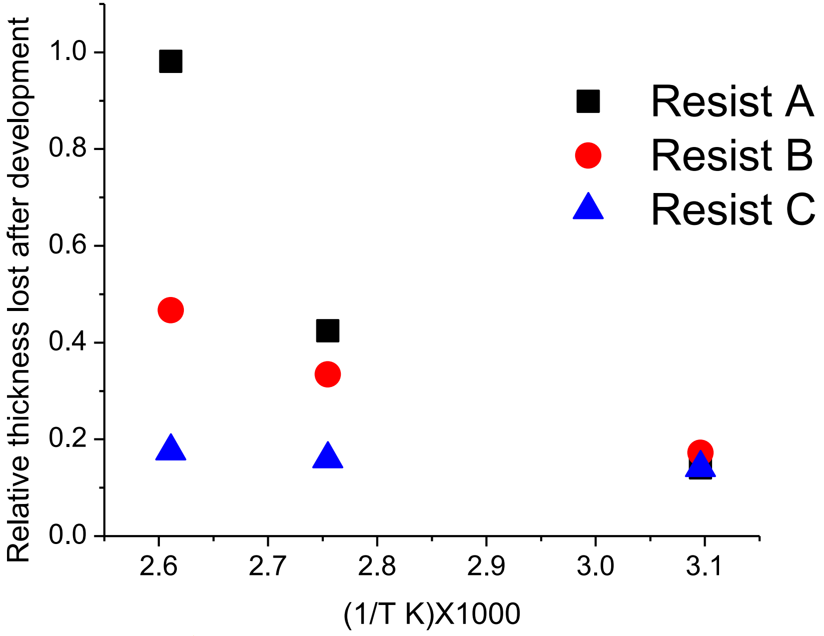
Sensitivity measurements at different PEB temperatures



EUV radiation

Fixed EUV dose

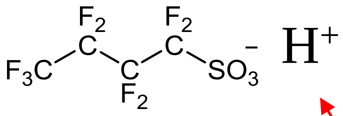
Expose
↓
PEB (3 temperatures)
↓
Develop in base
↓
Thickness measurements



← **Increasing temperature**

- Deprotection reaction cleaves protection sites to release isobutene
- For the same number of acids generated, more deprotection at higher temperatures – higher reaction rates and diffusivity of acids
- Increase in deprotection makes the resist more soluble in aqueous developer

Resist A and Resist C

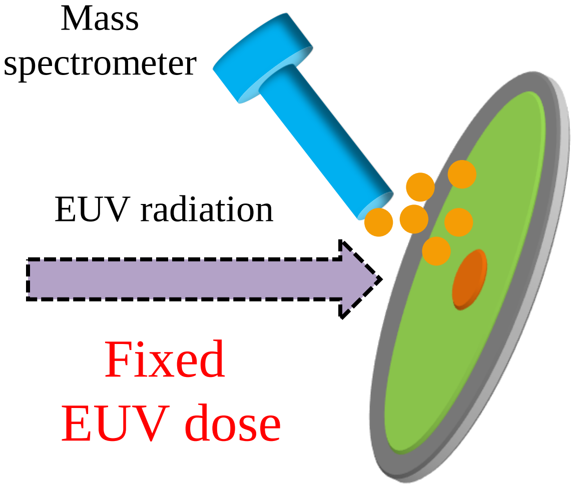


Resist B

$F_3C{-}SO_3^-$ H^+

Photoacid

Comparison of outgassing data to thickness measurements



Fixed EUV dose

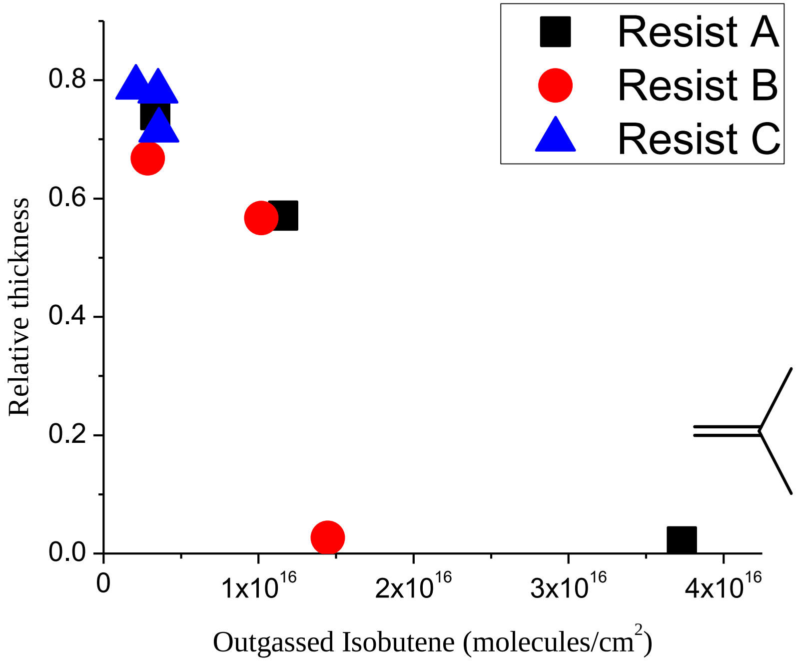
Expose sample at different temperatures

↓

Develop in base

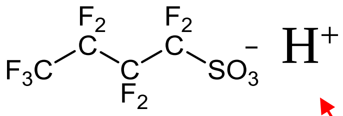
↓

Thickness measurements



- As the protecting group on the polymer is depleted, the polymer becomes more soluble in the developer.

Resist A and Resist C


$F_3C{-}CF_2{-}CF_2{-}CF_2{-}SO_3^-\ H^+$

Resist B

$F_3C{-}SO_3^-\ H^+$

Photoacid

Summary

- Outgassing data can provide insight to reactions occurring in resist films.
- We observed different levels of PAG decomposition depending on the PAG anion present in the resist film.
- We observed higher deprotection with increase in temperature and showed evidence of inhibited deprotection reactions with larger base quencher content.
- The mass spectrometer measurements correlated reasonably with sensitivity measurements on a hot plate.
- Not clear from measurements the dominant reaction pathway for PAG decomposition upon EUV exposure.
  - Photo-absorption of PAG or
  - Reactivity with generated electrons from ionization of polymer

Future directions

- Repeat measurements to confirm preliminary results
- Use of outgassing method to investigate and understand dominant mechanism leading to PAG decomposition reaction.
  - Evaluate and test more PAG types
  - Evaluate different polymers types
- Possibly extract acid diffusion information from deprotection trends

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SEMATECH

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