Fundamentals of the Reaction-Diffusion Process in Model EUV Photoresists

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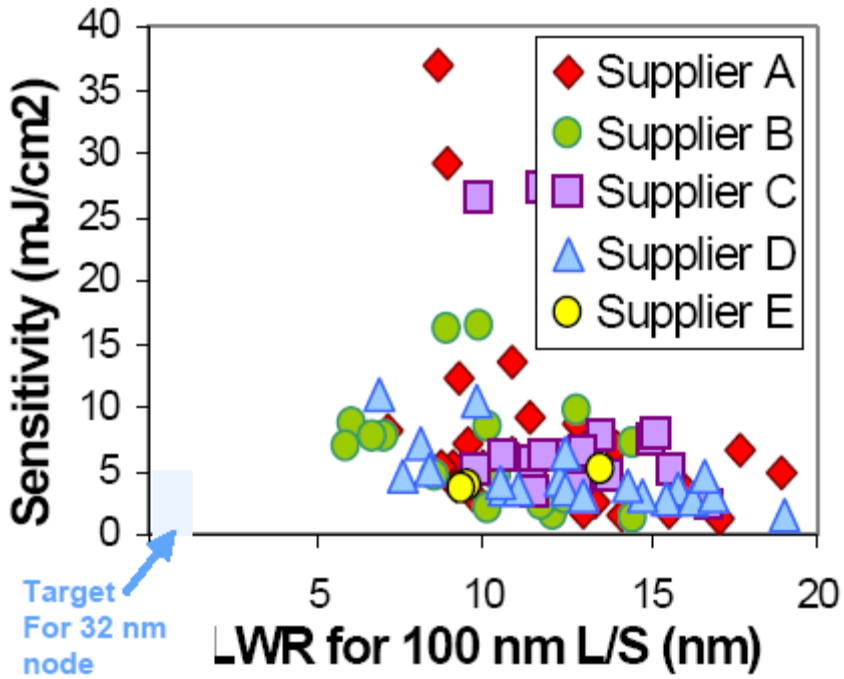
CRADA 1893

Motivation and Industry needs



•Simultaneously meeting resolution, sensitivity, and line width roughness

Adapted from : Melissa Shell Sematech EUV perspectives Meeting 5/10/05

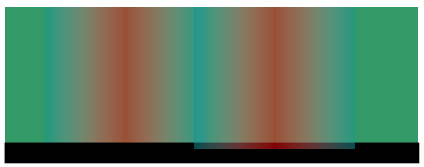
Current Challenges

1. Photoacid distribution at line-edge – dose related

- Few photons → statistical origin to LER?
- ➢ Higher PAG loadings → improve sensitivity

2. Acid diffusion

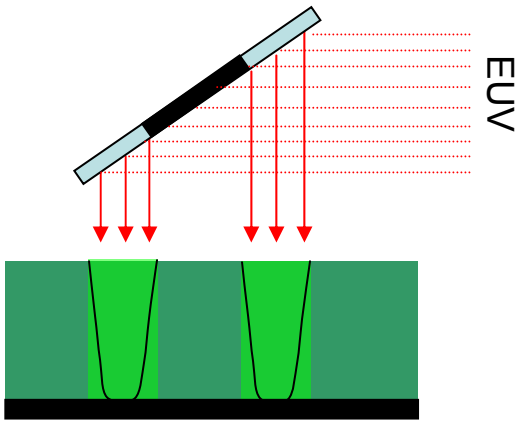
- How much is good / bad?
- ➢ Sharp latent image interfaces → Beneficial to LER



Identify the resist characteristics that lead to sharp latent image profiles

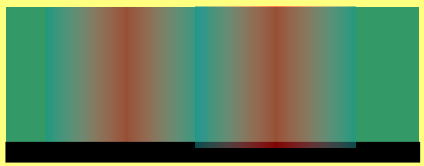
Lithography Process

Optical

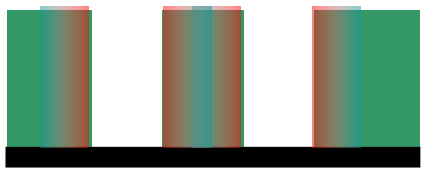


Post-Exposure

- PEB conditions
- Acid diffusion

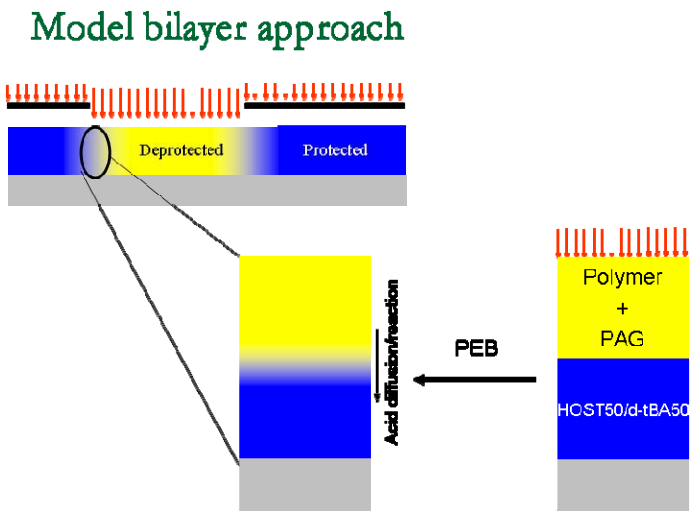


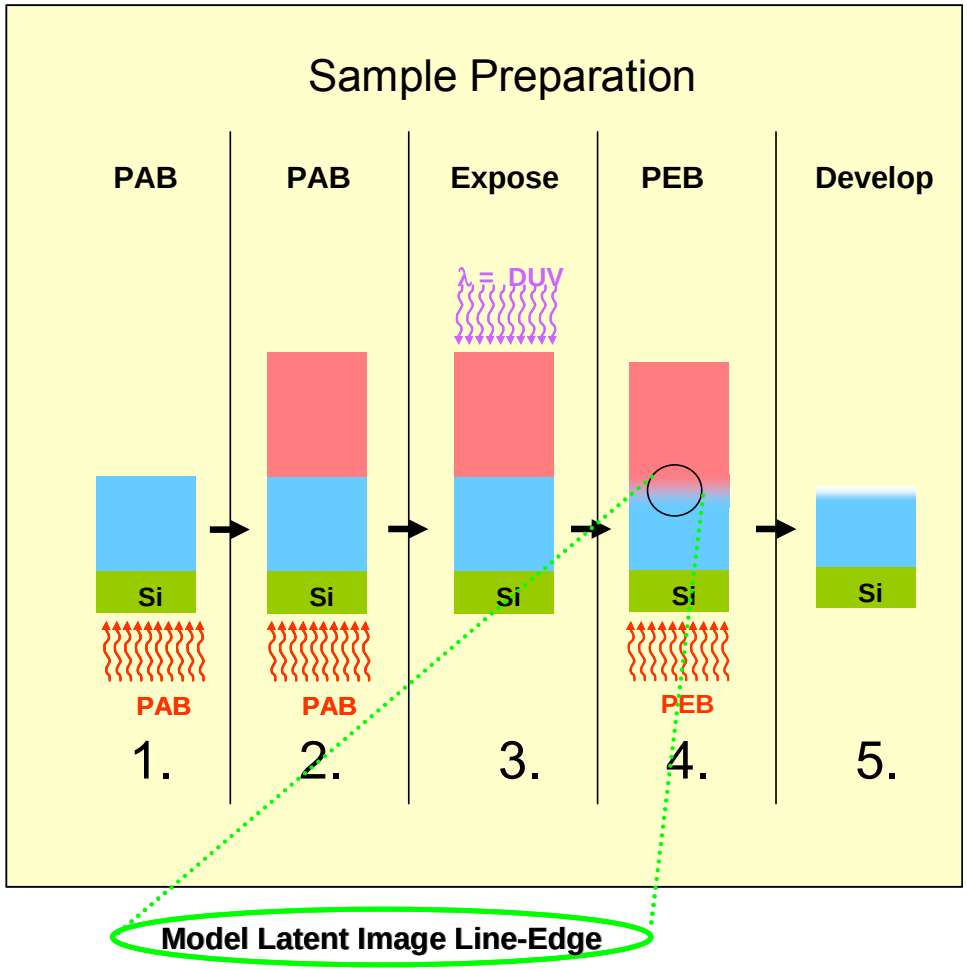
Development



How to measure the interface formation without optical effects?

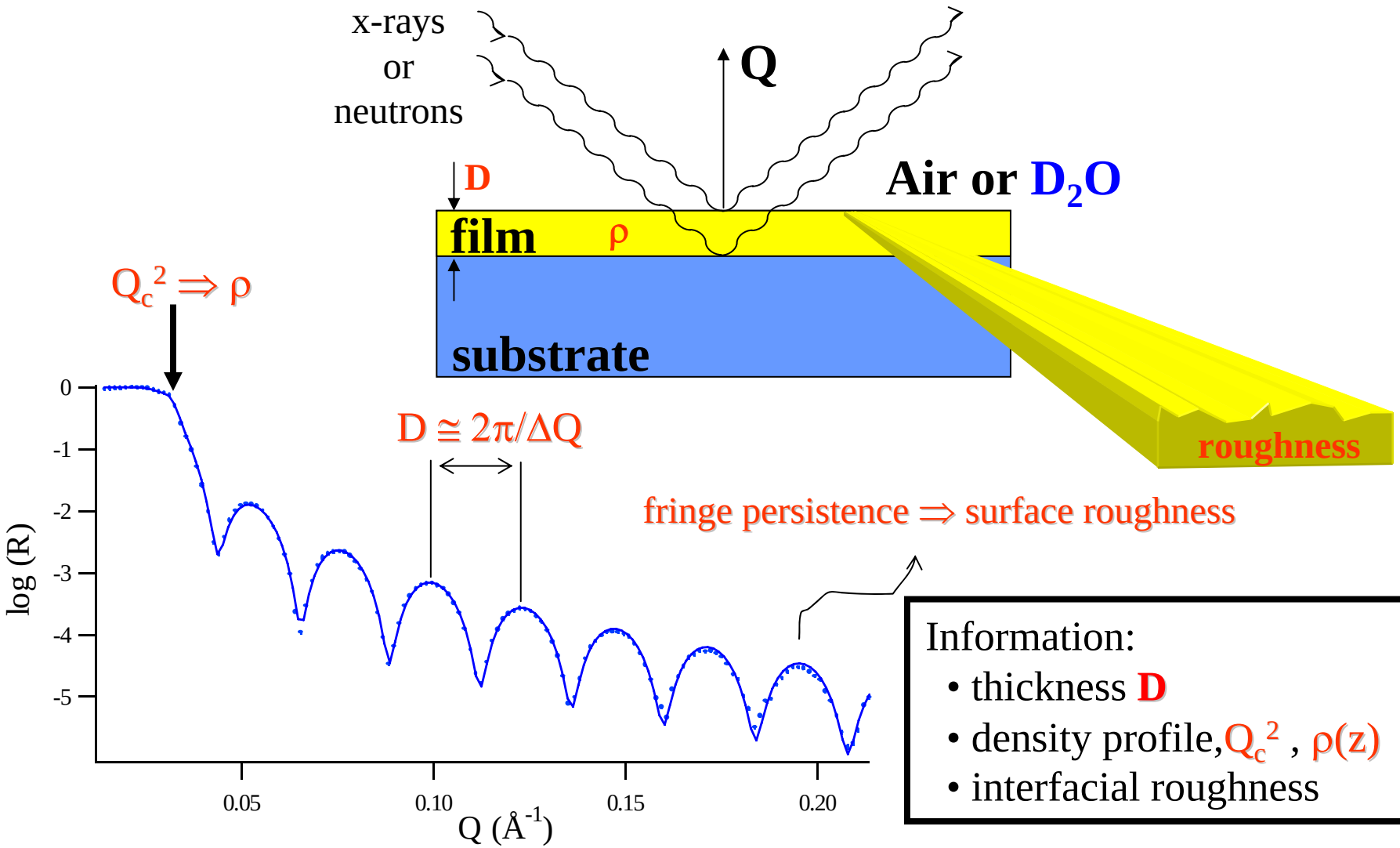
Ideal Step-Exposure Profile: Bilayer Geometry





- Multiple spin coat steps
  1. Acid feeder layer
  2. Resist layer
- *Currently* – using broadband DUV (248-nm) for experimentation

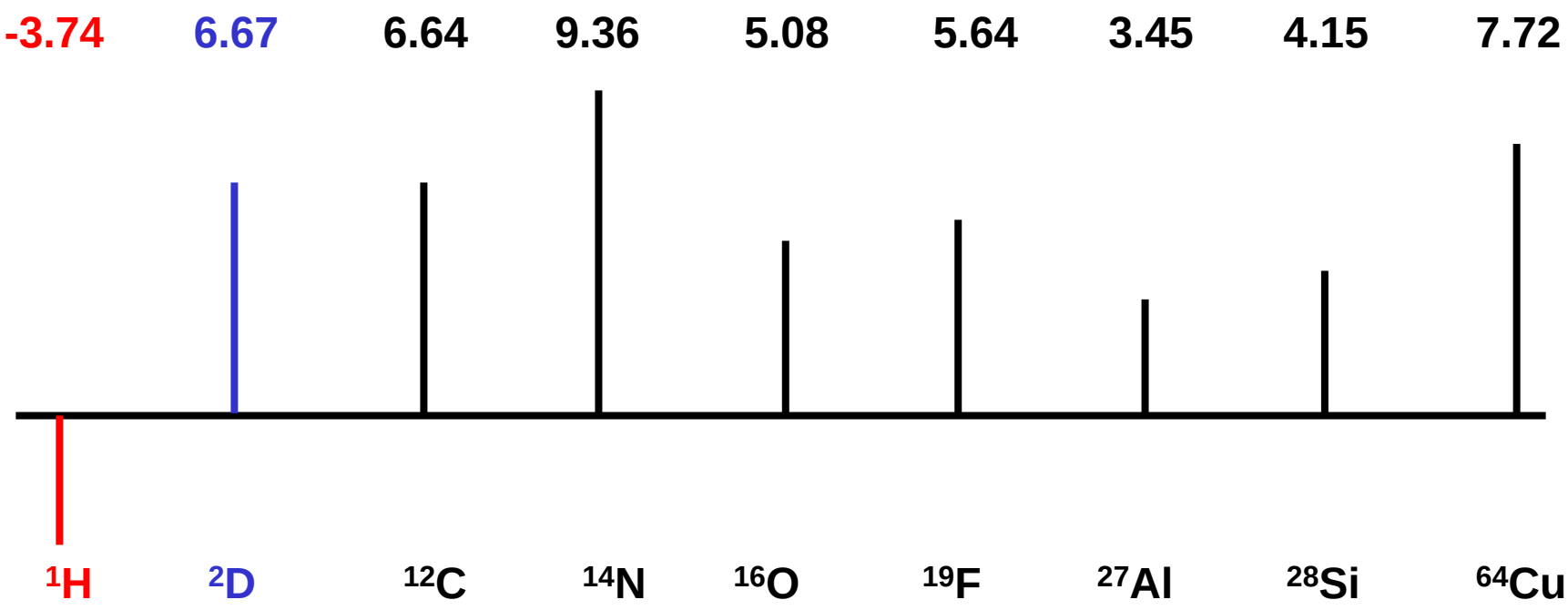
Measurement: Neutron Reflectivity



Information:

- thickness **D**
- density profile, Q_c^2 , $\rho(z)$
- interfacial roughness

Neutron scattering length densities

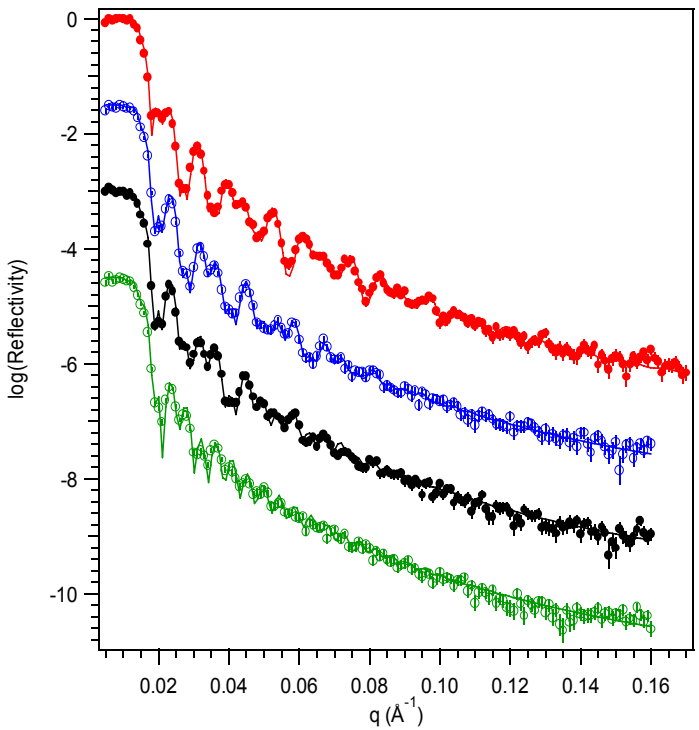


- Contrast largest between hydrogen and deuterium – very sensitive measurements
- Introduce isotopic substitution (H,D) to measure resist latent image profiles

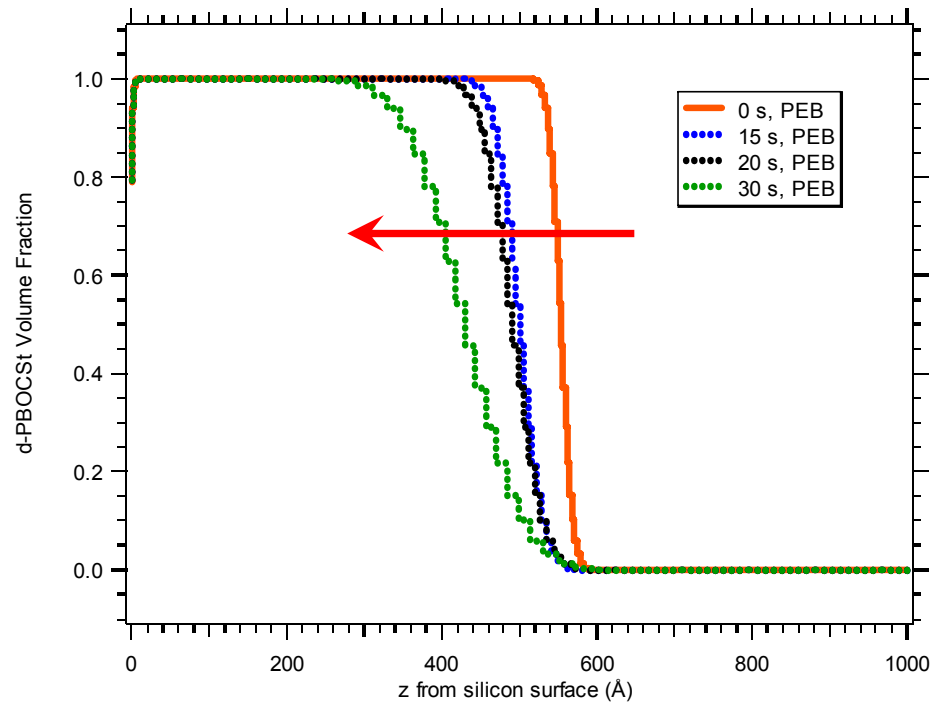
Reaction Front Evolution

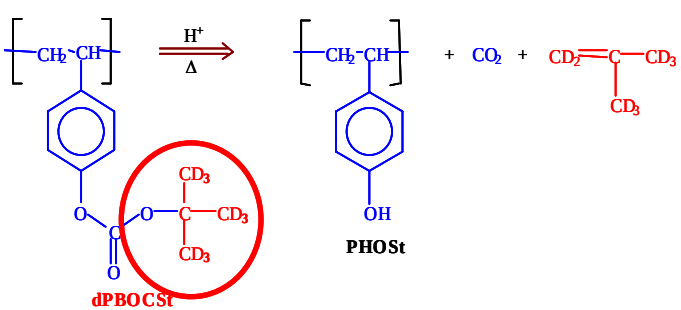
•Deuterium-labeled protection group provides neutron reflectivity contrast

Neutron Reflectivity Results



in situ protection profiles

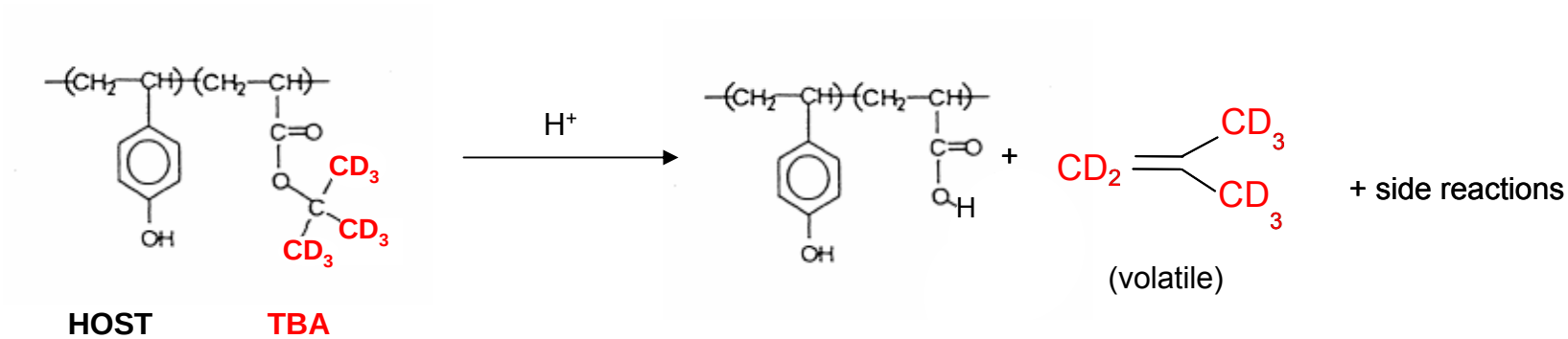




•*Ideal* Line-Edge leads to broadening (110°C PEB)
•Wide-range of protection levels at reaction-front
•Lin et al., Science 2002, 297, 372

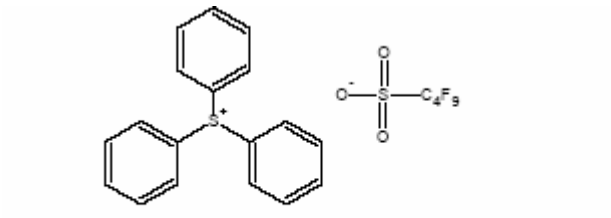
Experimental : Model EUV resist

- Deuterium labeling to directly measure the reaction-diffusion front
- Model system resist copolymer with photoacid generator



50/50 copolymer*

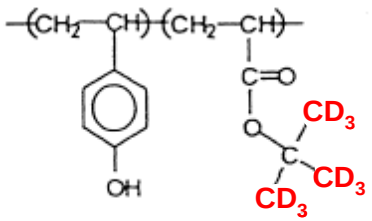
Photoacid generator



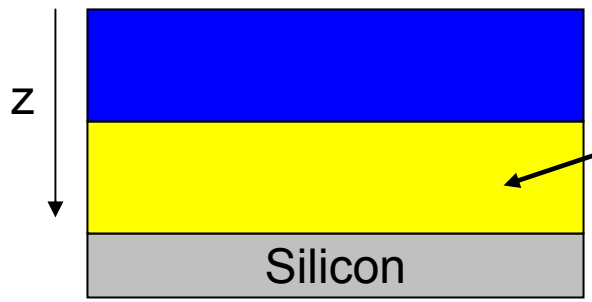
TPS-PFBS (Perfluorobutane sulfonate)

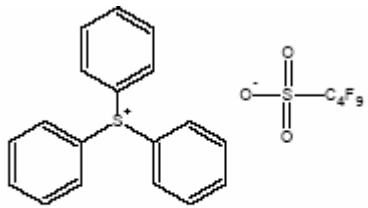
* DuPont Electronic Technologies

Neutron Reflectivity : Copolymer



HOST **d-TBA**

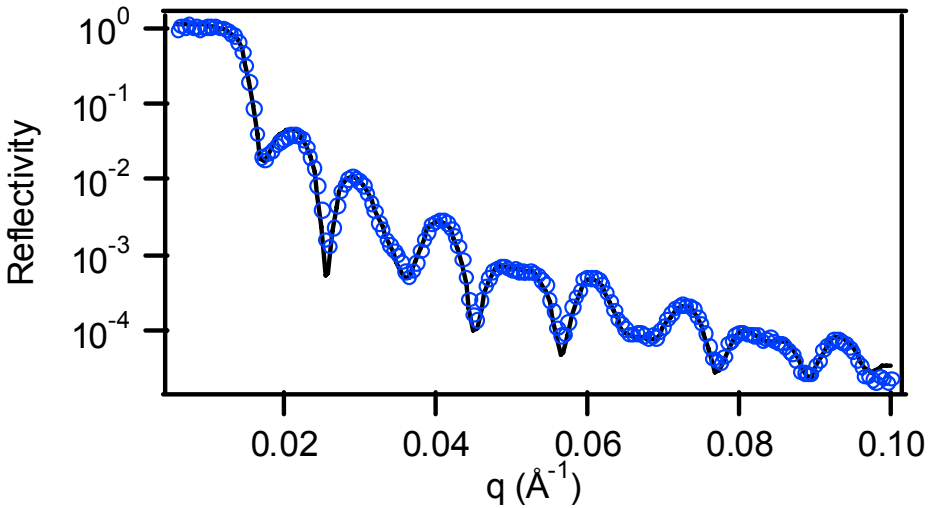


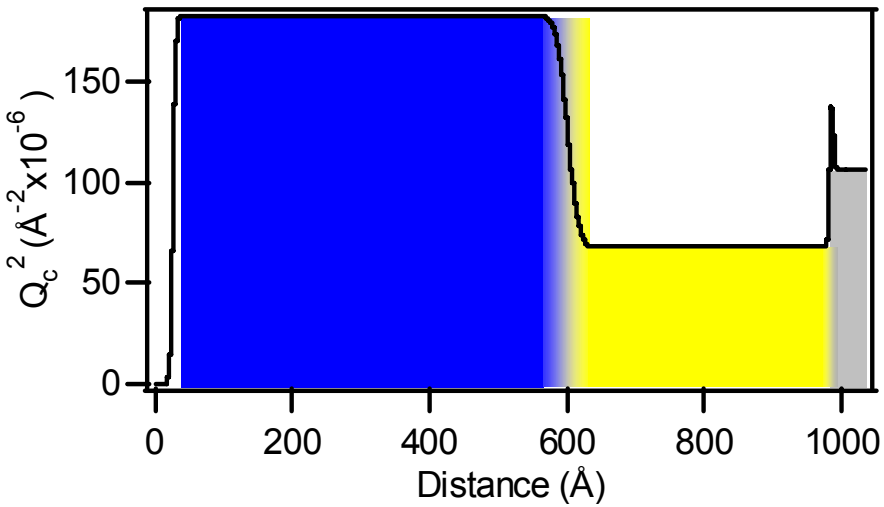


TPS-PFBS (Perfluorobutane sulfonate)

+

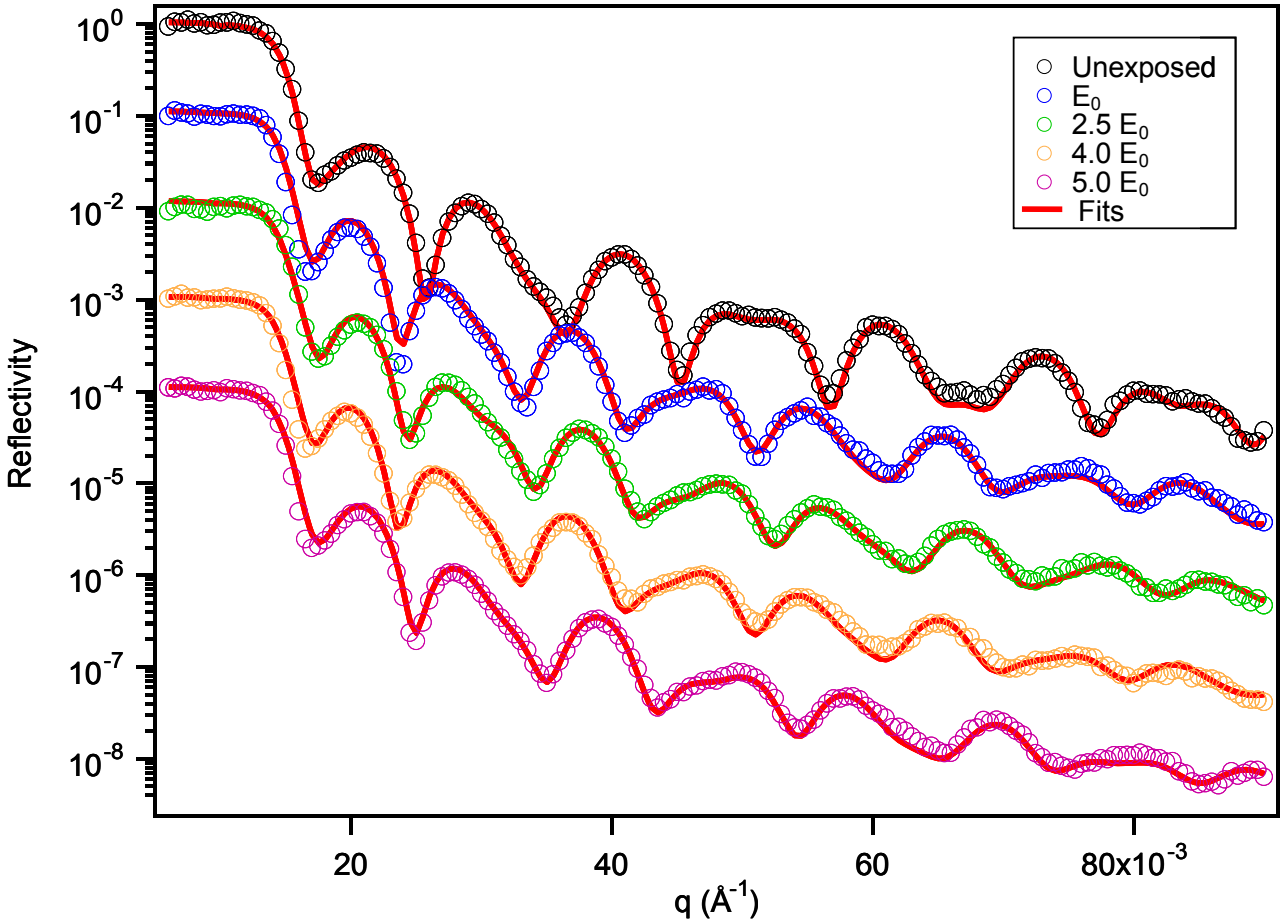
Polymer Feeder





- No PEB, interface between acid feeder and copolymer is < 2 nm
- Follow interface evolution with processing (varied dose & Fixed PEB 130 °C/30s)

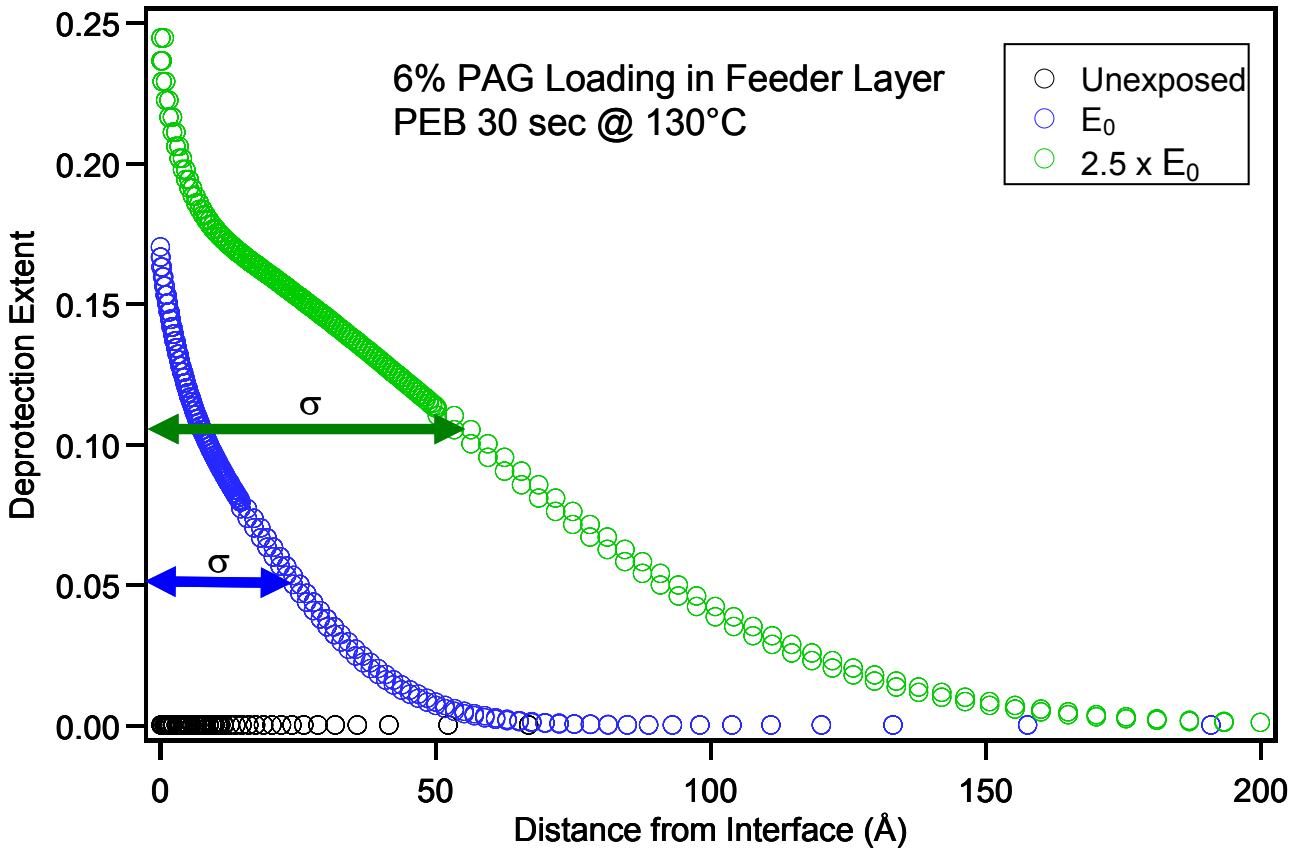
Results - Reaction Front



•Neutron reflectivity indicates bilayer structure

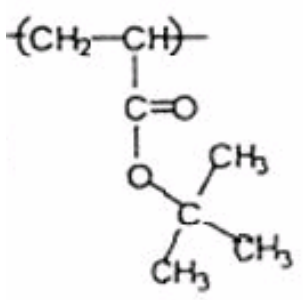
Data vertically offset for clarity
E_o : Dose-to-clear for bilayer

Results - Reaction Front



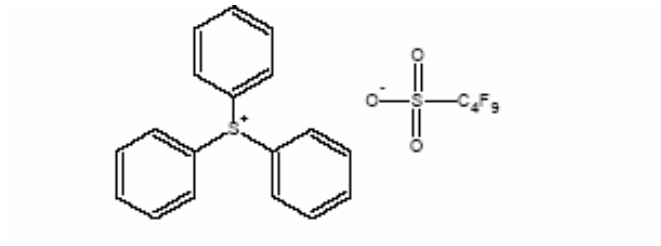
- ***Deprotection profile*** : Length-scale (σ) is (248 nm) dose sensitive
- ***Acid profile*** : Unknown – initially sharp
  - ➢Higher dose → more acid ⟶increased reaction-rate
  - ➢Acid reaction-diffusion models to determine mechanism of reaction length scale – many factors
    - ➢Complexity of acid diffusion in HOST-TBA copolymer – F.A. Houle et al. (2000)
    - ➢Potential for auto-accelerated reaction and thermal deprotection - Wallraff et al. (1994)

Results – PAG Loading



TBA homopolymer

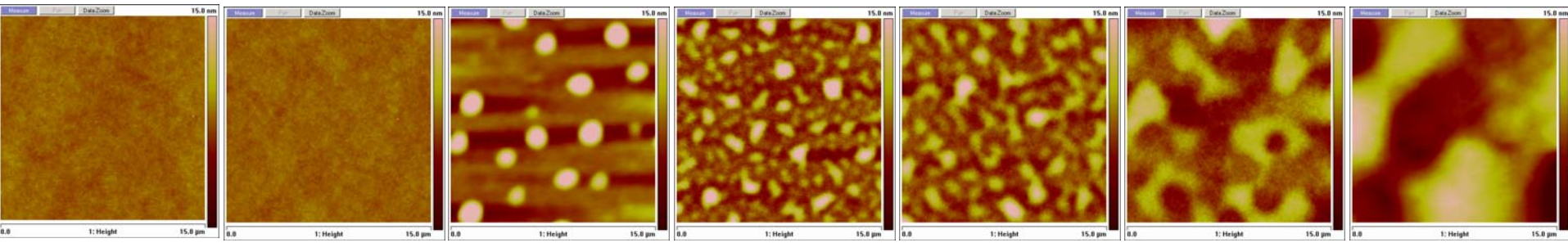
+



TPS-PFBS (Perfluorobutane sulfonate)

Increasing PAG loading

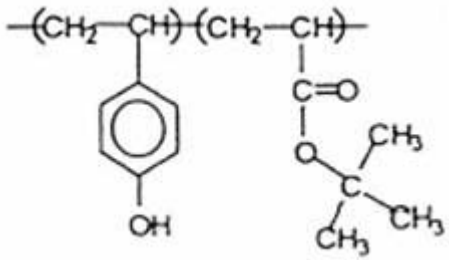
0 % **2 %** **5 %** **10%** **15 %** **20 %** **25 %**



(90°C PAB)

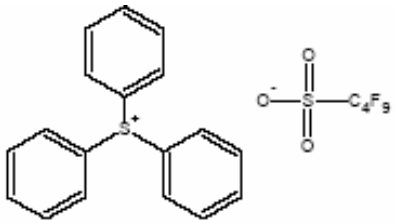
- Segregation within homopolymer increases with loading
- Fixed PAB temperature and time

PAG loading with HOST-TBA resist



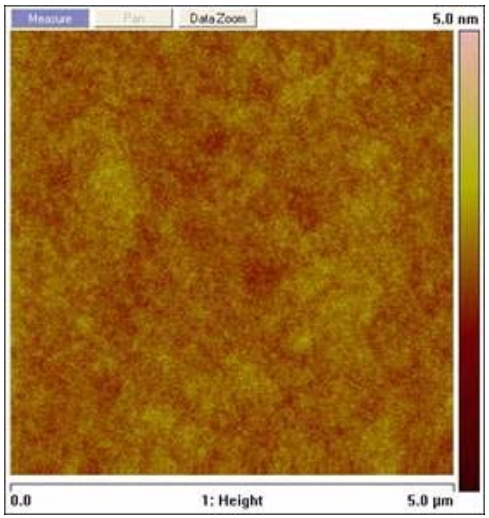
60 / 40 HOST / TBA

+

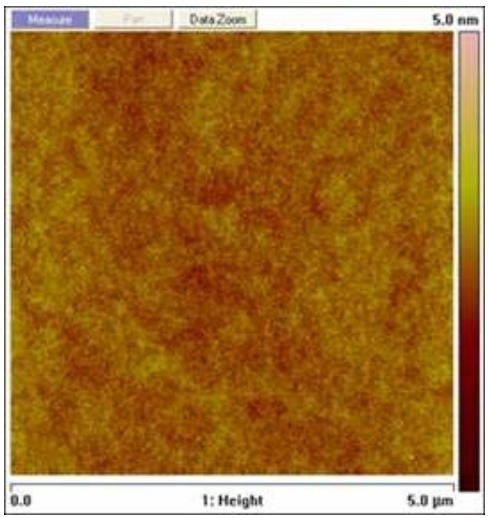


TPS-PFBS (Perfluorobutane sulfonate)

20 %



30 %



- PAG segregation dependent upon resist HOST composition
- Chemical force microscopy See poster (2-ME-09) by JT Woodward

Conclusions

- Reaction front profile *width* dependent upon dose
- High PAG loading leads to phase separation in TBA homopolymer
- PAG segregation at high loadings not observed for TBA-HOST copolymers
    - Copolymers confer miscibility

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