New developments in resist-outgas testing at NIST

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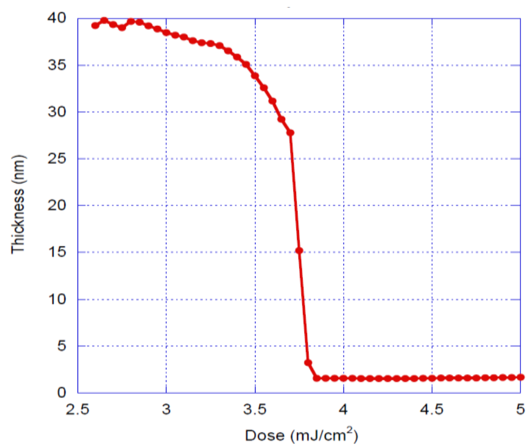
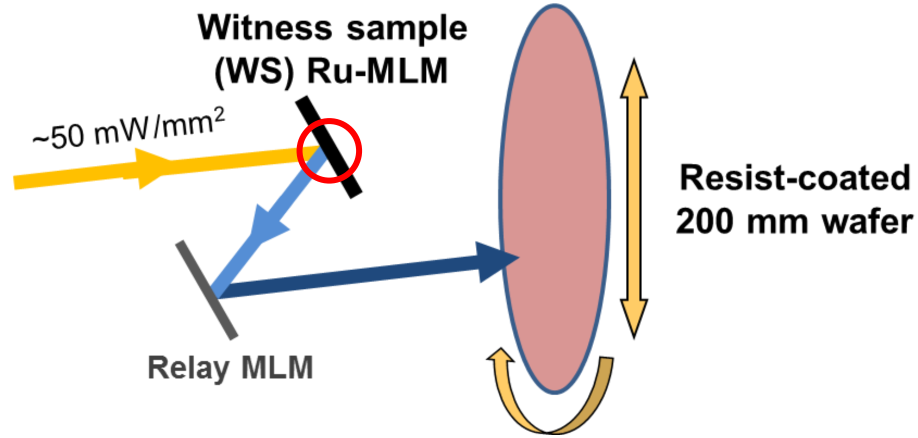
Outline

- Implementation of ASML EUV-based resist-outgas testing at NIST
  - Update and observed trends
  - Preliminary scaling studies
- EUV-exposed polymers containing S and F (proxies for EUV-C)
  - Composition
  - Atomic-H cleaning
- Comparison of contamination potential from various species related to resist-outgassing.

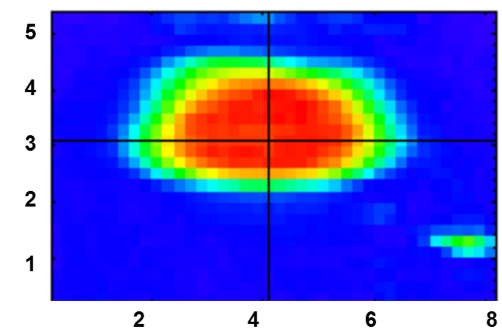
ASML Resist-Outgas Testing Protocol at NIST



(1) Determine E0

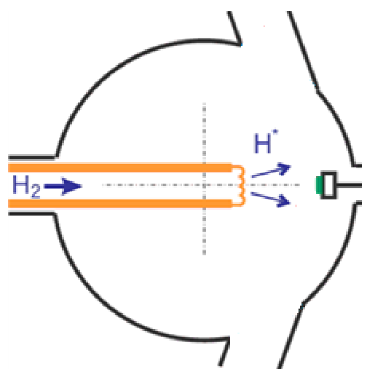


(2) Co-expose witness sample & resist-coated 200 mm wafer to E0 in 1 hr.



(3) Measure C-thickness with spectroscopic ellipsometry and scale to 300 mm wafer

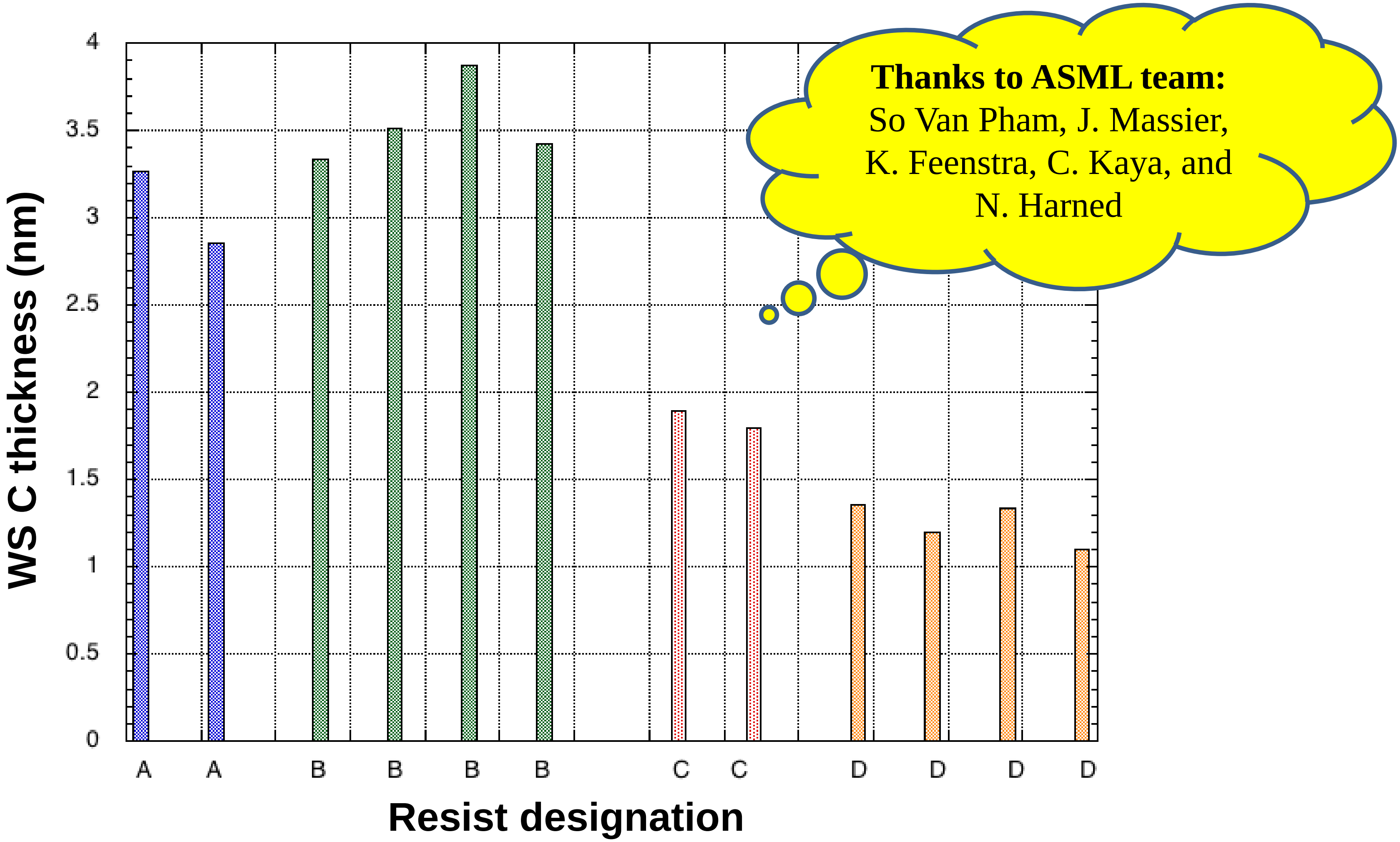
<3nm



(4) Clean C with atomic H

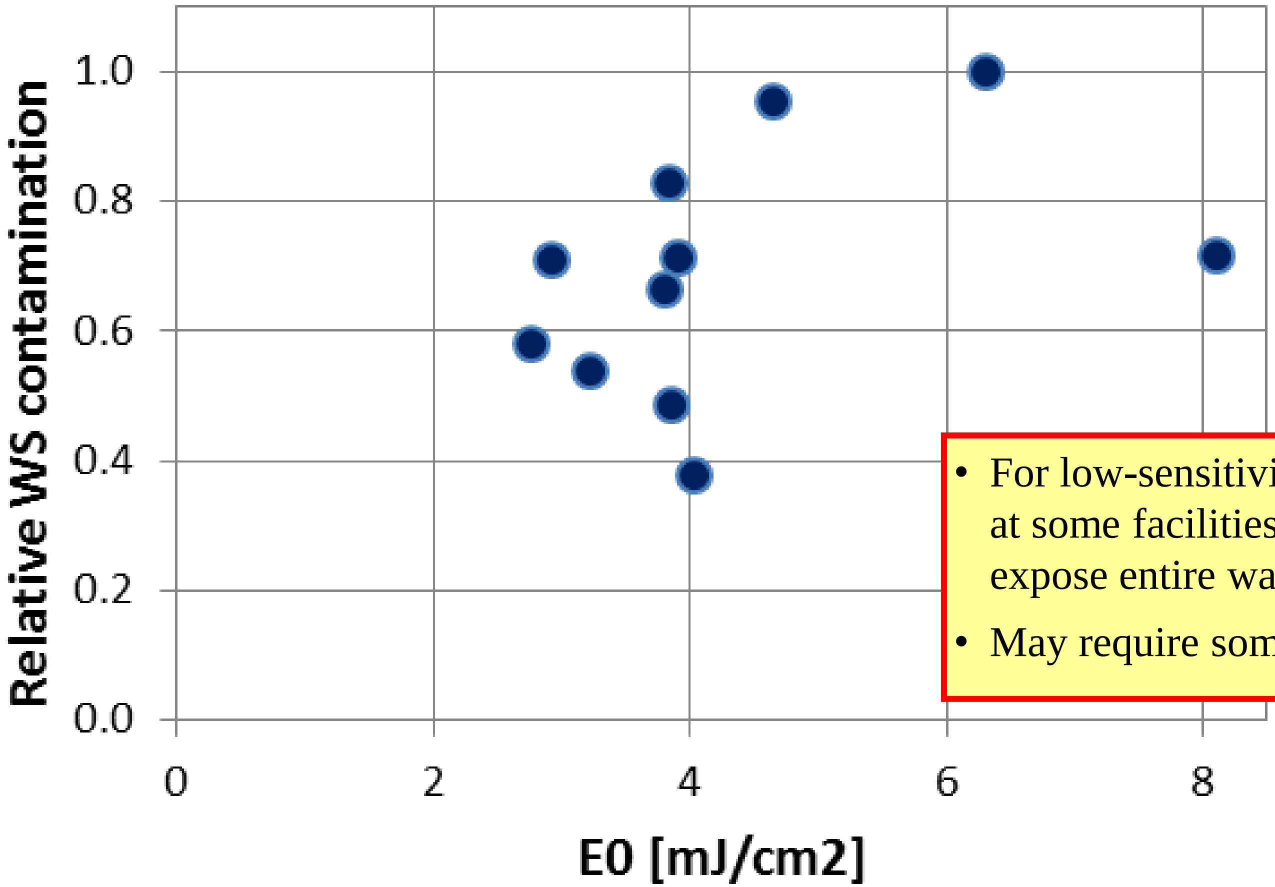
(5)
Measure amount of residual non-C {S, P, F, I, Cl, …} with XPS.

Reproducibility of outgas testing at NIST



- 200 mm wafer exposed in 1 hr
- C thickness scaled by 9/4 to get 300 mm wafer exposure equivalent
- Reproducibility within ±10%

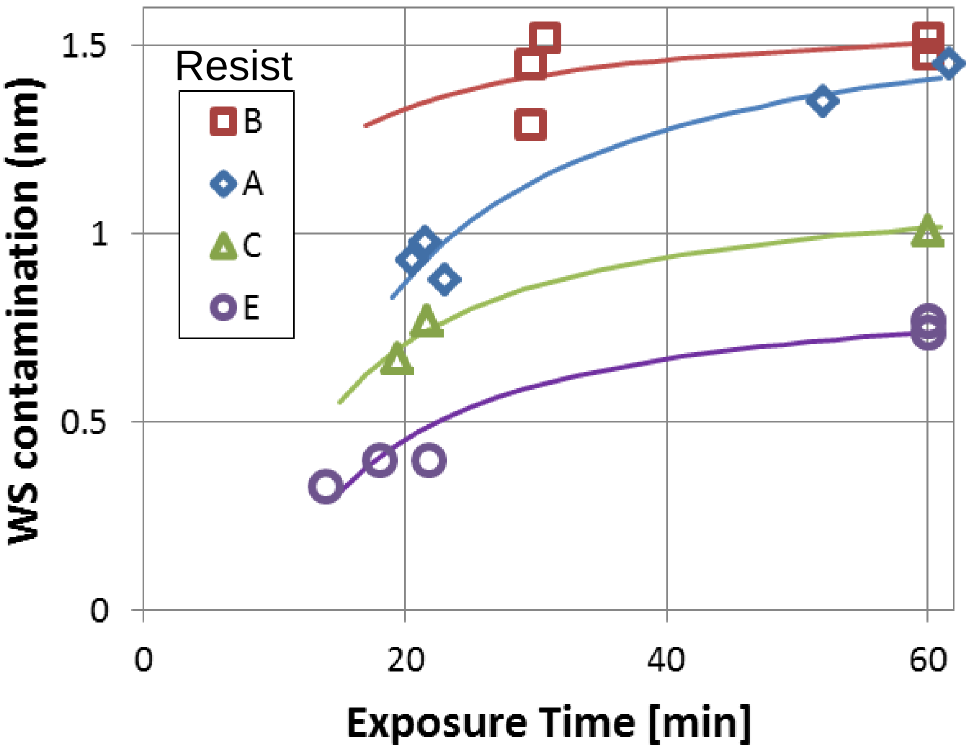
Poor correlation of outgas contamination with E0



- For low-sensitivity resists, EUV power at some facilities may be insufficient to expose entire wafer in 1 h.
- May require some type of scaling.

- Normalized witness sample (WS) C thickness for 11 different resists does not correlate with dose-to-clear, E0. Other parameters dominate:
  - Outgas species
  - Time evolution of outgassing products: diffusion, PAG reactions, etc.

Measured outgas contamination for different exposure times

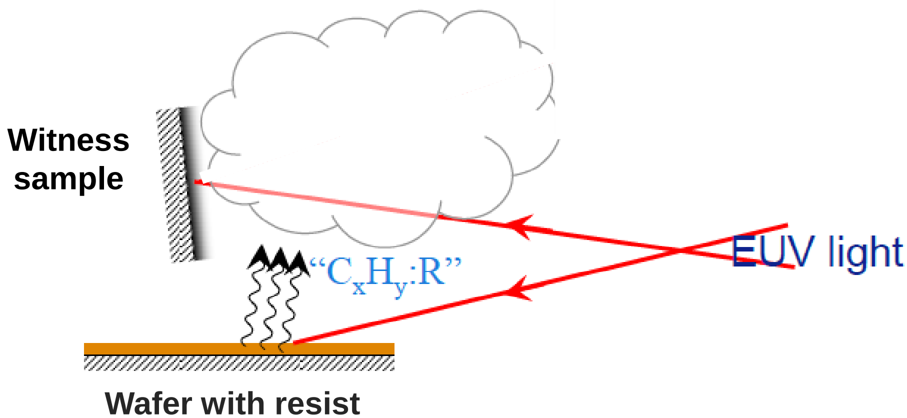


- E0 delivered to entire 200 mm wafer in all cases.
- Exposure time decreased from standard 60 min by increasing EUV power.

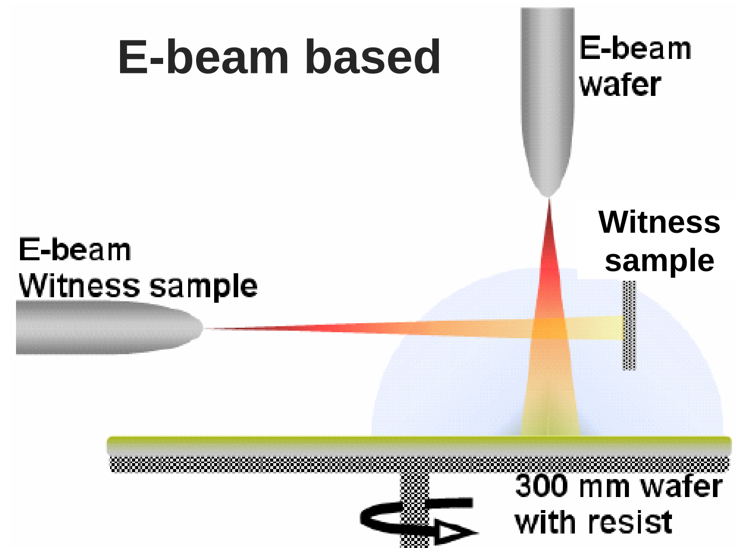
- Lines are fits to simple model assuming some fraction of outgas products do not escape resist before end of exposure and hence do not contribute to contamination.
- Due to complicated, resist-specific dependence on exposure time, if available source power is insufficient to provide E0 over the entire wafer in 1 h, exposure time should **not** be increased to compensate.
- Investigating possibility of sequential exposures each delivering E0 to as much area as possible with given EUV power in 1 hour.

E-beam test enables fast and low cost resist screening

EUV based



E-beam based



- E-gun advantages over photon testing
  - Abundant intensity means contamination can be grown quickly
  - Single wafer exposure therefore small amounts of resist is needed
  - Easier maintenance (no EUV source)

Courtesy of N. Harned, ASML

Outline

- Implementation of ASML EUV-based resist-outgas testing at NIST
  - Update and observed trends
  - Preliminary scaling studies

- Correlation of EUV and e-beam contamination containing C and residuals (S, F, P, I, Cl, Br)
  - Composition
  - Atomic-H cleaning

- Comparison of contamination potential from various species related to resist-outgassing.

Atomic-H cleaning of non-C contaminants

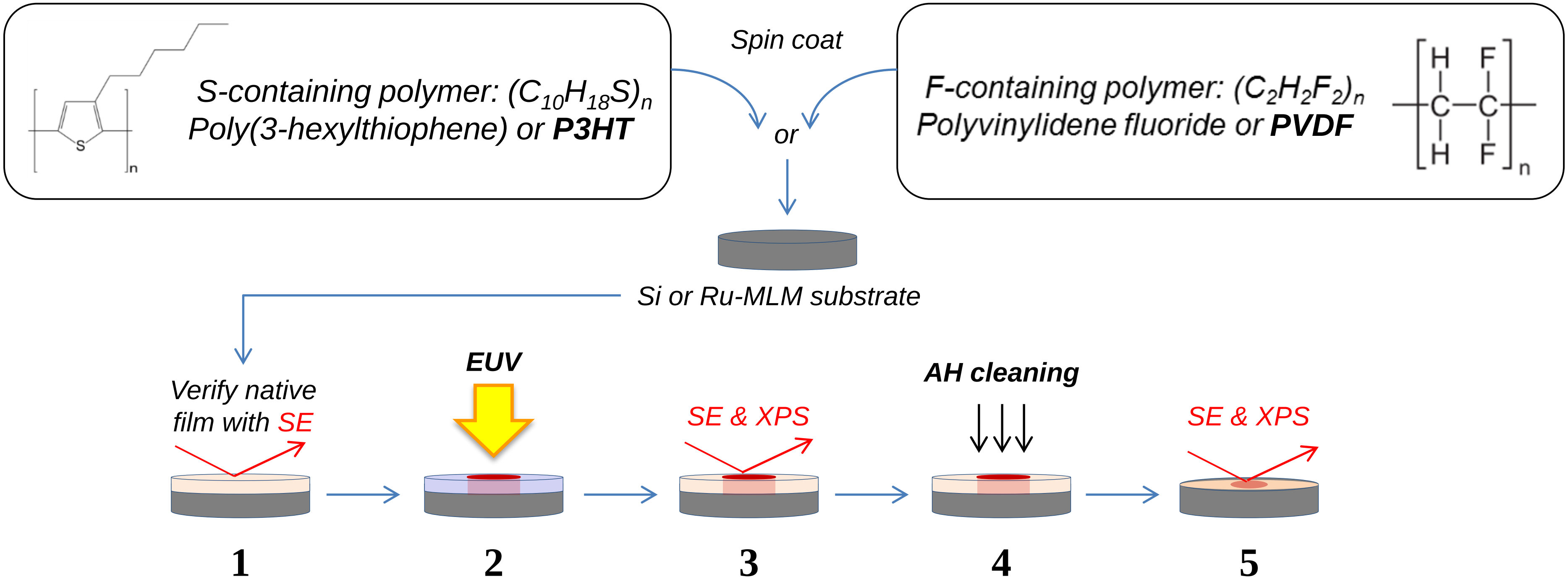
- Little/no data on efficacy of atomic H cleaning of "*non-cleanables*": S, P, I, F, Cl, Br

- Previously only two data points on AH cleaning of S at NIST
  - ~3 At% of S was completely removed from one outgas WS. (Performing XPS before and after AH cleaning significantly reduces throughput.)
  - All C and S removed from ~6 nm deposited by EUV exposure in presence of diphenyl sulfide.

- NIST recently completed new "high-contamination" facility to make EUV-induced deposits of highly contaminating species containing S, P, I, etc.

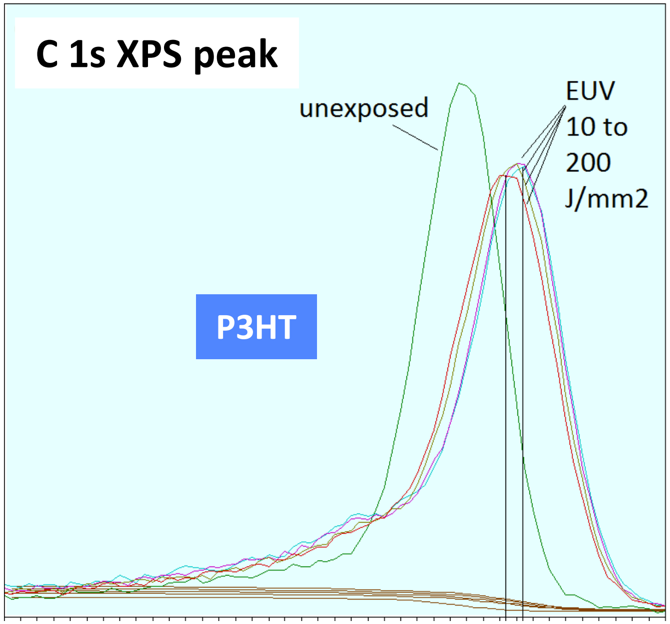
- In interim, investigated AH cleaning of EUV-exposed spin-coated polymers containing appropriate species (S and F).

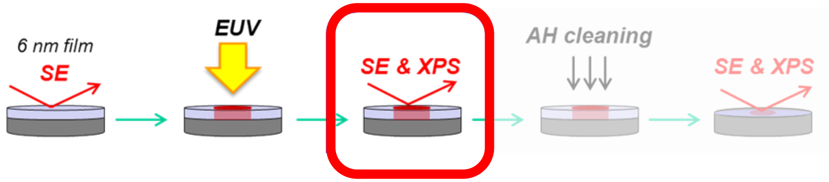
Polymer-based AH-cleaning study of S & F

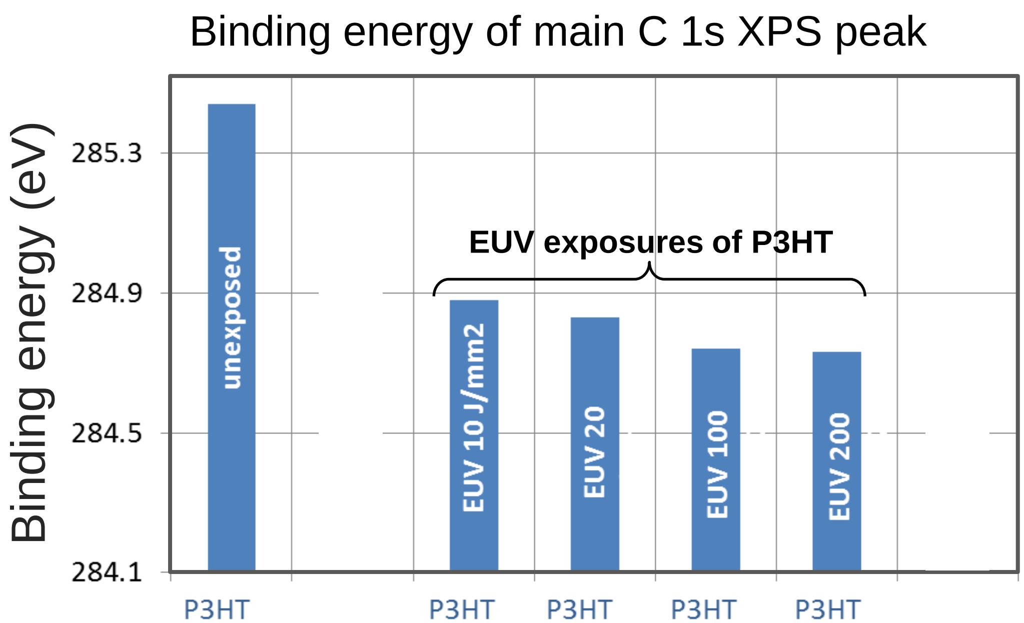


1) Spin coat <10 nm film of polymer onto Si or Ru-cap MLM substrate
2) Perform EUV exposures with varying dose (1-200 J/mm^2)
3) Inspect with spectroscopic ellipsometry (SE) and XPS
4) Clean with atomic-H (AH)
5) Inspect with SE and XPS

Effect of EUV on C 1s XPS peak

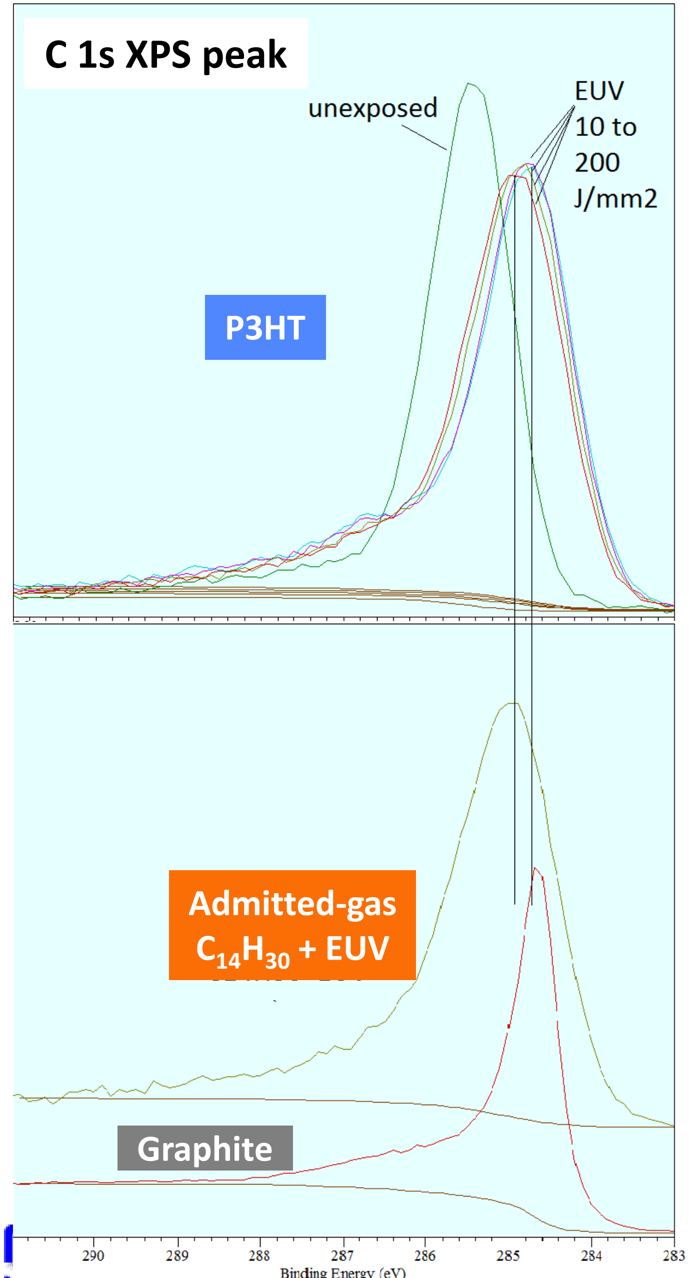


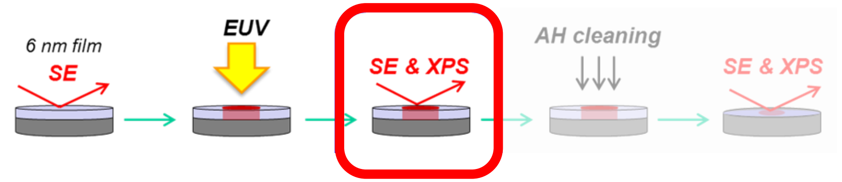


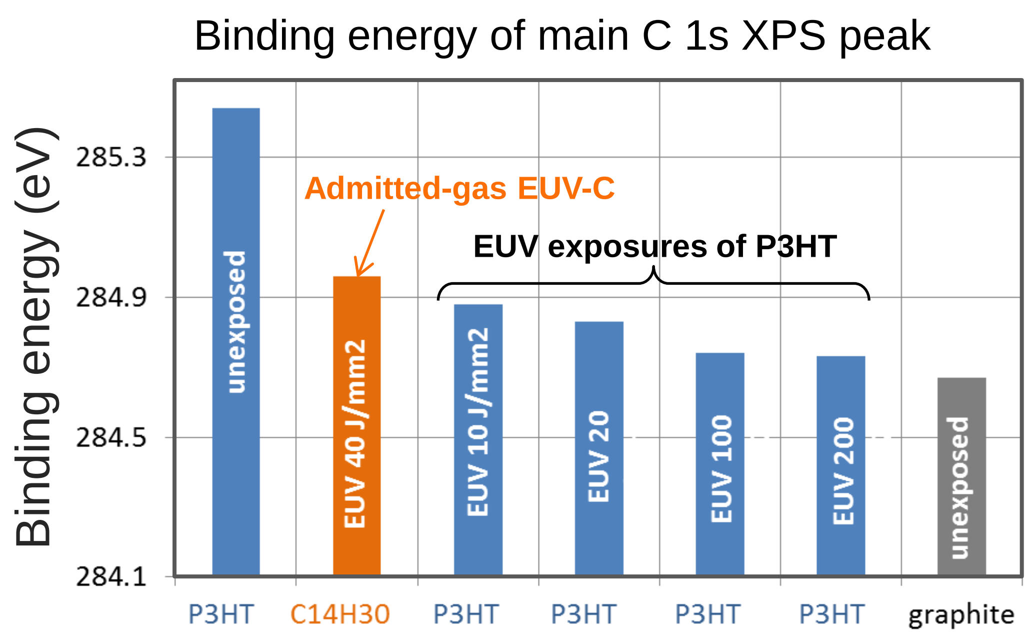


- Lowest EUV dose dramatically alters P3HT C1s peak to similar shape and energy of typical admitted-gas EUV-C.

Effect of EUV on C 1s XPS peak

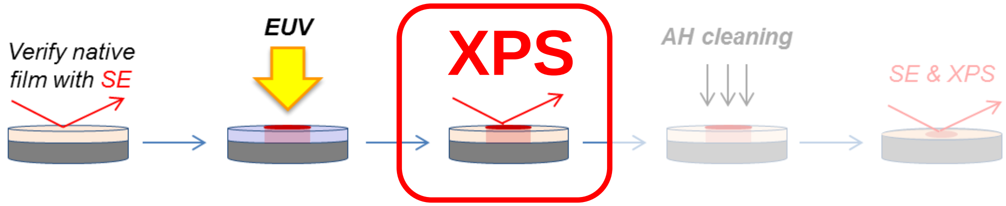


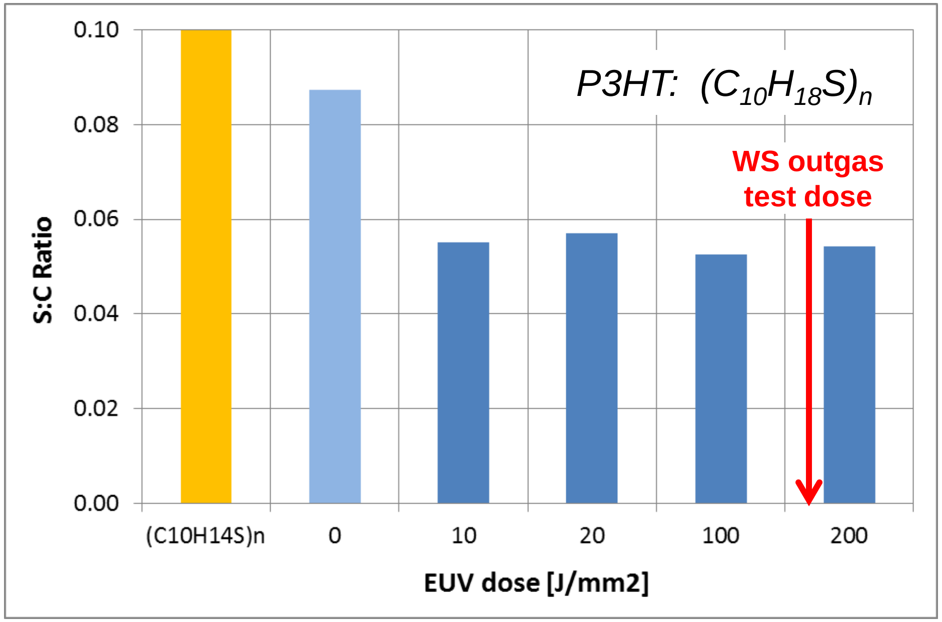




- Lowest EUV dose dramatically alters P3HT C1s peak to similar shape and energy of typical admitted-gas EUV-C.
- C1s binding energy shifts toward graphitic state with increasing EUV dose – as observed with admitted-gas EUV-C deposits.
- Similar trend in PVDF **and** *all admitted-gas exposures*

EUV-induced desorption of S and F



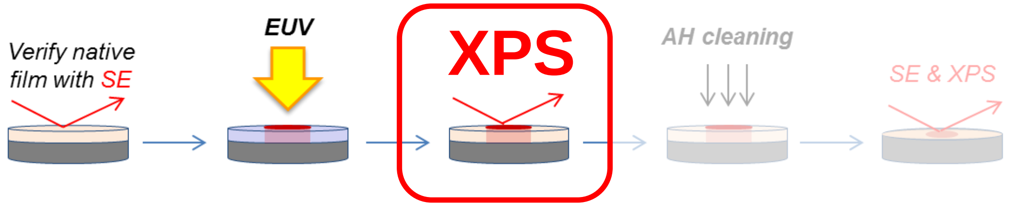


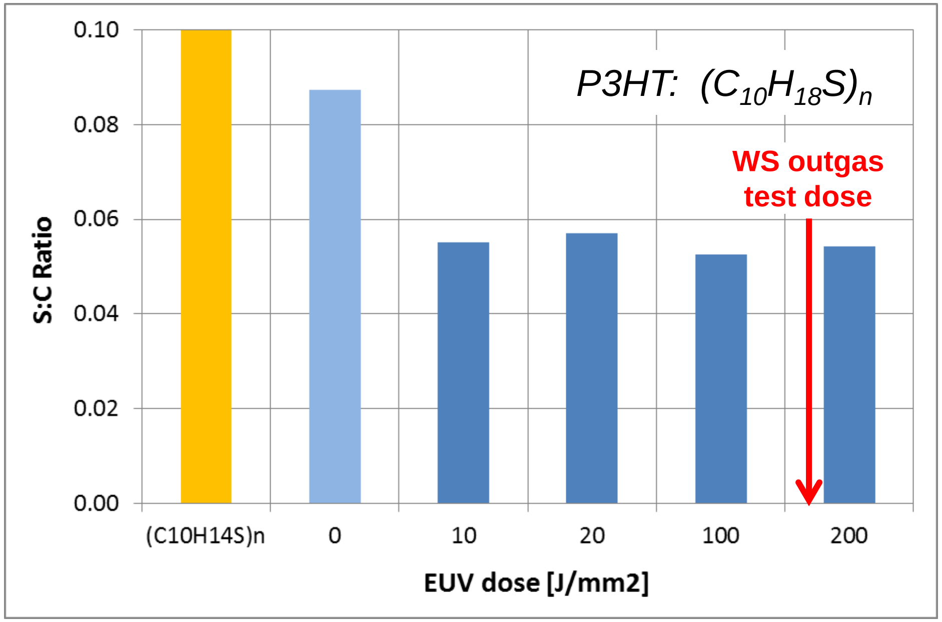
➢ Amount of C remains relatively constant with EUV dose for both polymers

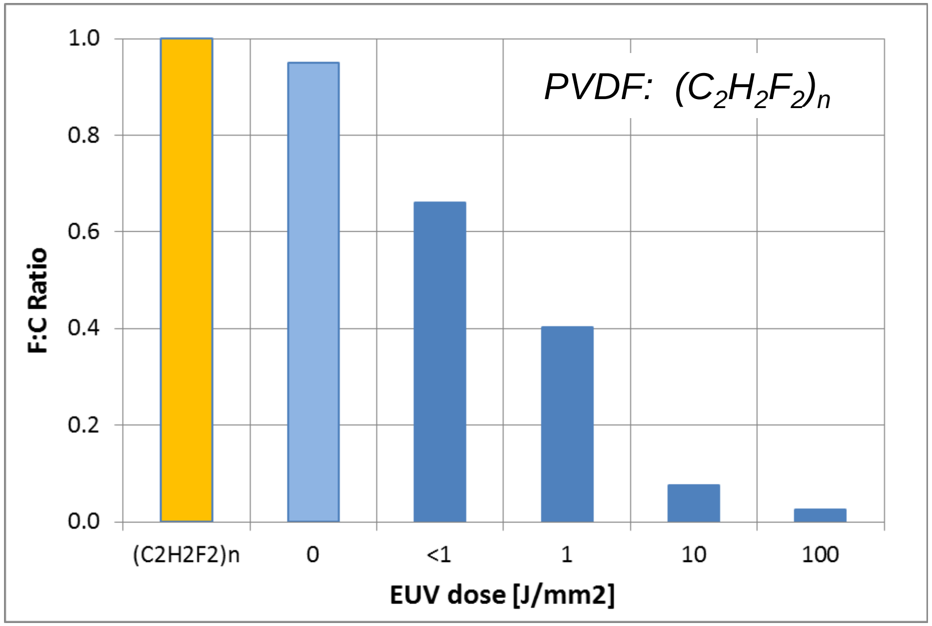
<u>S is partially desorbed by EUV</u>

- ~ 40% of S is rapidly desorbed by EUV (<10 J/mm2)
- ~60% of S is resistant to desorption by highest doses

EUV-induced desorption of S and F







➢ Amount of C remains relatively constant with EUV dose for both polymers

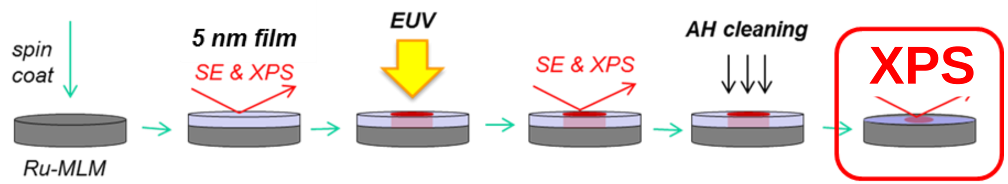
S is partially desorbed by EUV

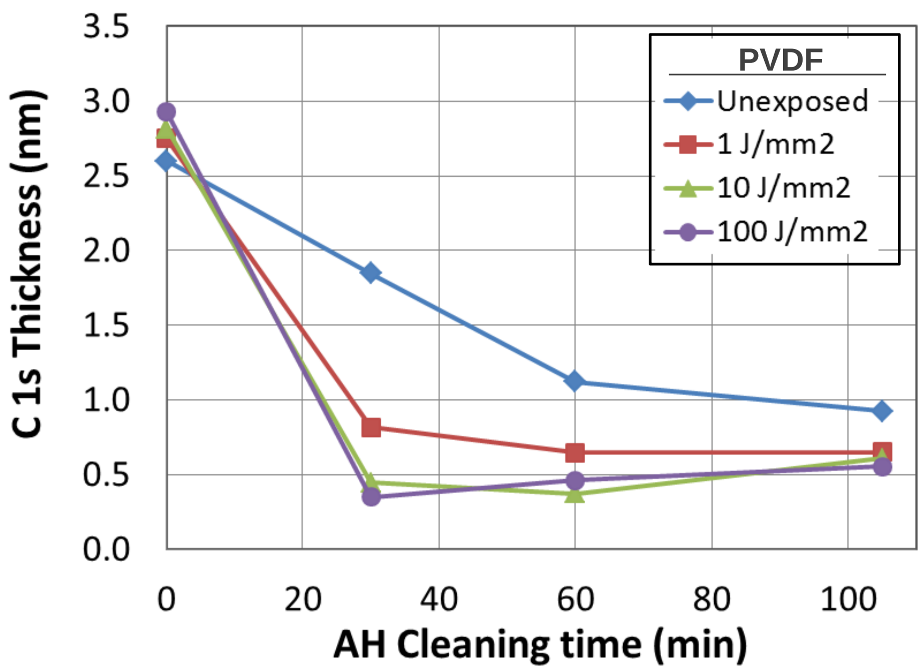
- ~ 40% of S is rapidly desorbed by EUV (<10 J/mm2)
- ~60% of S is resistant to desorption by highest doses

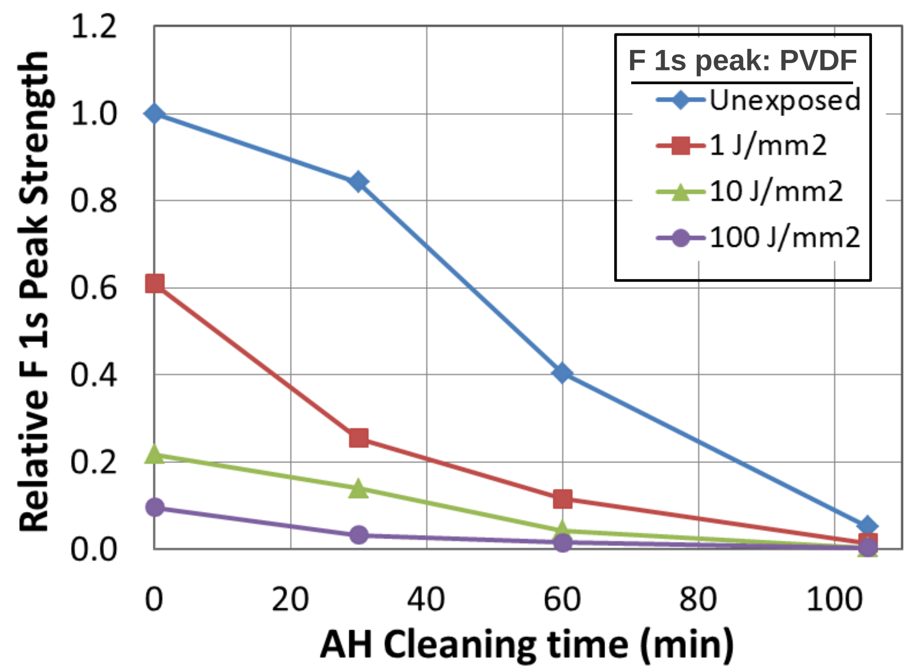
F is highly susceptible to desorption by EUV

- ~50% of F is rapidly desorbed by lowest doses
- F continues to desorb with increasing dose

AH cleaning of F from EUV-exposed polymers

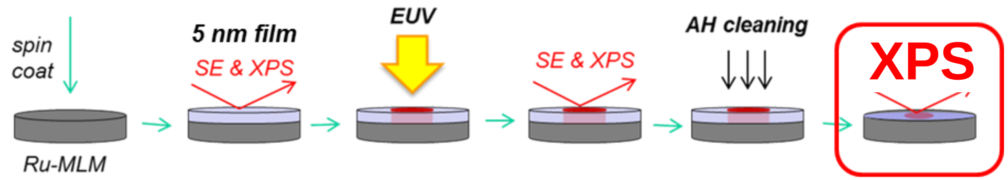


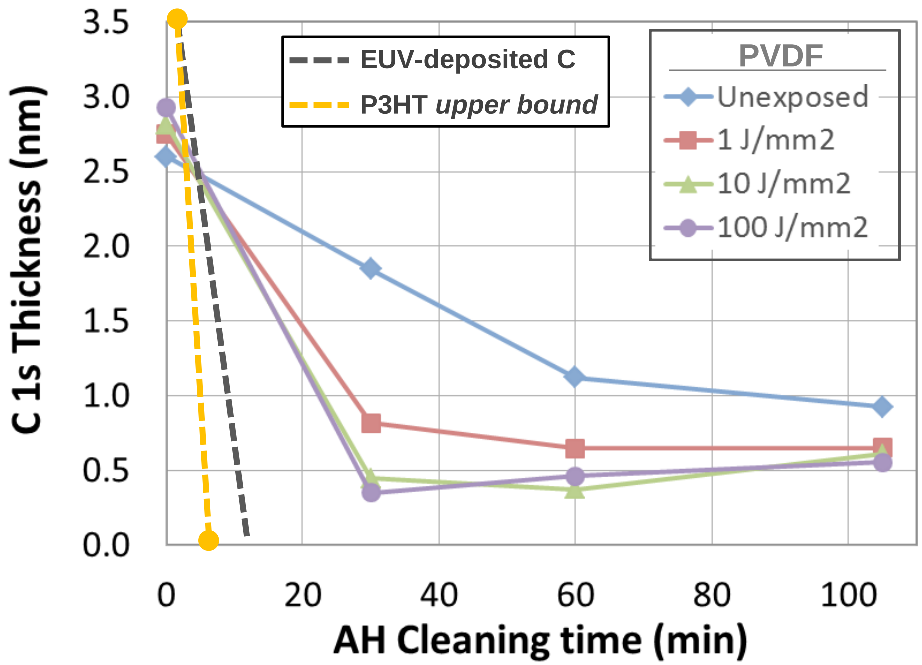


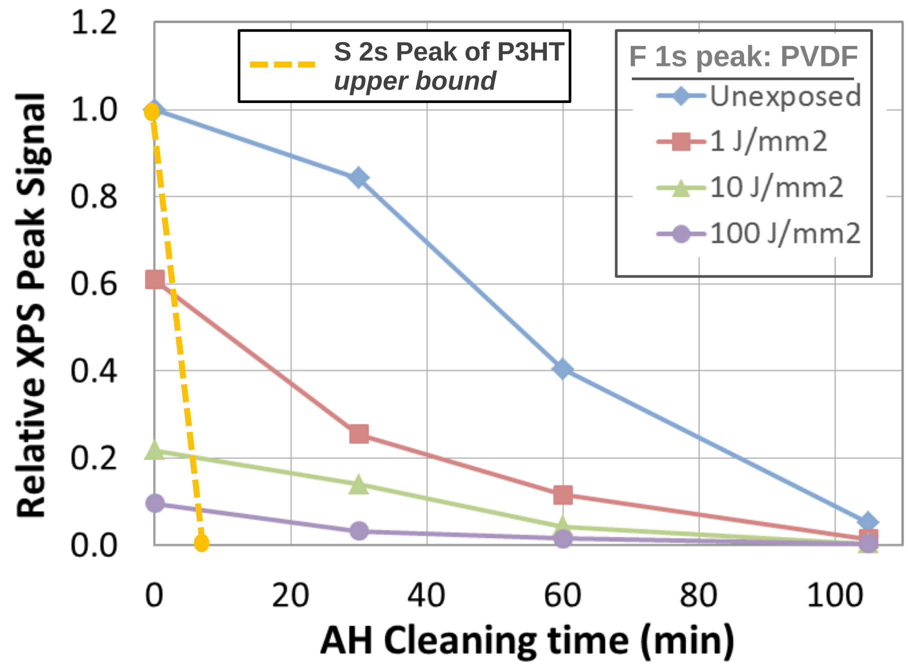


- Presence of F significantly slows AH cleaning of C
- AH removes F much more slowly than C
- F is rarely observed as “non-cleanable” outgas contaminant because it is efficiently desorbed by EUV **not** because it is easily cleaned by AH.
- Similar e-beam exposures are planned to compare role of desorption.

AH cleaning of F and S from EUV-exposed polymers







- AH cleans both EUV-exposed and native P3HT
  - >10x faster than PVDF
  - >2x faster than pure C from EUV exposure in admitted hydrocarbon vapor.
- AH cleaning rate of **first deposit made by e-beam-exposure** in admitted diphenyl sulfide was at least as fast as the rate for pure C from EUV exposure in admitted hydrocarbon vapor.

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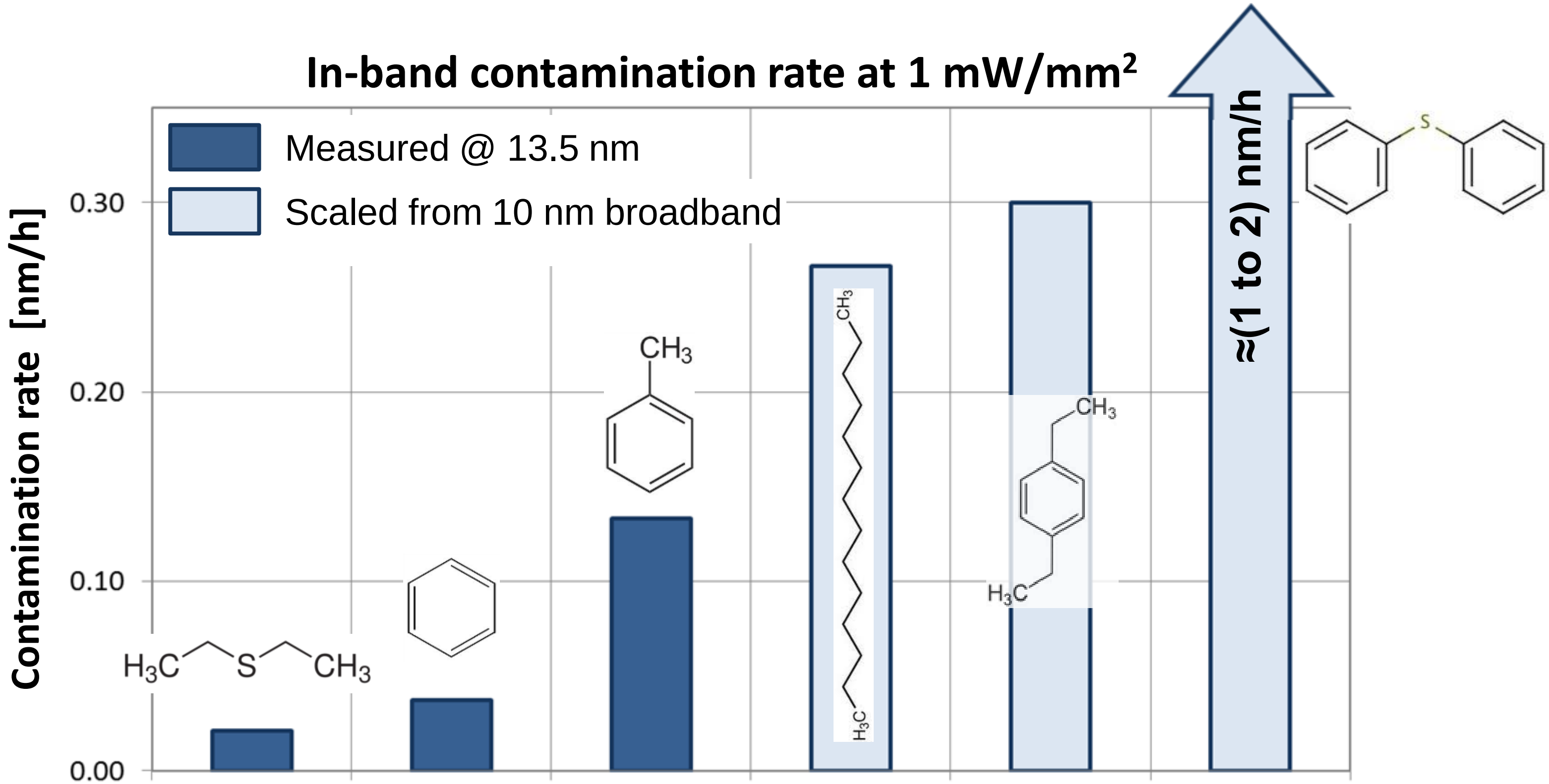
- Comparison of contamination potential from various species related to resist-outgassing.

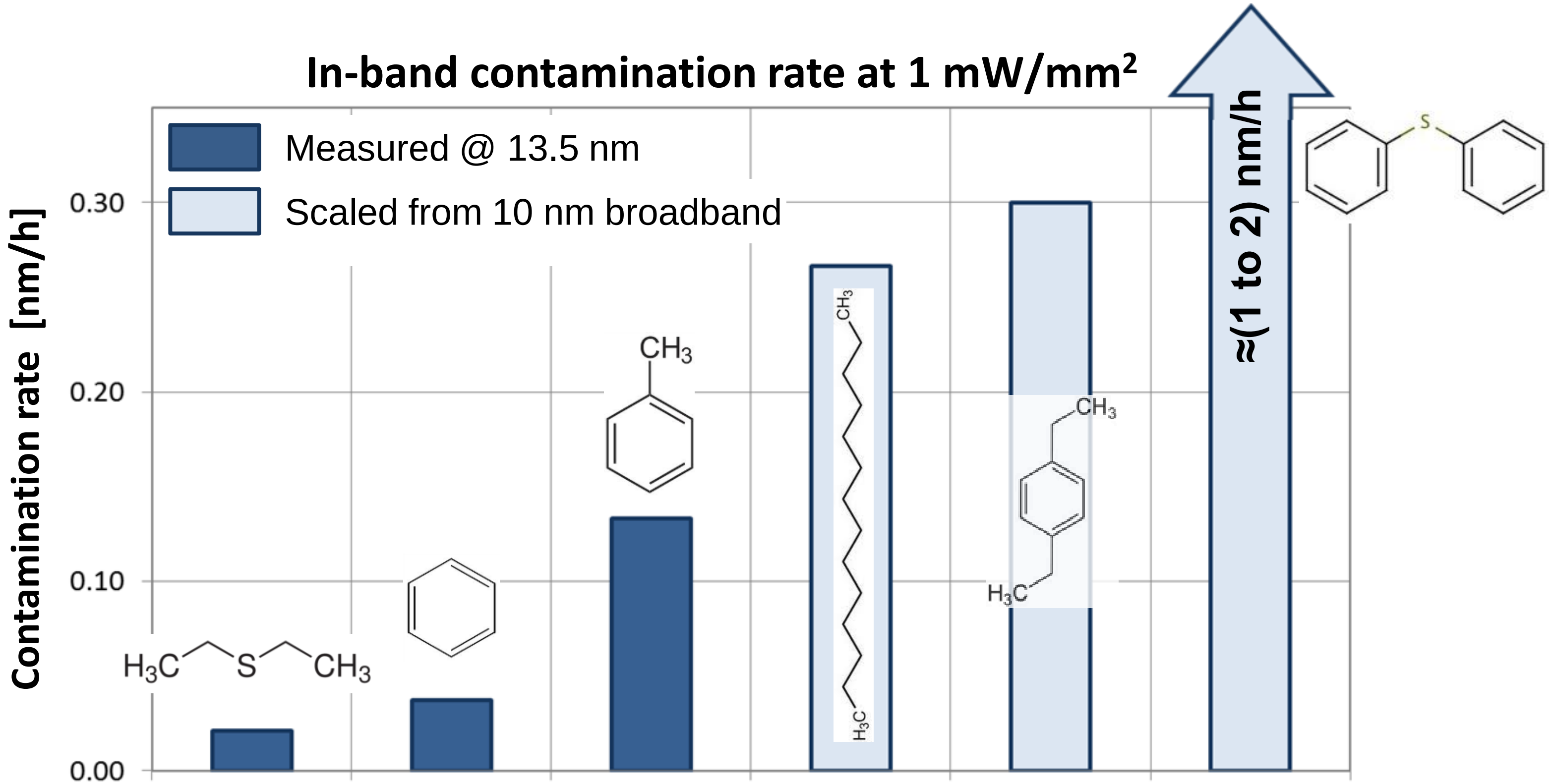
Contamination rates for various species



	Diethyl sulfide	Benzene	Toluene	Tetra-decane	Diethyl benzene	Diphenyl sulfide
Exposure pressure	2×10^{-6} Torr	1×10^{-6} Torr	1×10^{-6} Torr	1×10^{-6} Torr	1×10^{-6} Torr	5×10^{-7} Torr

- Presence of S (or F) does not necessarily result in high contamination rate

Contamination rates for various species



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Exposure pressure	2×10^{-6} Torr	1×10^{-6} Torr	1×10^{-6} Torr	1×10^{-6} Torr	1×10^{-6} Torr	5×10^{-7} Torr
Vapor pressure	**58 Torr**	**94 Torr**	**27 Torr**	**3×10^{-3} Torr**	**1 Torr**	**2×10^{-3} Torr**

- Presence of S (or F) does not necessarily result in high contamination rate.
- Vapor pressure is better indicator of contamination potential, but not universal

Ongoing research

1. **Establish correlation of e-beam vs. EUV resist outgas testing**
   - WS contamination for expanded set of resists - benchmarks
   - AH cleaning efficacy of C and non-C residuals (S, P, Cl, I, Br)
     - Deposits from exposures in admitted gases
     - Exposures of spun-on polymers

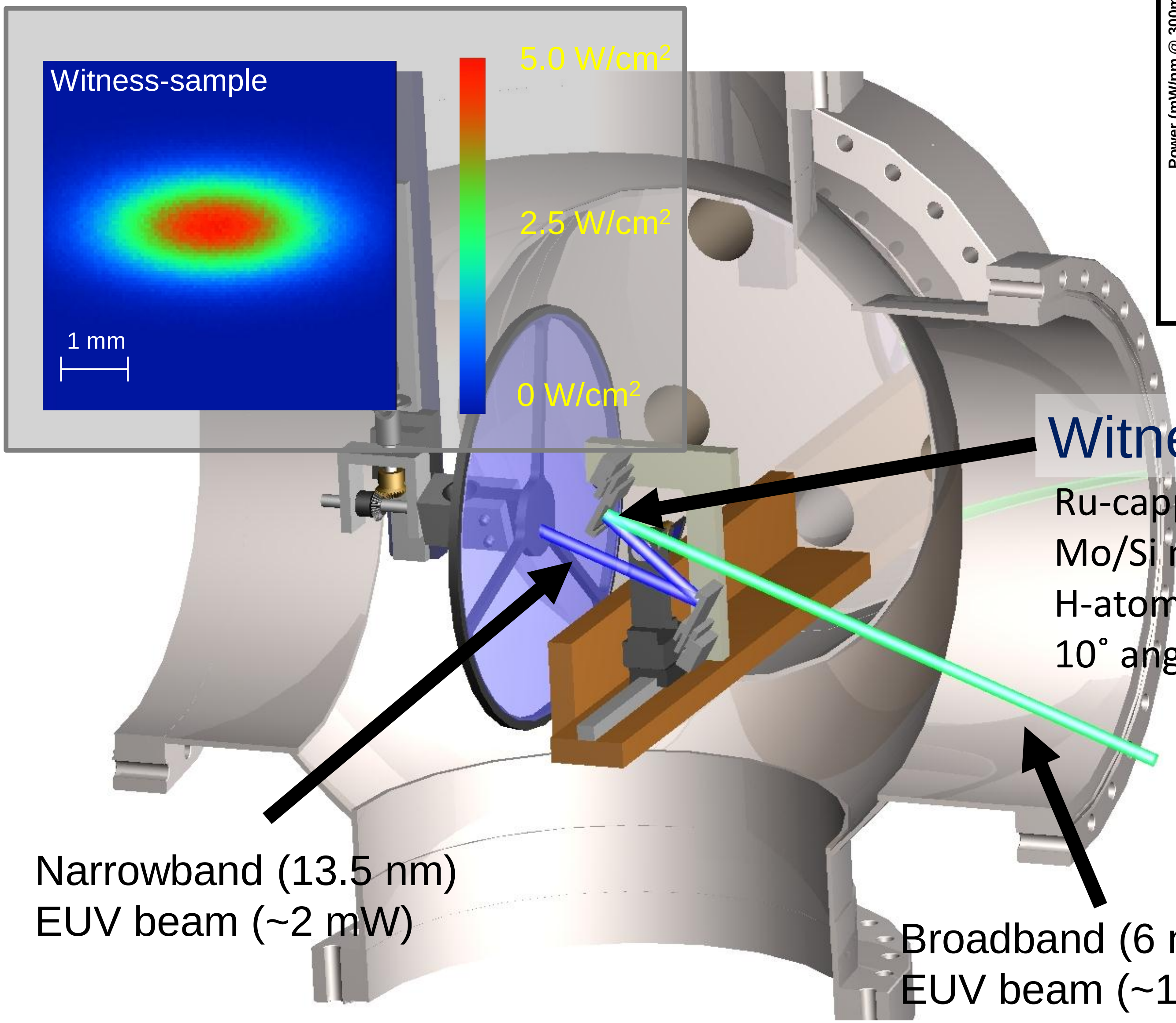
2. **Investigate scaling of WS outgas contamination with area, dose & sequential exposures.**

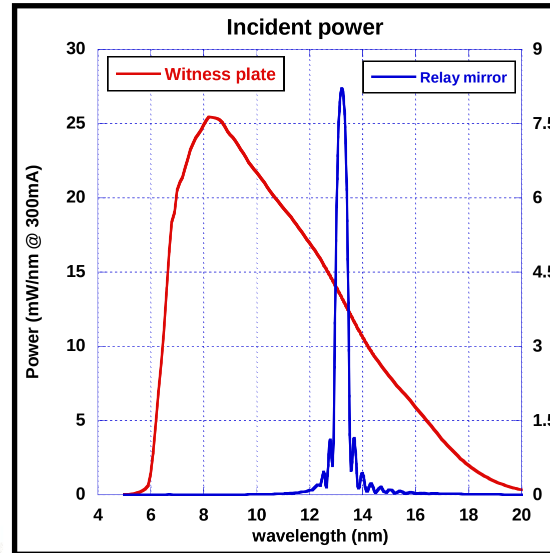
3. **Possible new phenomena associated with high-dose EUV exposure in HVM**
   - "graphitization" of contamination and impact on AH cleaning
   - Reflectivity loss due to repeated AH cleaning

Thank you!

Supplemental Slides

BL-1B Sample chamber





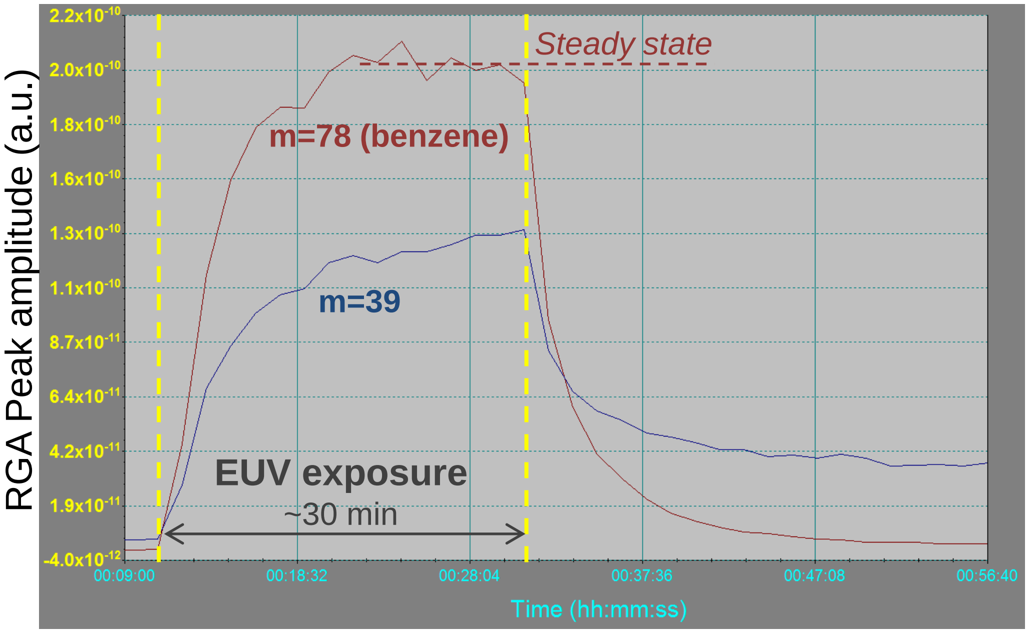
Witness sample

Ru-capped
Mo/Si multilayer
H-atom cleaned
10˚ angle of incidence

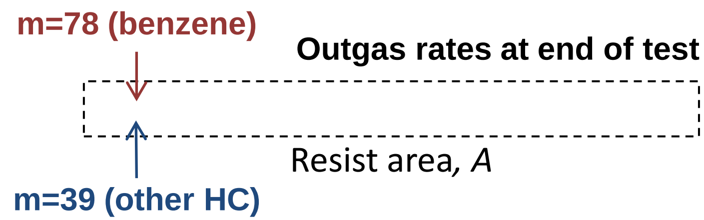
Narrowband (13.5 nm)
EUV beam (~2 mW)

Broadband (6 nm - 18nm)
EUV beam (~150 mW)

Time evolution and scaling of resist outgassing



- Some species (e.g., benzene) will evolve more readily from resist than others (e.g., m=39)
- Outgassing rate reaches steady state once initially irradiated area is depleted.



Total volatilized molecules that will *eventually* outgas from area, *A*, exposed to E_0

Fraction of volatilized molecules yet to outgas by end of test time, *T*

- Effective outgas time for species s, τ_s, during test.
- Varies with *T* if steady state not attained
- Resist dependent

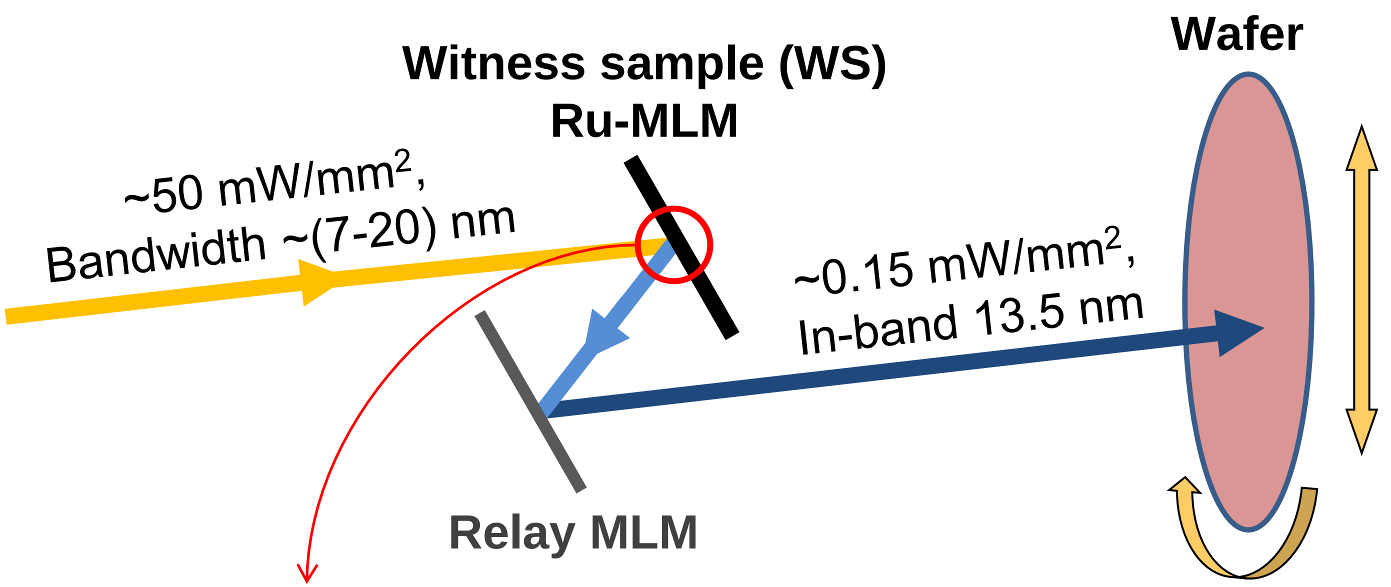
$$\left(\begin{array}{c}\text{Num species-}s\text{ molecules}\\ \text{emitted during test time, }T\end{array}\right) = N_s = \alpha_s A\, E_0 \cdot \left(1 - \frac{\tau_s}{T}\right)$$

- Resist dependent.
- May vary with dose.

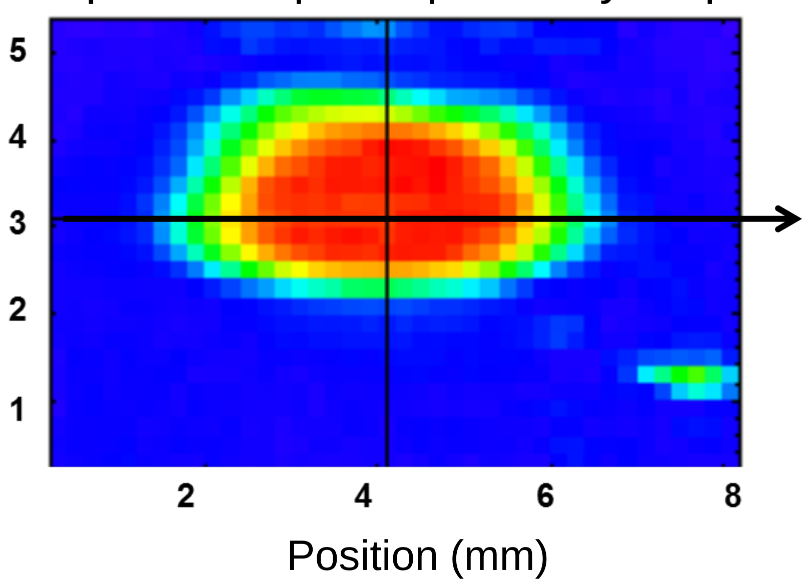
$$\left(\begin{array}{c}\text{C thickness}\\ \text{on WS}\end{array}\right) = \sum_{s}^{species} \beta_s N_s = A\, E_0 \sum_s \alpha_s \beta_s \left(1 - \frac{\tau_s}{T}\right)$$

- **Outgas contamination scales with exposed area, *A*, for fixed test time *T*.**
- **No simple scaling law for *T*.**

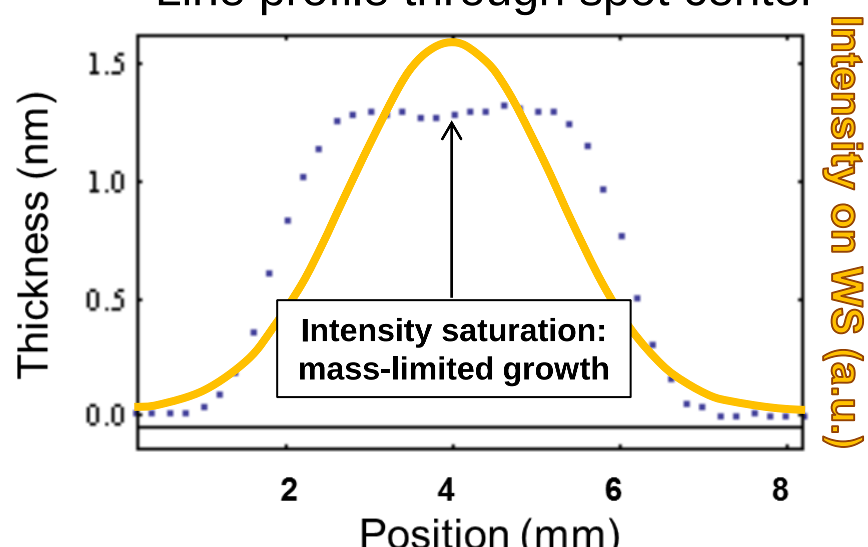
Outgas testing requires "mass-limited" C growth



Spectroscopic ellipsometry map

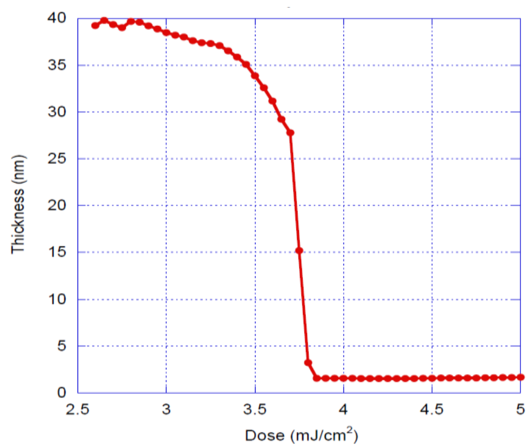


Line profile through spot center



National Institute of Standards and Technology

AH cleaning in resist-outgas testing



(1) Determine E0

Hybrid systems

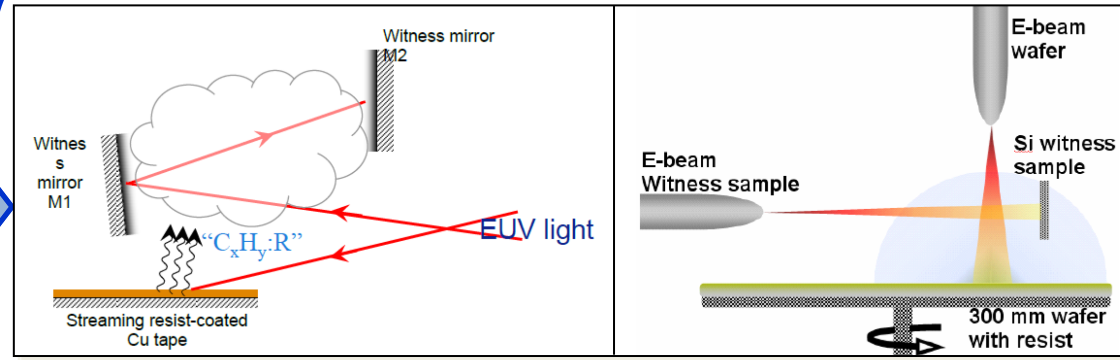
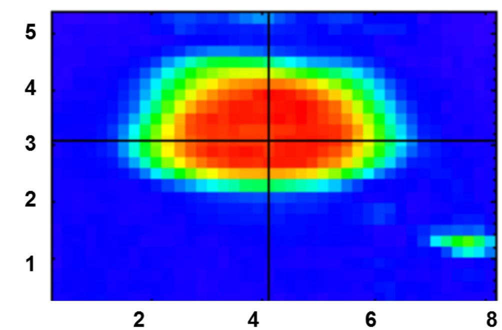


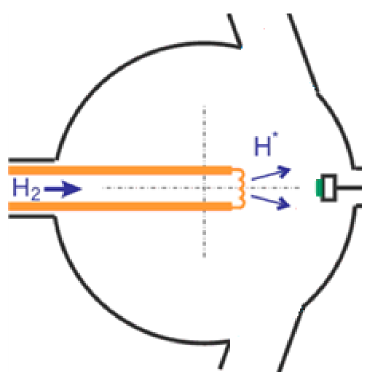
Figure courtesy of N. Harned, ASML

(2) Expose WS (with e^- or EUV) & resist (with e^- or EUV) to E0 in 1 hr.



(3) Measure C-thickness with spectroscopic ellipsometry and scale to 300 mm wafer

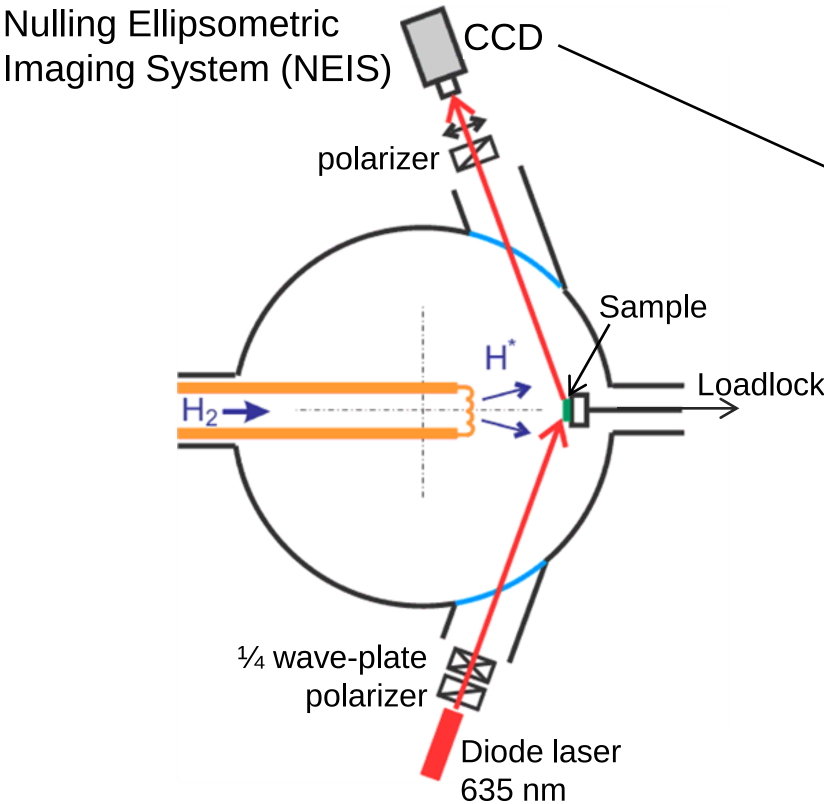
<3nm



(4) AH cleaning of C and residuals (S, P, F…)

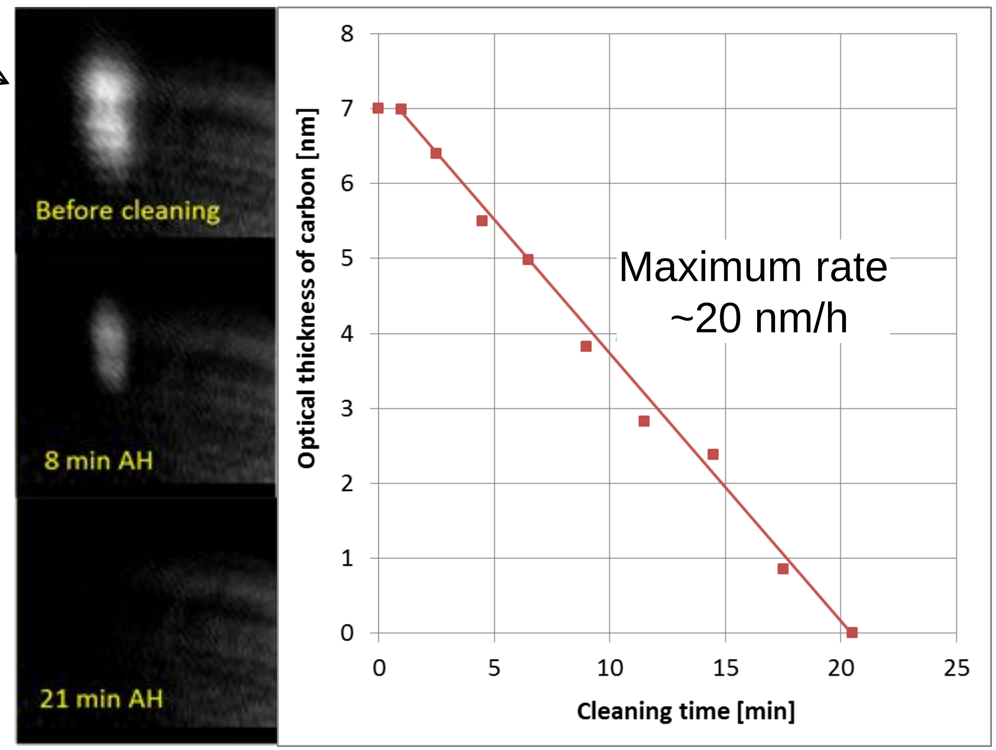
(5) Measure amount of residual non-C {S, P, F, I, Cl, …} with XPS.

NIST atomic-H cleaning facility



- Base pressure ~10^{-8} torr
- Filament-sample distance = 4.5 cm
- Filament material - W
- H_2 pressure ~ 1 Torr
- $T_{filament}$ = 1850°C
- $T_{sample} \leq 60$°C

AH cleaning of EUV-deposited carbon

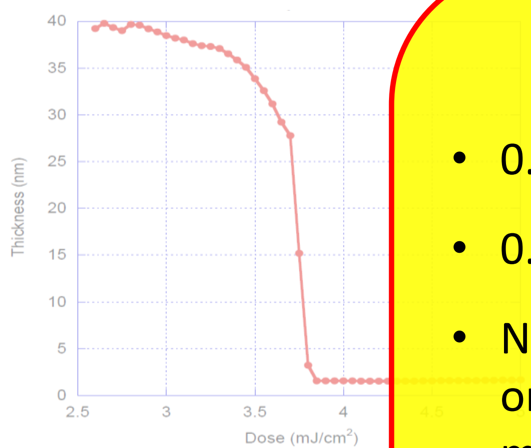


- Thickness monitored *in situ* by NEIS (Nulling Ellipsometric Imaging System)
- NEIS signal normalized to thickness measured by *ex situ* XPS before cleaning.

ASML Resist-Outgas Testing Protocol at NIST

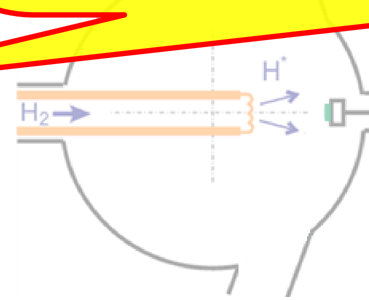
ASML announced relaxed XPS detection limit criteria

- 0.1 at% for I (highly absorbing)
- 0.25 at% for all others
- New limits allow acquisition in ¼ of the time compared with original (0.1 at% for all) and provide enhanced sensitivity for most harmful species (I).
- NIST developed spreadsheet tool relating XPS acquisition parameters to desired "detection limit" to improve uniformity in XPS sensitivities at different resist outgas testing facilities.



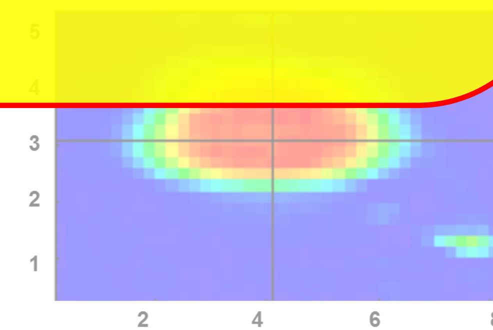
(1) Determine E0

(5) Measure amount of residual non-C {S, P, F, I, Cl, …} with XPS.



(4) Clean C with atomic H

<3nm



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