

Limits to accelerated MLM lifetime testing: TiO₂ in hydrocarbons and Ru in H₂O

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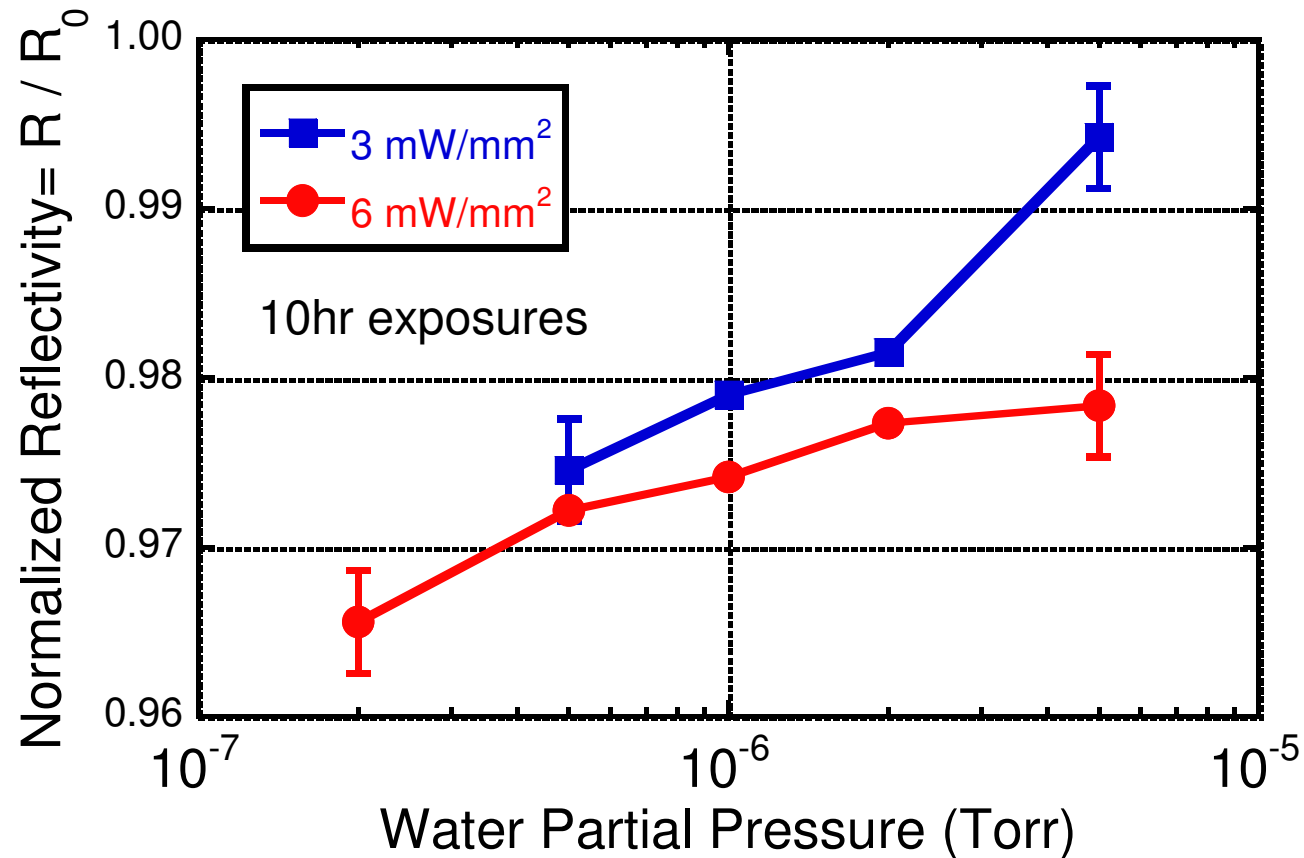
Outline

- 1) Damage of Ru-cap MLMs in H₂O environment
 - Inverse dependence of damage rate on H₂O pressure
 - NIST results confirmed by PTB

- 2) C-deposition on MLMs with non-optimized TiO₂-cap
 - Resist-related HCs: acetone, benzene, MMA, toluene
 - Non-linear behaviors observed

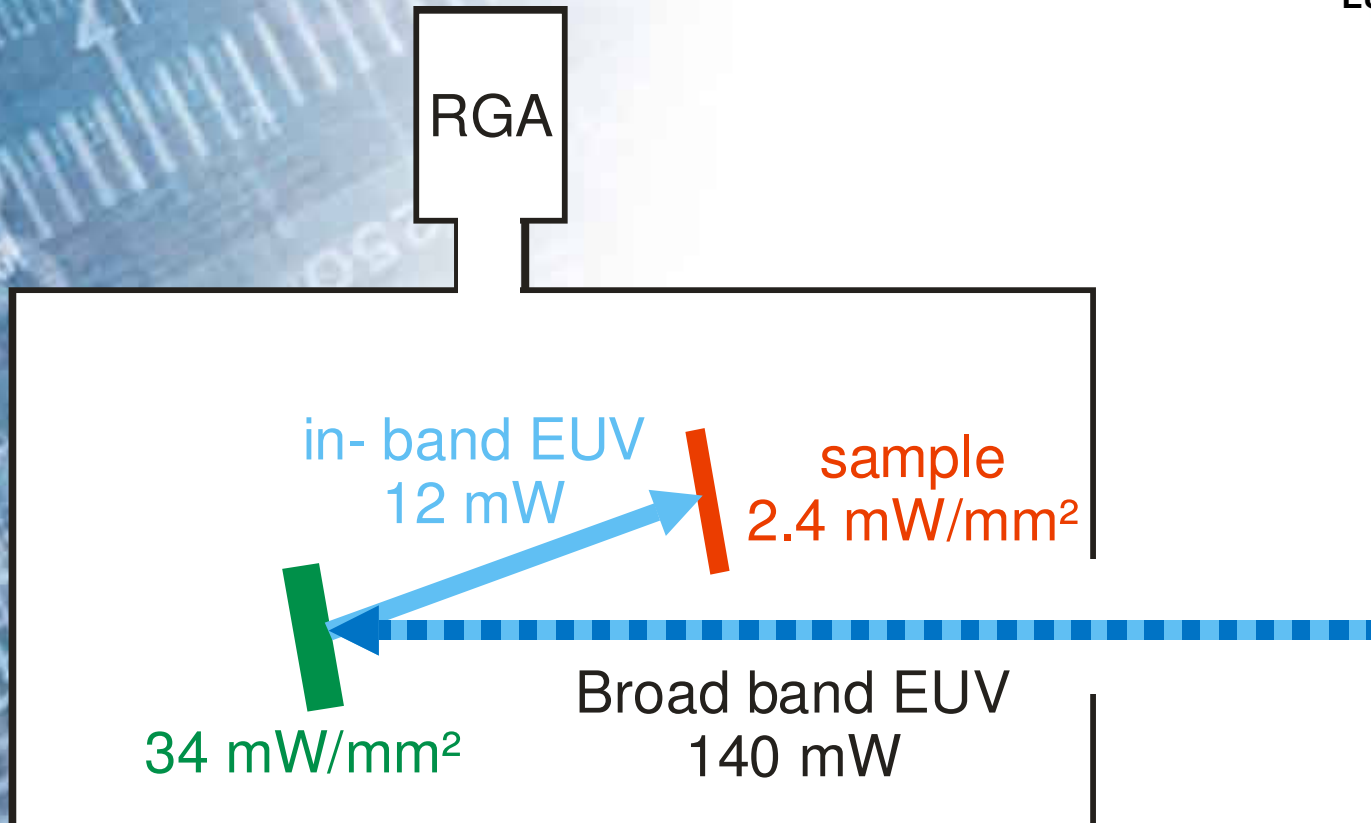
- 3) Simple thick-C-growth model
 - Application to NIST and Intel MET data
 - Limits of model: thick C-growth only

Inverse dependence of Ru-cap MLM damage on H₂O level (Early 2005)



- Hypothesized that competition between oxidation and C-deposition responsible
- But RGA showed no significant hydrocarbon presence
- XPS not available at the time for confirmation

Recent EUV irradiation at PTB



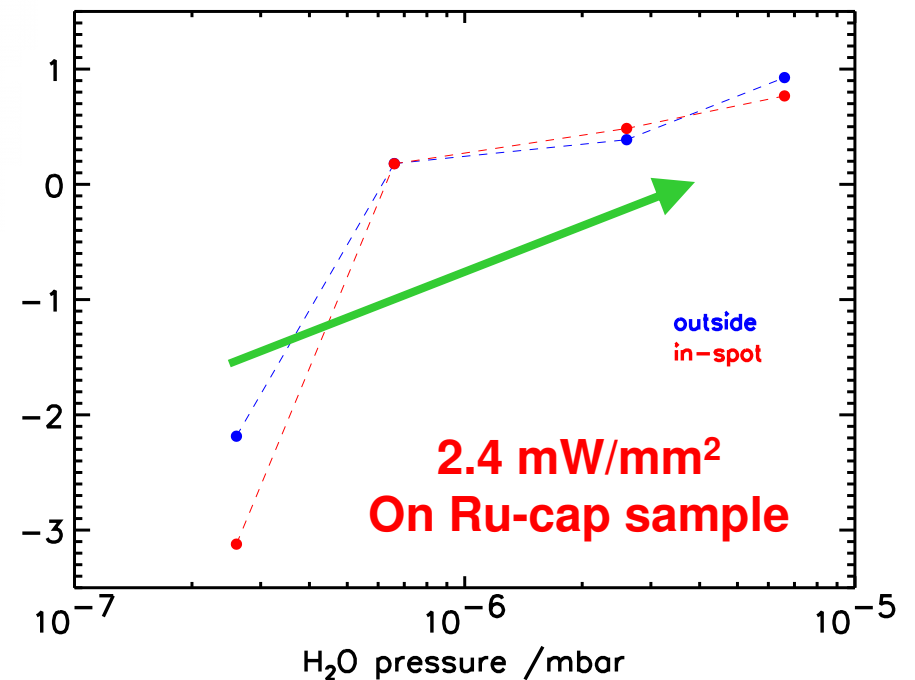
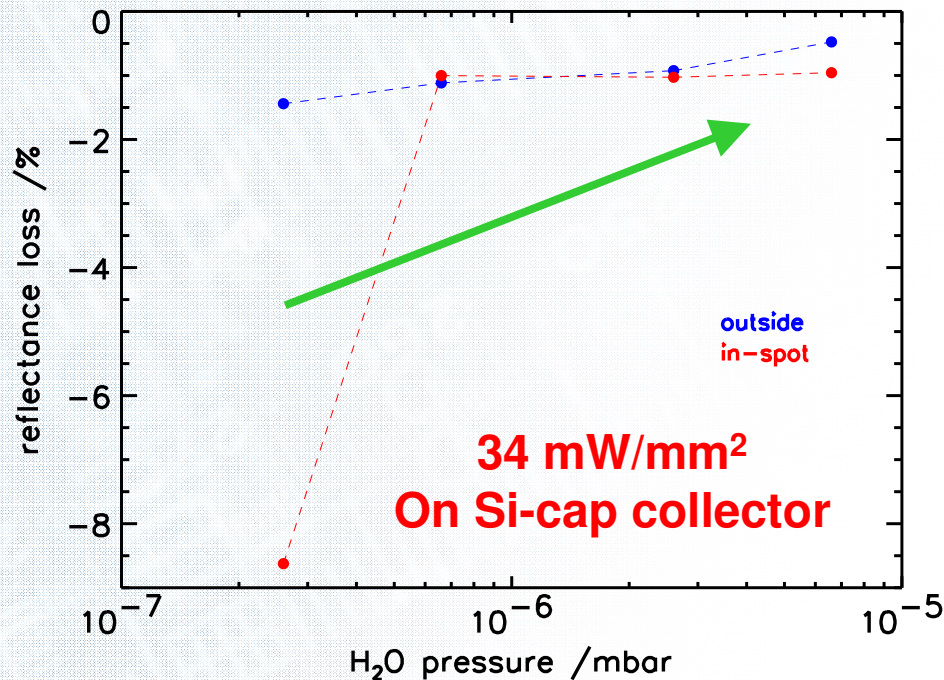
Irradiation test chamber at PTB:

- broad band EUV radiation (10° grazing incidence mirror and Si-Filter)
- in-band EUV filtering by Mo/Si mirror inside irradiation chamber

PTB results consistent with NIST

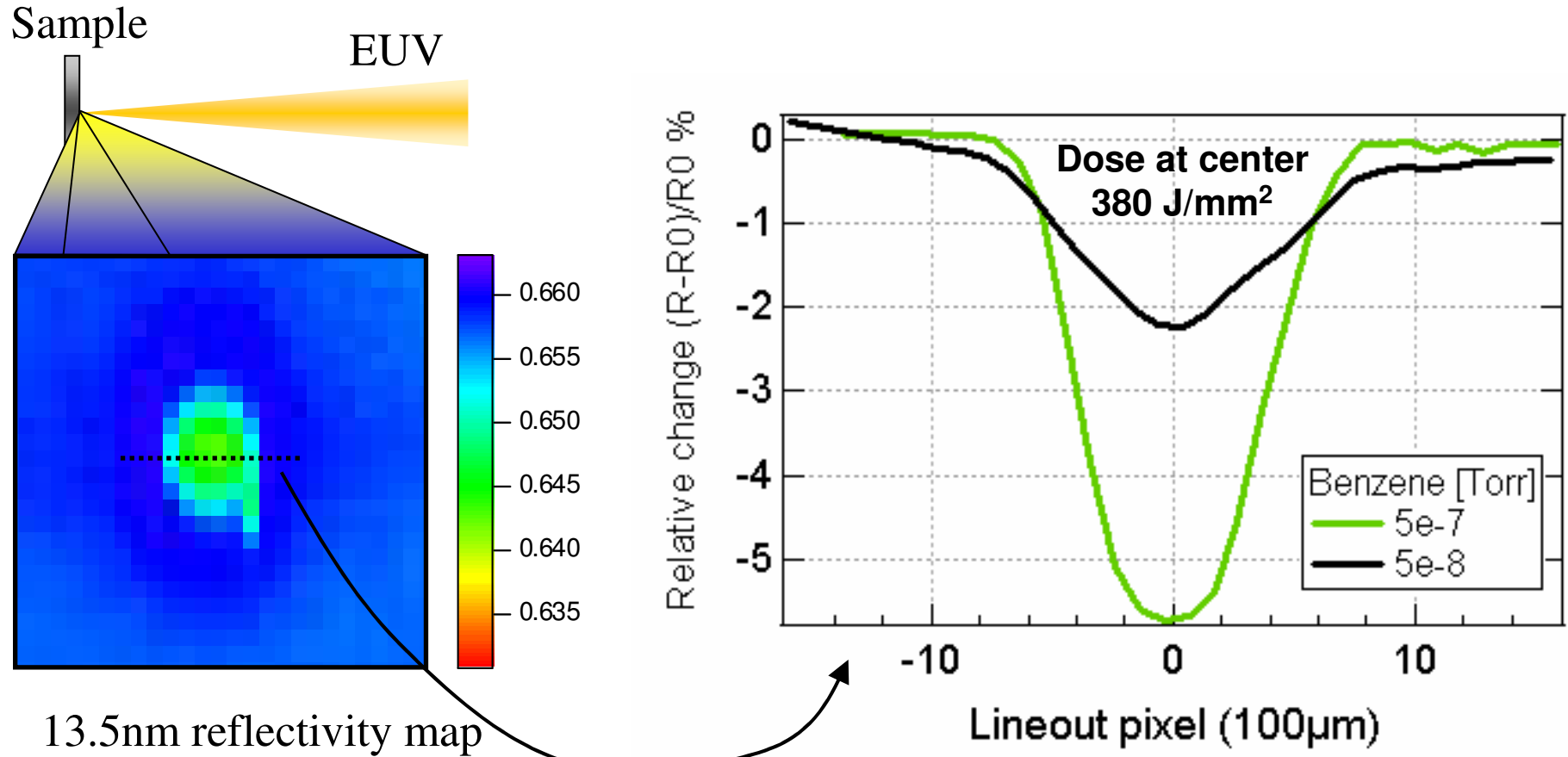


EUV Radiometry



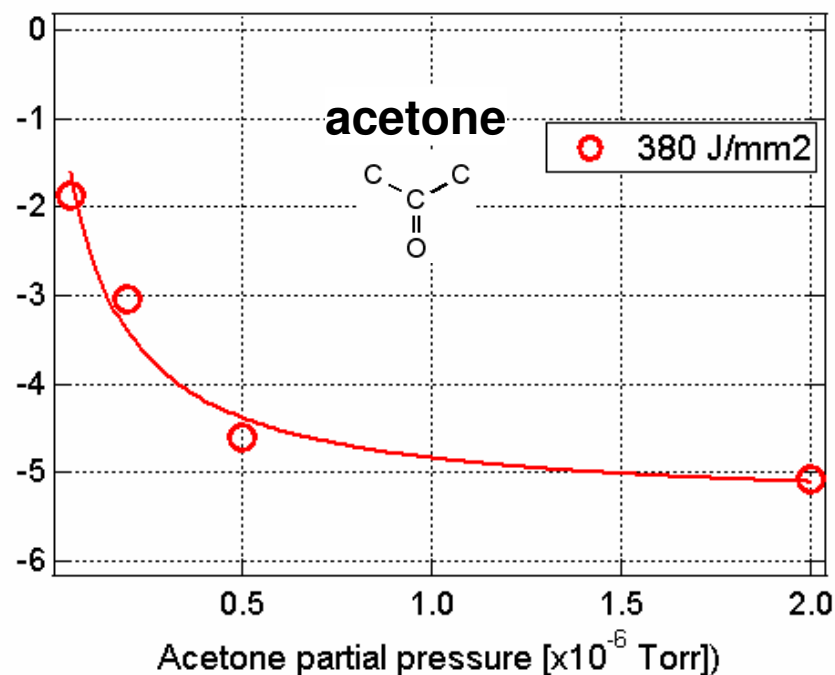
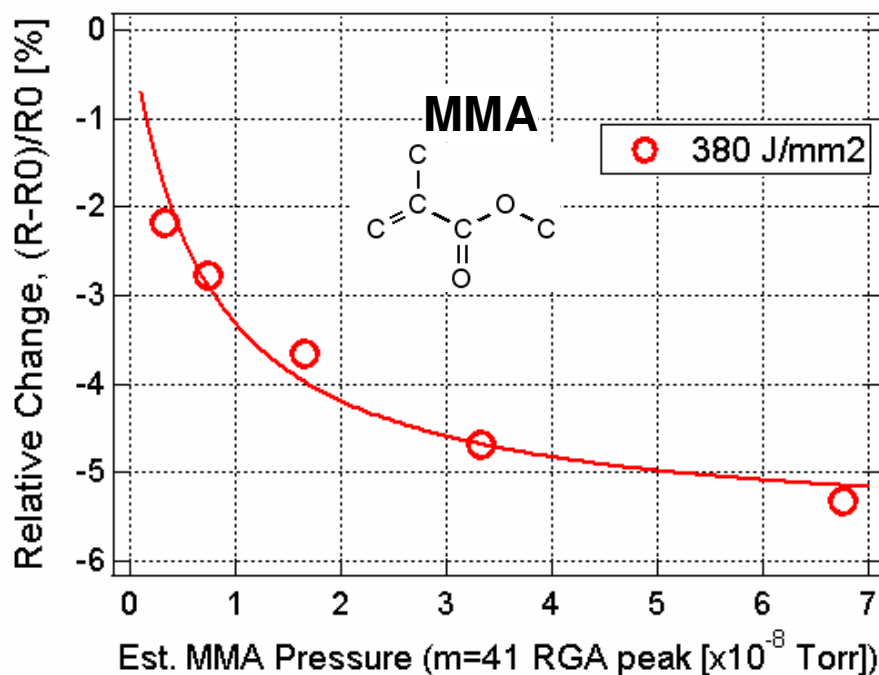
- Same trend of less damage at greater water pressures in PTB system
- Similar behavior for both LLNL Ru-cap MLM and Si-cap collector mirror
- XRF analysis confirms
 - C deposition at low H₂O pressures
 - C deposition mitigated by intermediate H₂O pressures
 - Oxidation begins to dominate at highest H₂O pressures

NIST exposures of generic TiO_2 in resist-related HCs



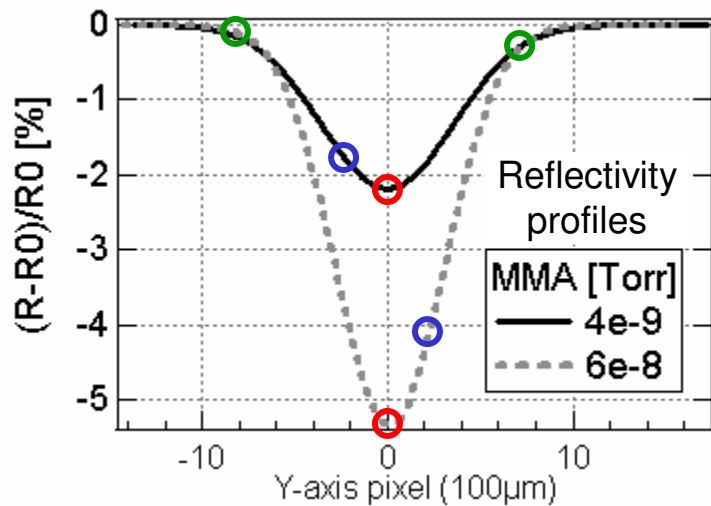
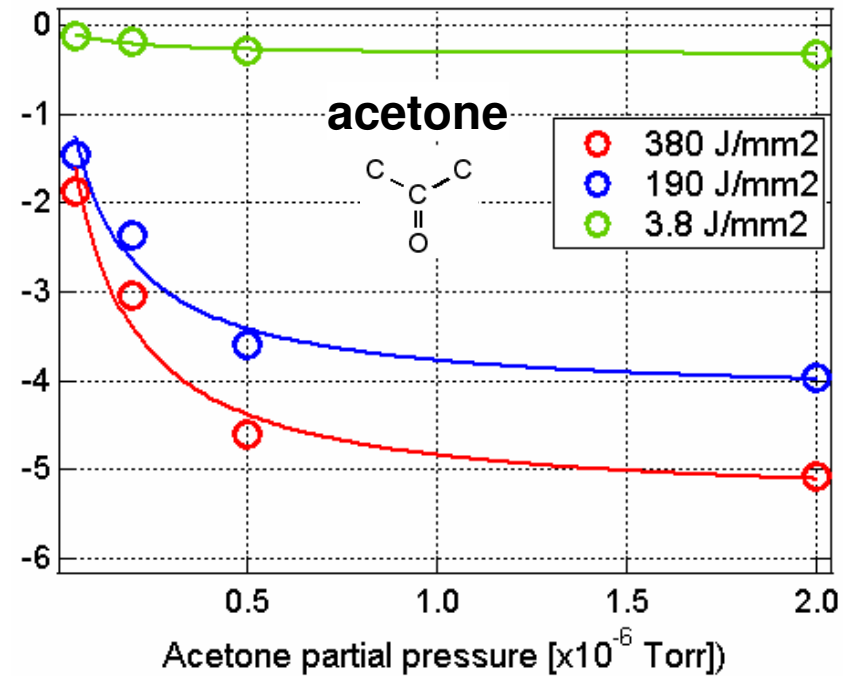
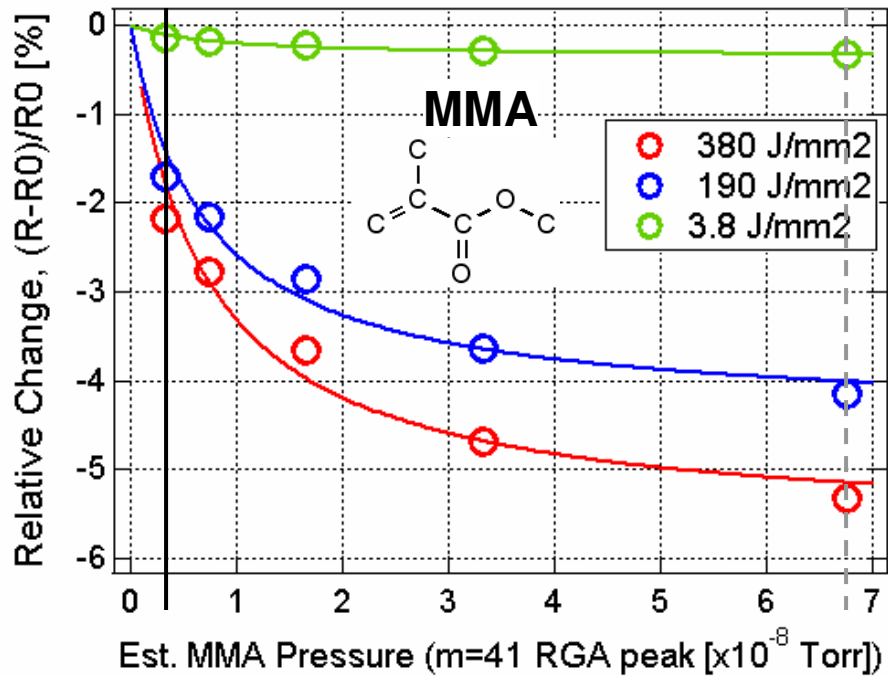
- Generic TiO_2 cap layer was not optimized to resist C deposition
- Reflectivity loss **nonlinear in pressure**: ($10\times$ pressure \neq $10\times$ loss)
- Significant ($>0.5\%$) loss at low doses ($<10 \text{ J/mm}^2$) in tails of intensity distribution

Generic TiO₂-cap MLMs exposed in resist-related HCs



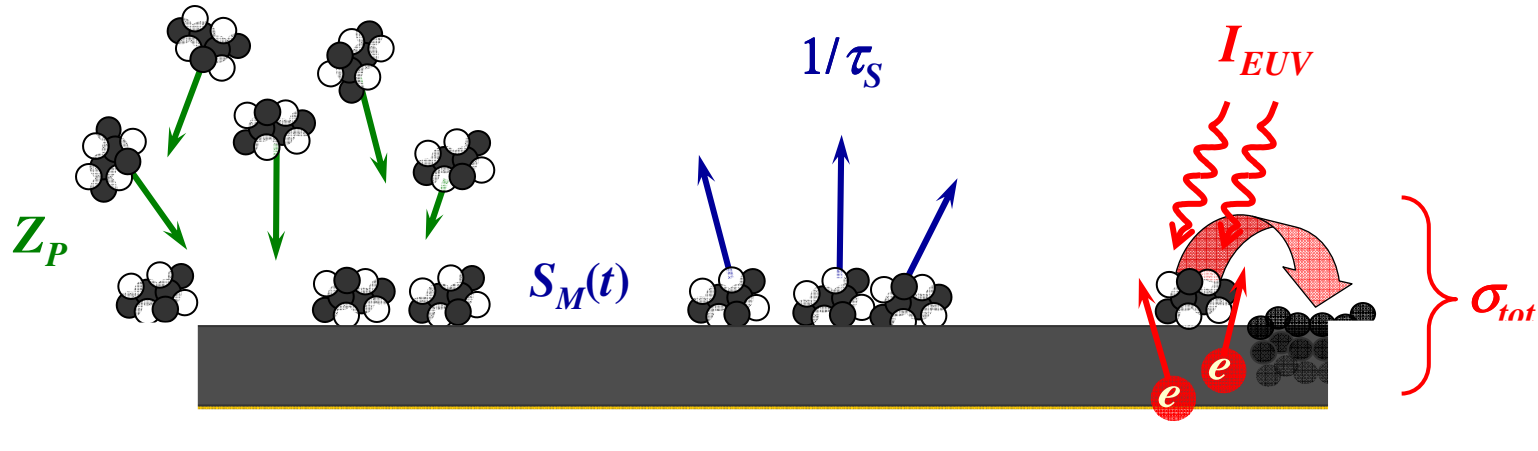
- Significant losses for all species, doses and pressures examined ($<10^{-8}$ Torr)
- Saturation possibly due to site competition as coverage approaches 1 ML

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- Saturation possibly due to site competition as coverage approaches 1 ML
- Widths of Gaussian reflectivity profiles suggests square-root dependence on intensity – similar to Canon's results!
- **Suggests low-intensity exposures should not be accelerate by increasing pressure**

NIST simple thick-C-growth model



Single-species contaminant

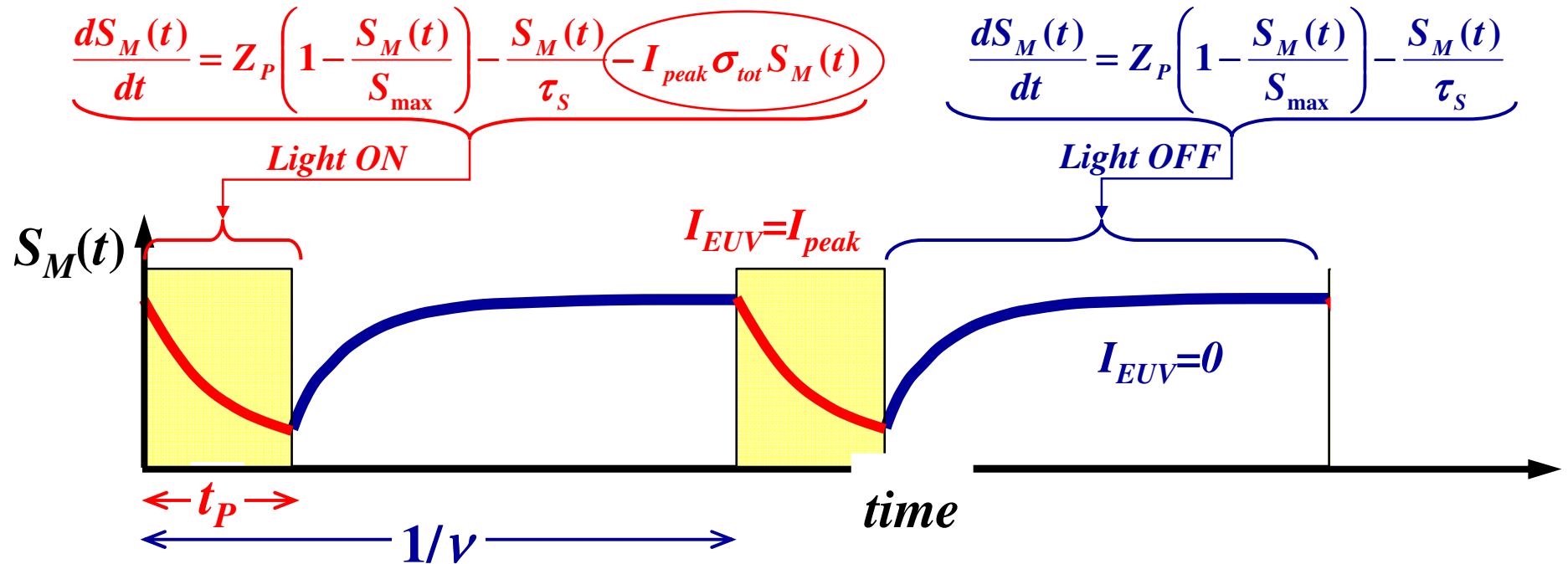
- Coverage of adsorbed intact molecules, $S_M(t)$ [molecules cm^{-2}]
- Site-limited max coverage $S_{max} \sim 1$ ML
- Impingement rate Z_P [molecules $\text{cm}^{-2} \text{s}^{-1}$]
- Surface-residence time τ_S [s]

First-order photo reaction

- Incident EUV intensity I_{EUV} [photons $\text{cm}^{-2} \text{s}^{-1}$]
- Total cross section σ_{tot} [cm^2]
 - Secondary e^- dissoc. dominates
 - Photo-desorption negligible
- Linear in S_M and I_{EUV}

$$\frac{dS_M(t)}{dt} = Z_P \left(1 - \frac{S_M(t)}{S_{max}} \right) - \frac{S_M(t)}{\tau_S} - I_{EUV} \sigma_{tot} S_M(t)$$

Evolution during pulsed irradiation



Carbon-growth rate, k [C atoms $\text{cm}^{-2} \text{s}^{-1}$]

$$k = \nu N_C \int_0^{t_p} I_{\text{peak}} \sigma_{\text{tot}} S_M(t) dt$$

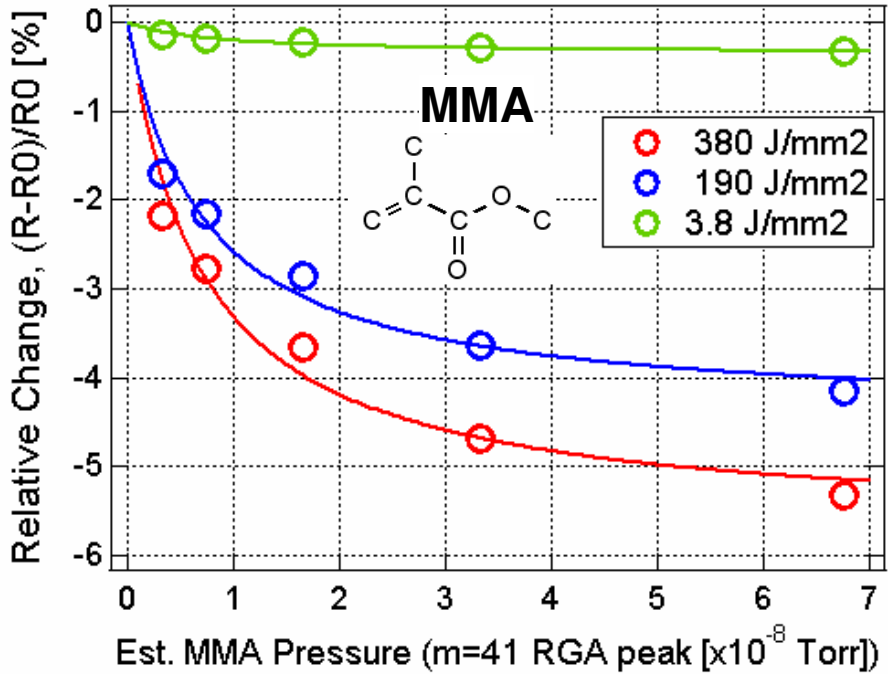
Damage rate for Equilibrium Approximation

Carbon-growth rate: $k = \nu N_C \int_0^{t_p} I_{peak} \sigma_{tot} S_M(t) dt \cong (\nu t_p) I_{peak} \sigma_{tot} S_{eq}$

$$k = N_C \frac{Z_P \tau_S I_{avg} \sigma_{tot}}{1 + I_{avg} \sigma_{tot} \tau_S + Z_P \tau_S / S_{max}}$$

Assuming: Duty $\ll 1$, and residence time, $\tau_s \ll$ pulse period

- **Equilibrium approximation:** photon-induced reactions produce only small perturbation of light-off equilibrium coverage
- Independent of time structure
- NOT useful as *ab initio* predictor due to exponential uncertainties in τ_S and σ_{tot}
- Predicts observed “pressure saturation”
- Application to MET contamination data predicts reasonable residence times of 10-100s and contaminant pressure $\sim 10^{-10}$ Torr



Summary

- 1) Initial non-intuitive damage rates of Ru in H₂O confirmed by PTB
- 2) Exposures of generic TiO₂-cap MLMs (not designed for optimal C-growth resistance) in resist-related hydrocarbons
 - Damage rate not linear with HC pressure at high levels
 - Saturation of damage can occur at surprisingly low pressures (10⁻⁸ - 10⁻⁷ Torr)
 - Accelerated testing should only be performed at pressures below saturation regime for each gas.
- 3) Simple thick-C-growth model
 - Only applicable after first few MLs of C have been deposited
 - Predicts non-linear pressure and intensity dependences
- 4) Ongoing work to explore resonance effects and growth of first MLs