Update on NIST resist-outgas testing program

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Outline

- Status and progress of resist testing at NIST
- Investigation of atomic-H cleaning efficacy for non-carbon contaminants
- Propose study to compare contamination rates of electrons and EUV photons

Update on resist-outgas testing at NIST

- Agreements to perform testing with four resist manufacturers

- NIST witness sample (WS) resist-outgas test
  - E0 measurement
  - Includes 2 separate WS exposures to verify reproducibility
  - Cost $9,363 per resist test
  - Current throughput ≈ 1.5 resists per week

- Once reproducibility is established for several resists, may lower cost and increase throughput by performing only one WS exposure per resist.

- NIST will adopt one or two widely used resists as working standards for comparison with other testing facilities.

- Limited data base of 8 different resists tested to date. All but one met NXE-3300 specifications.

Atomic-H cleaning of non-C contaminants

- At 2011 EUVLS Resist TWG ASML indicated little/no data on efficacy of atomic H cleaning of non-C contaminants (S, P, I, F, etc.)

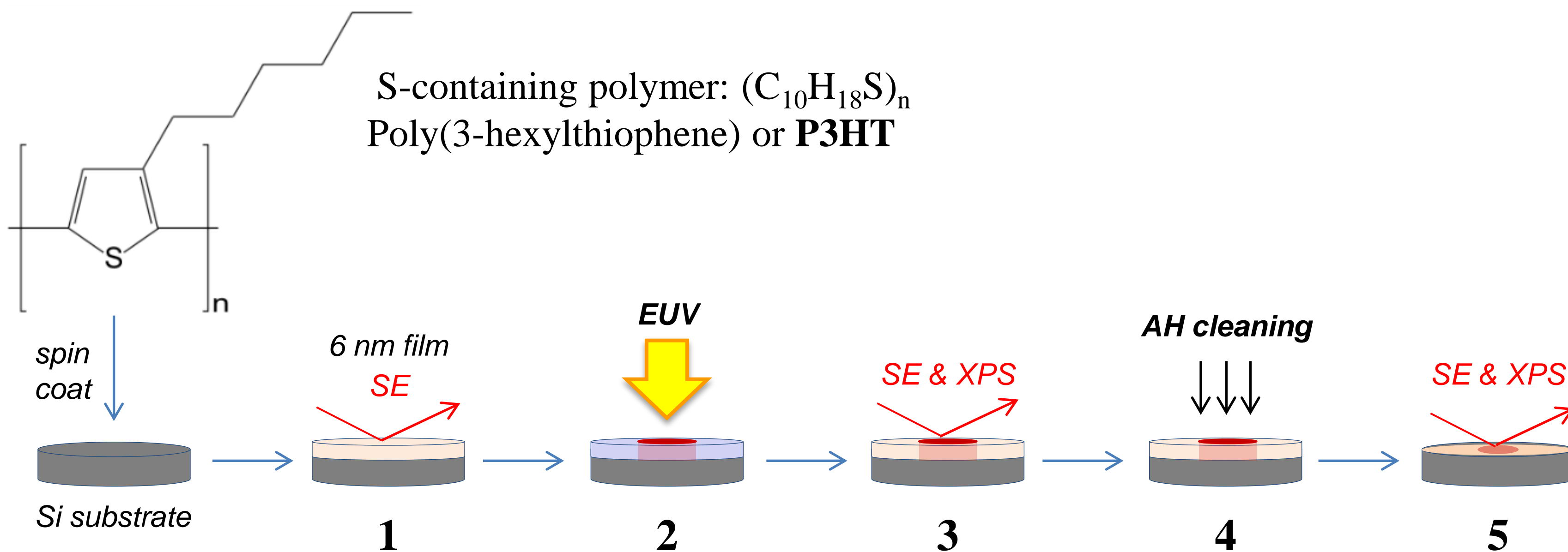
- Direct comparison of XPS before and after AH cleaning of resist-outgas samples is constrained by limited XPS time and low levels of non-C contaminants from resist outgas test to date.

- In **one** case when XPS could be performed before and after cleaning of resist outgas sample, ~3 At% of S was completely removed by AH.

- NIST is attempting a more systematic investigation by AH cleaning of EUV-exposed spin-coated polymers containing appropriate species.

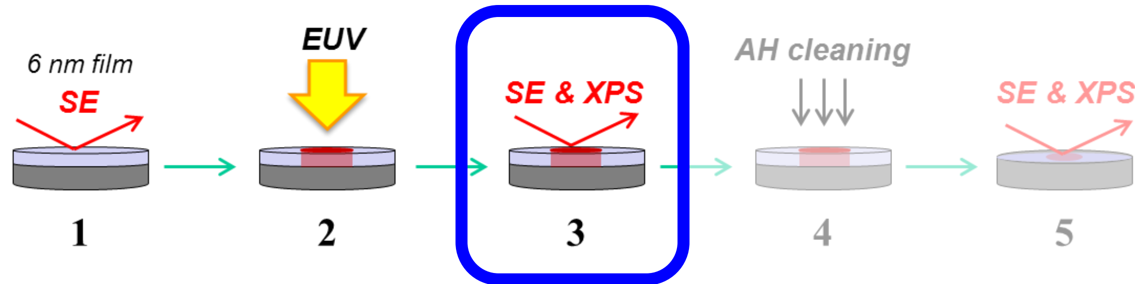
- First test of S-containing polymers on Si substrate have been completed

Polymer-based atomic-H cleaning study



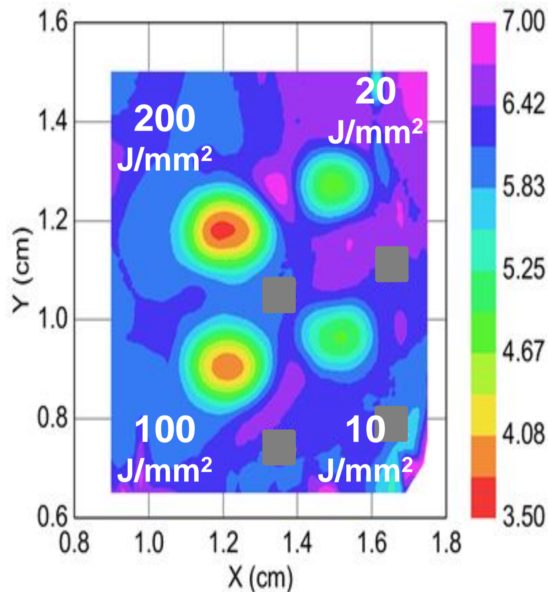
1) Spin coat 6 nm film of P3HT onto Si substrate
2) Perform 4 high-EUV-dose exposures (10-200 J/mm^2) on single sample
3) Inspect with spectroscopic ellipsometry (SE) and XPS
4) Clean with atomic H (AH) for time to remove equivalent amount of EUV-deposited C
   - Preliminary results suggest : (unexposed P3HT cleaning rate) ≥ (EUV-deposited carbon rate).
5) Inspect with spectroscopic ellipsometry (SE) and XPS

P3HT after EUV exposures: SE & XPS



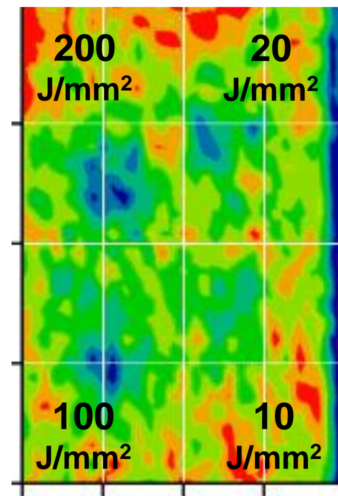
Spectroscopic ellipsometry

(using optical constants of unexposed resist)

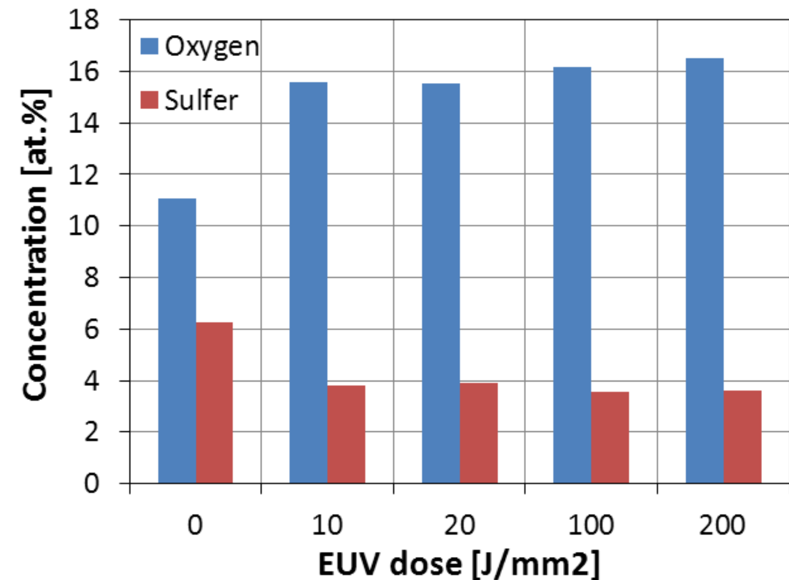


XPS

Map of S 2s peak

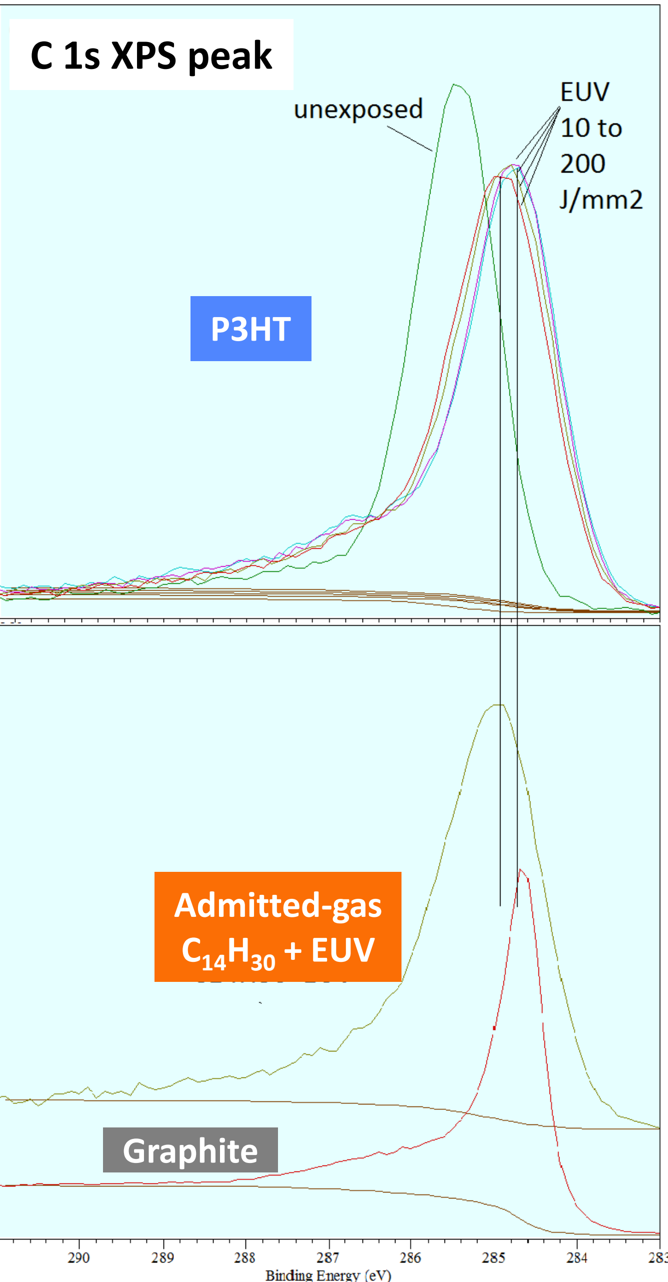


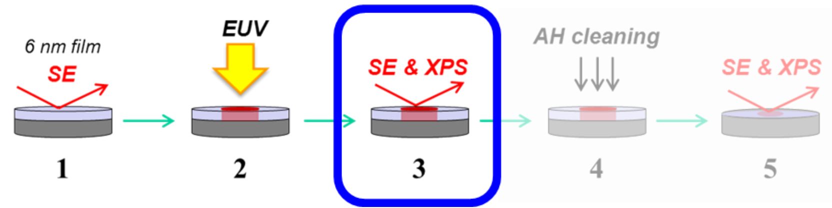
Effect of EUV on composition

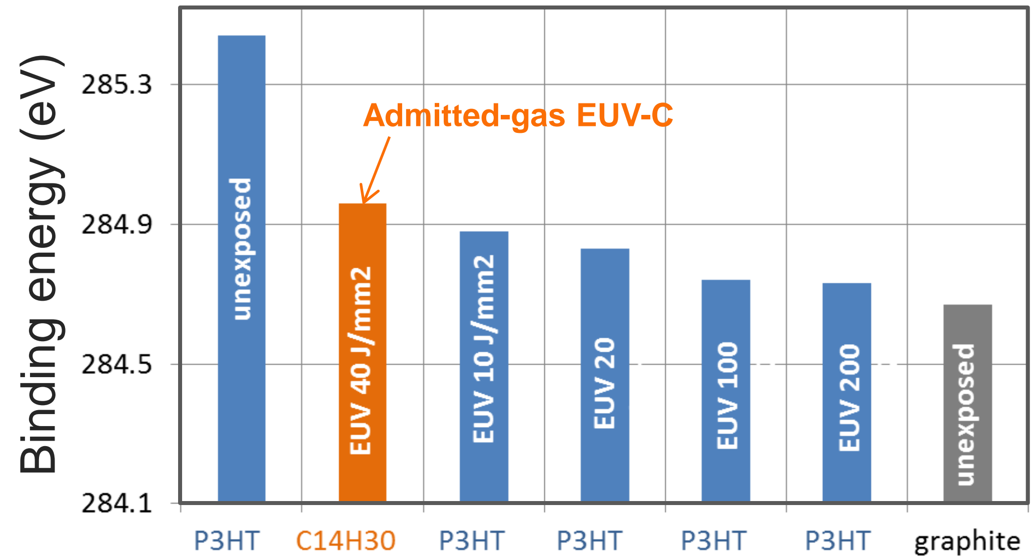


- Lowest-dose of EUV significantly affected S and O content
- Increasing EUV dose had little effect: suggests EUV saturation

Effect of EUV on C 1s XPS peak

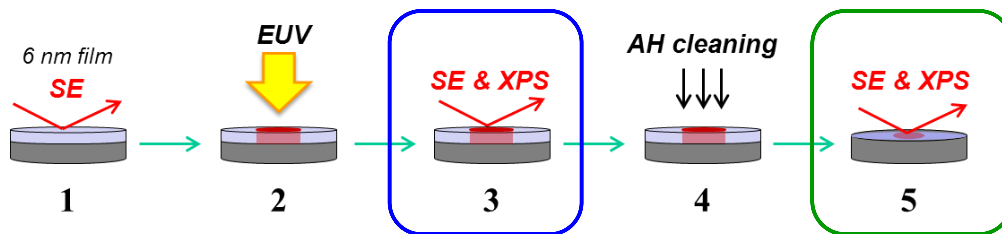






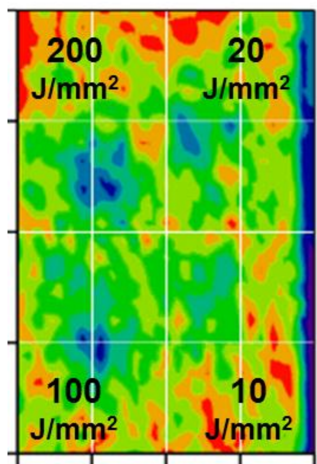
- EUV decreases C concentration only slightly
- Lowest EUV dose dramatically alters P3HT C1s peak to similar shape and energy of typical admitted-gas EUV-C.
- C1s binding energy shifts toward graphitic state with increasing EUV dose – as observed with admitted-gas EUV-C deposits.

Compare before & after AH cleaning



Before cleaning

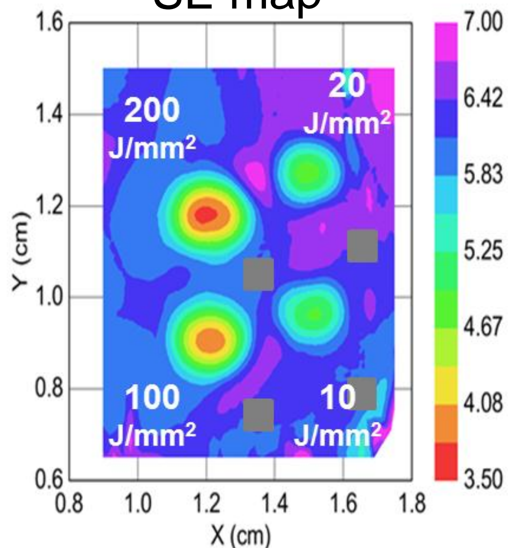
XPS S 2s map



XPS Atomic concentration

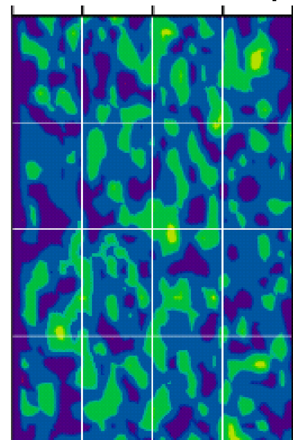
EUV dose J/mm2	C 1s at%	O 1s at%	S 2s at%	Si 2p at%	N 1s at%
0	72	11	6.3	11	0.2
10	69	16	3.8	12	0.3
20	69	16	3.9	11	0.3
100	67	16	3.5	13	0.2
200	67	17	3.6	13	0.4

SE map



After cleaning

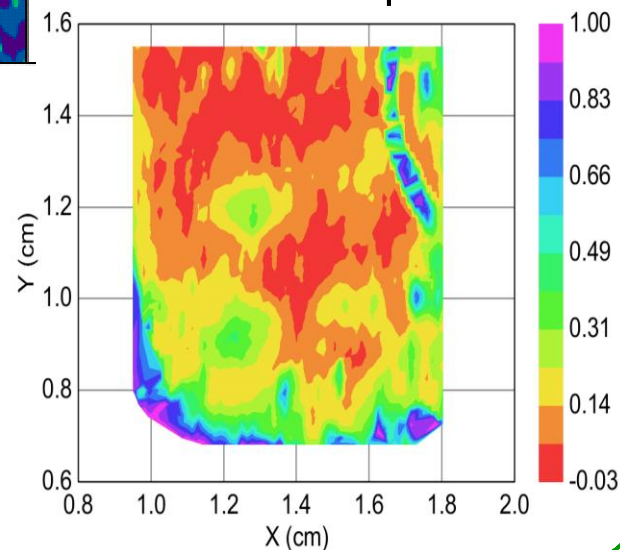
XPS S 2s map



XPS Atomic concentration

EUV dose J/mm2	C 1s at%	O 1s at%	S 2s at%	Si 2p at%	N 1s at%
0	13	34	<0.5	53	0.1
10	14	34	<0.5	52	
20	14	34	<0.5	52	
100	17	33	<0.5	49	
200	15	35	<0.5	51	

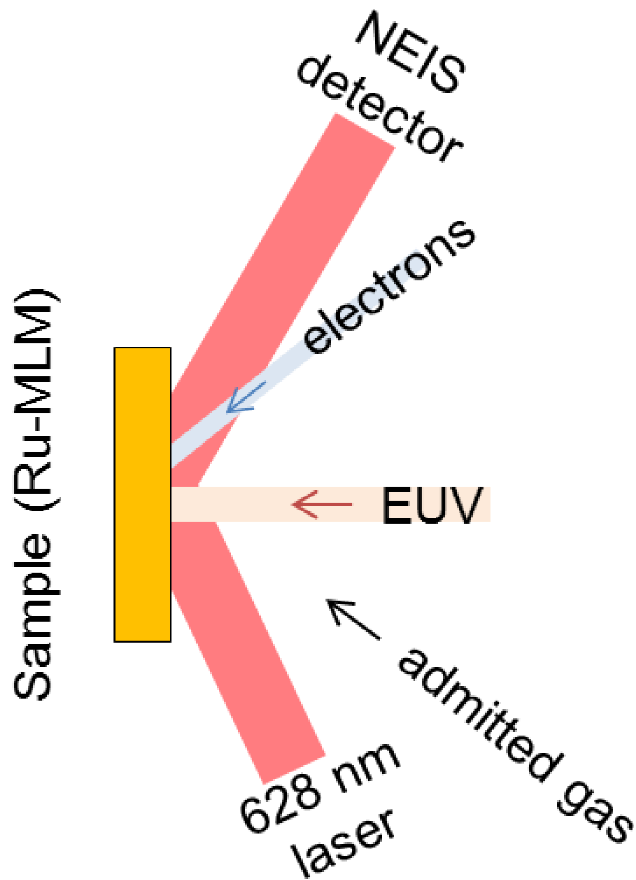
SE map



Atomic-H cleaning of non-C contaminants

- Initial results indicate AH can effectively remove S from native and EUV-exposed P3HT-coated Si
- XPS C 1s peak for EUV irradiated P3HT is similar to EUV-deposited C, but XPS provides only limited insight into chemical nature.
- Procedure will be repeated for P3HT on Ru-MLMs then other polymers will be explored.
- AH cleaning on contamination from actual admitted-gas exposures of diphenyl sulfide will be performed to test use of polymers as proxy.

Propose direct comparison of electron and photon contamination rates



- Exploring feasibility of adding a small electron gun to the NIST optics contamination facility.
- Perform e-beam and EUV-photon exposures on same sample in same vacuum environment of admitted gas.
- Real-time monitoring of carbon growth with Nulling Ellispometric Imaging System (NEIS)
- Comparison of contamination rates and morphology of deposits (XPS, SE, NEXAFS) from EUV and e-beam exposures in admitted-gas.