Predicting optics carbonization from a knowledge of resist outgas composition

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Outline

- Predictive method for ranking resist contamination potential
- Experimental elements
  - Quantitative analysis of resist outgas rates and composition
  - Measuring carbonization rates over large range of partial pressures
  - Estimating carbonization rates in HVM environment
- Summary

Ranking "contamination potential" of resists

- Measure resist total outgassing and composition
- Construct database of damage rates of principal outgas components
  - over large range of pressures and intensities to establish scaling
  - in the presence of water vapor at levels anticipated in tool
- Extrapolate rates of components to anticipated values of pressure based on measured outgas rate and tool geometry
- Calculate "contamination potential" as sum of scaled rates for each component
- Use this figure of merit to rank resists and identify promising candidates for witness-plate testing.

Ranking "contamination potential" of resists

Advantages

- Relatively rapid method to pre-screen resists as database grows
- More informative than total outgas qualification
- Can provide important feedback to resist manufacturers on how to improve composition

Sources of uncertainty

- Estimating effective partial pressure at optic in tool
- Validity of scaling laws outside measurement range
- Interactions between different adsorbed species (unlikely at low pressures)
- Differences in cleanability of deposits (*e.g.,* S, F, Cl are known to be problematic.)

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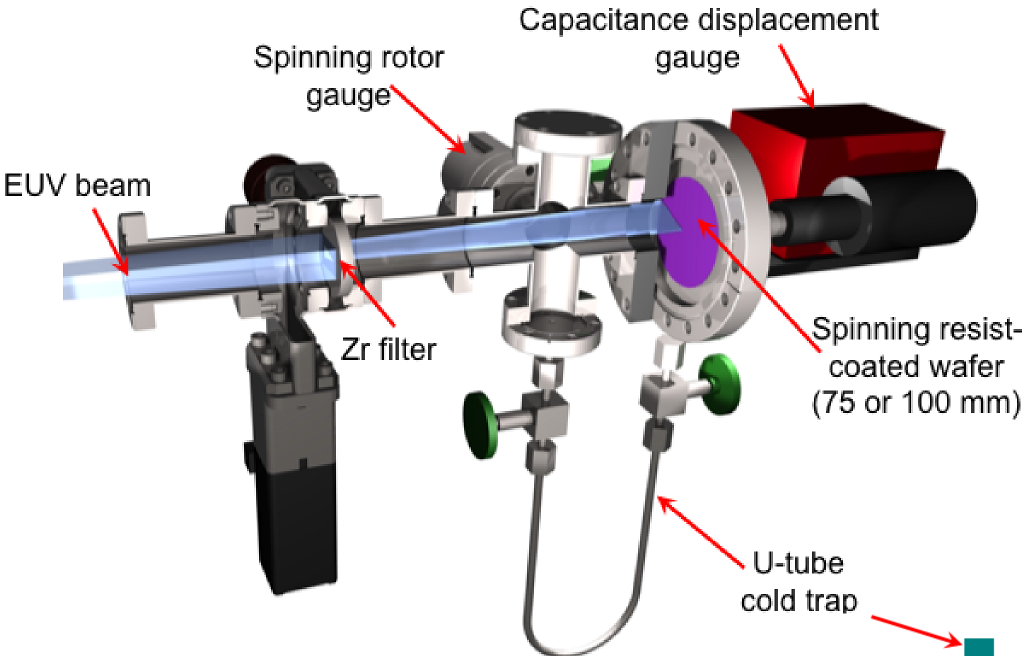
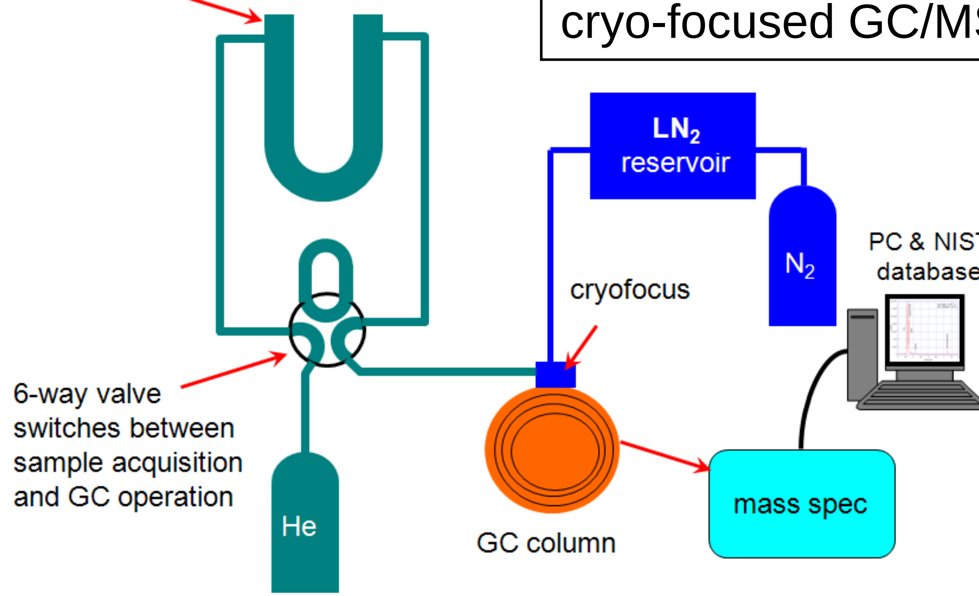
Outgassing measurements

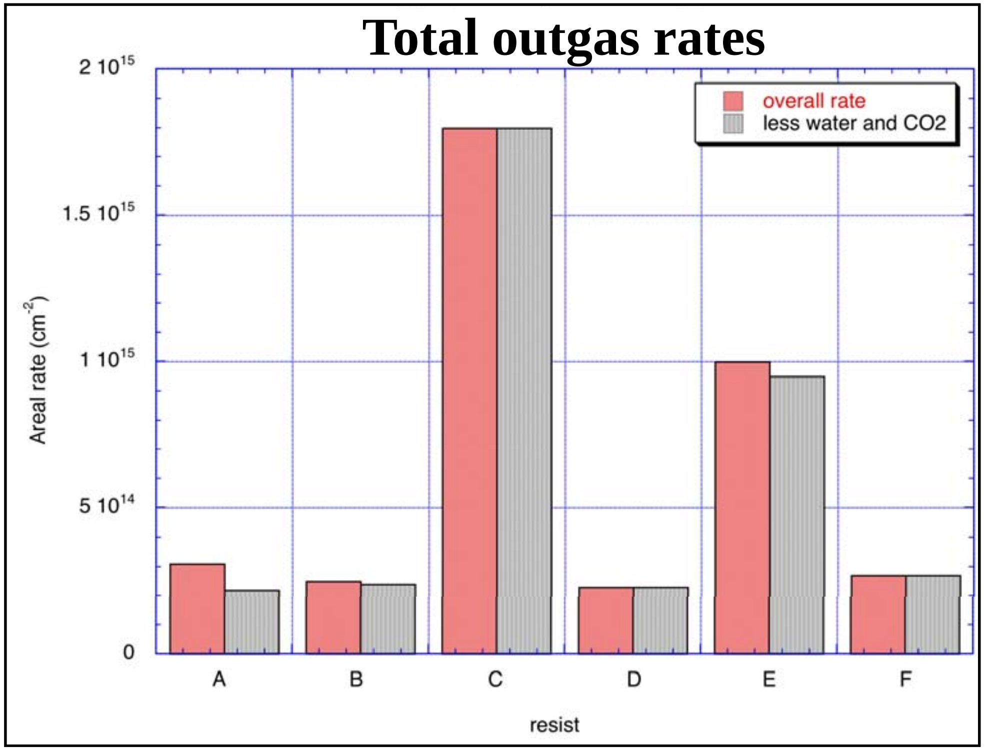


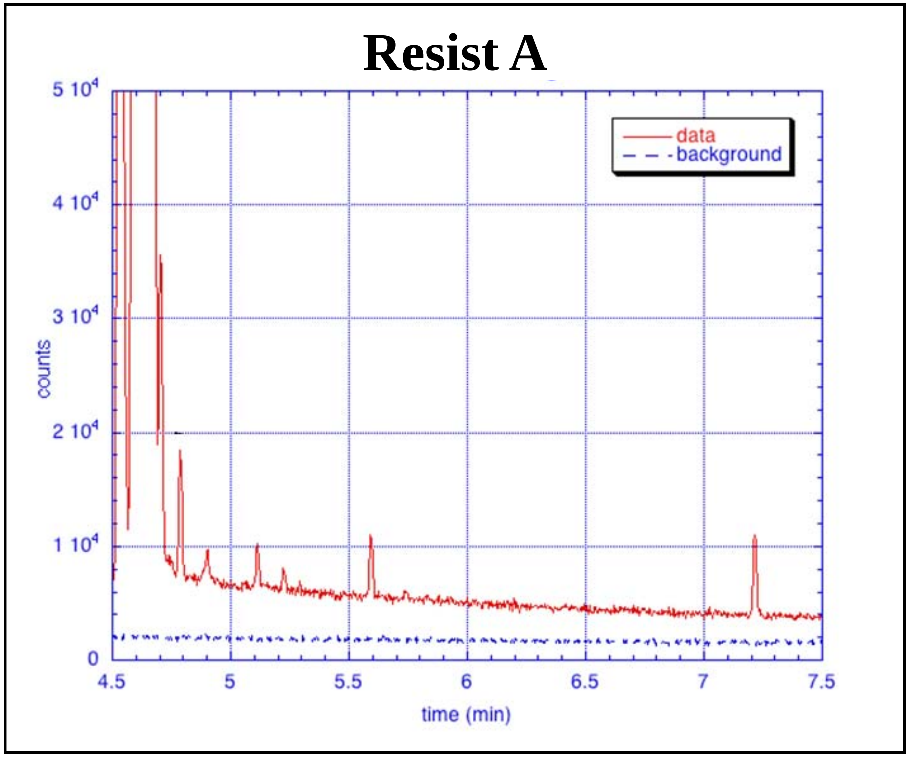
Outgassing-measurement end station on synchrotron

Chemical composition by cryo-focused GC/MS



An example of 6 resist compositional analyses





Significant components observed

1. Isobutene
2. Benzene
3. Acetone
4. Acetaldehyde
5. Isobutane
6. Diphenyl sulfide
7. Hexane
8. Tert-butylbenzene

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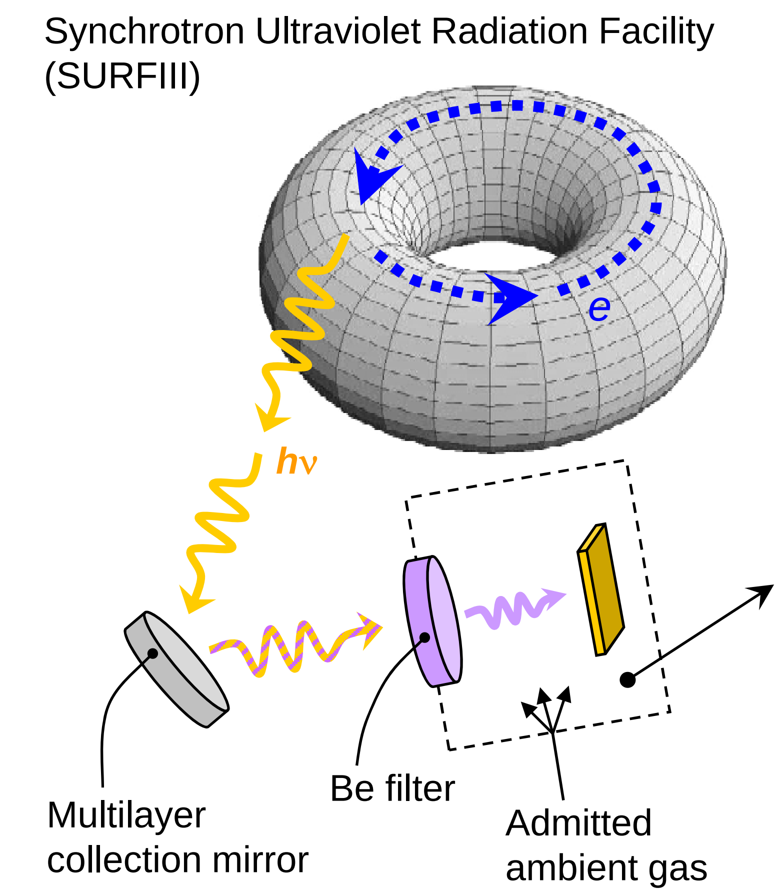
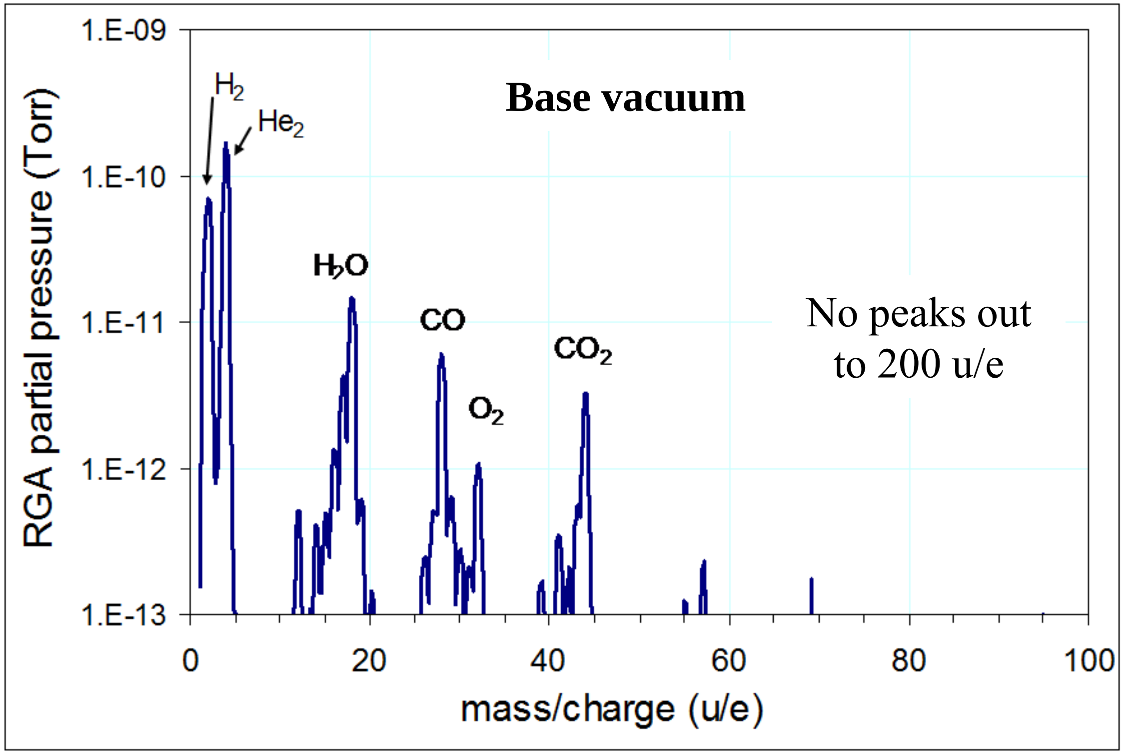
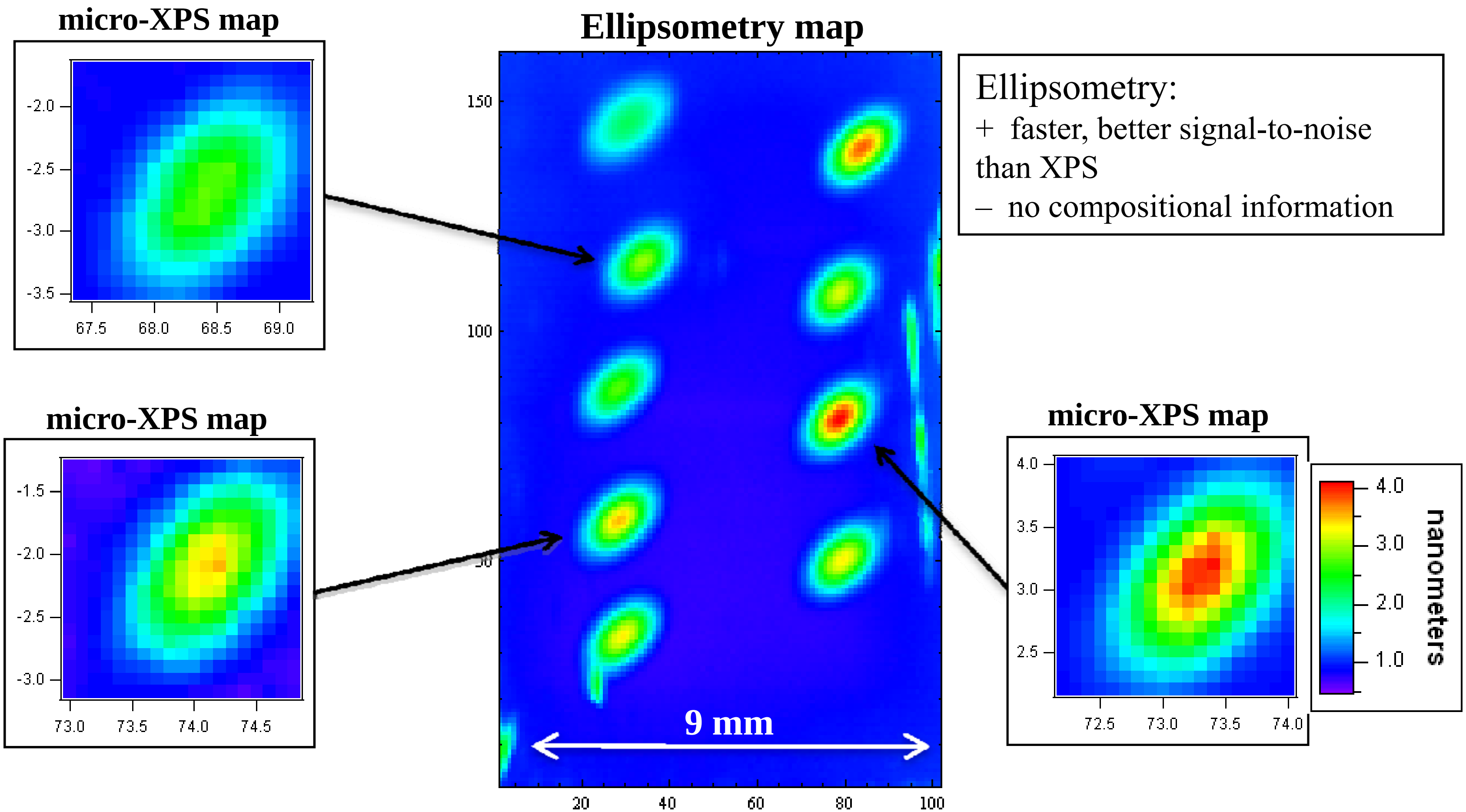
NIST optics lifetime testing facility





- Base H_2O partial pressure $\approx 1 \times 10^{-10}$ Torr
- Average, in-band (13.1-13.6nm) intensity 4-8 mW/mm^2
- Use TiO_2-capped tri-layer samples that match top 3 layers of standard Mo:Si multi-layer mirror.

Contamination characterized by XPS and ellipsometry



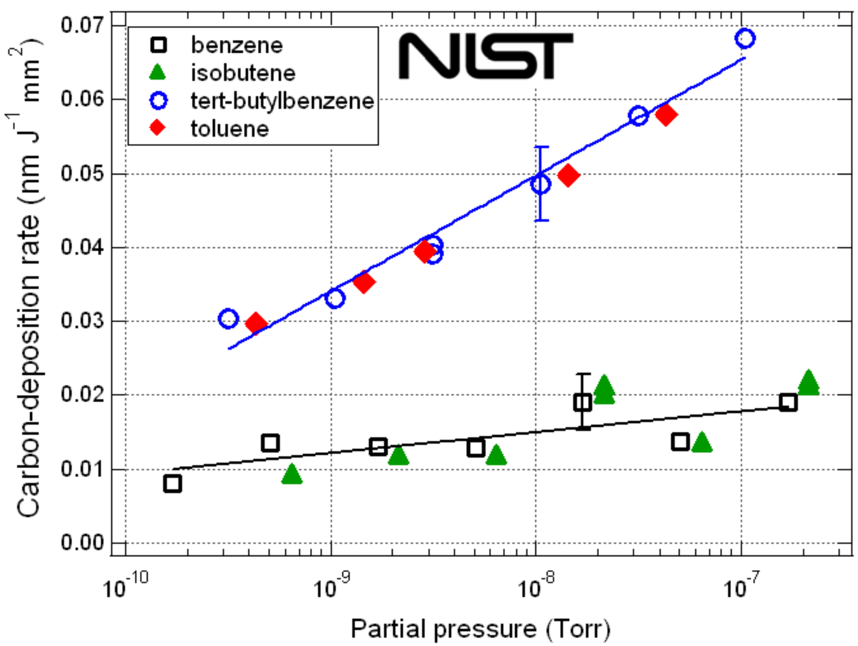
Ellipsometry:
+ faster, better signal-to-noise than XPS
– no compositional information

- C-deposition rates reported here based on XPS-measured thickness at center of spot.
- Good qualitative agreement between XPS and ellipsometry
- Quantitative correlation under way, but depends on unknown properties of deposits

Coverage and carbonization rates vary as log of pressure

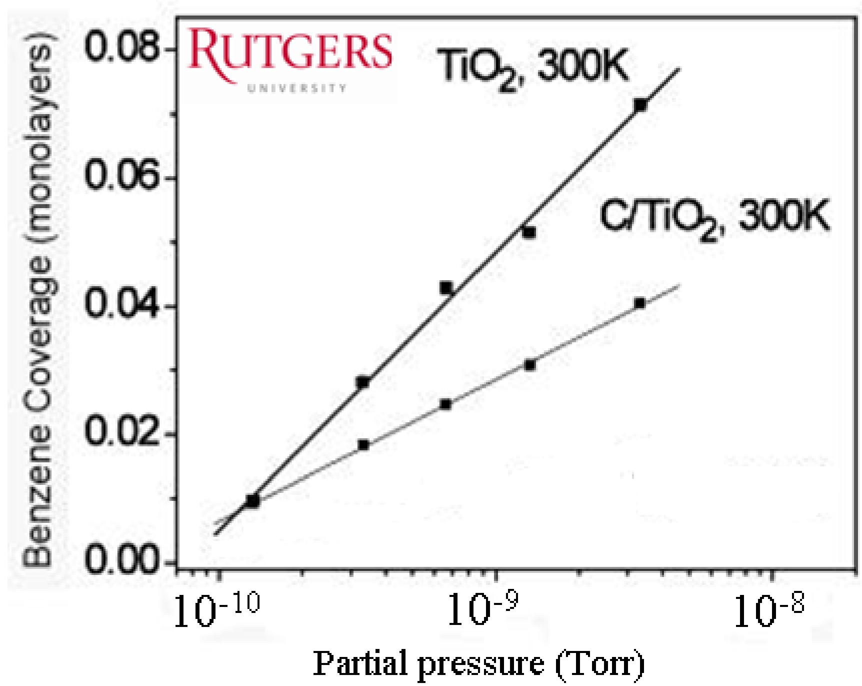
EUV-induced C-deposition rates

Hill, *et al*, Proc. SPIE, Vol. 7271, 727113 (2009)



Non-irradiated coverage measurements: Temperature-programmed desorption

Yakshinskiy, *et al*, Proc. SPIE 7271-36 (2009).



- Log(p) scaling of both EUV-induced carbon growth rates on TiO_2-cap MLs *and* steady-state coverage of molecules on non-irradiated TiO_2(011)
- Same coverage behavior on C-covered TiO_2 (011) suggests scaling not specific to TiO_2
- Log(p) behavior continues down to 10^{-10} Torr for all organic species tested

Correlation with physical properties of organics

NIST Measurements † (normalized)

Species	Vapor pressure at 20C, Torr	Relative C growth rate
Benzene	80.85	17
Toluene	21.86	38
isobutene	2267.55	14
Tert-butylbenzene	1.5	36

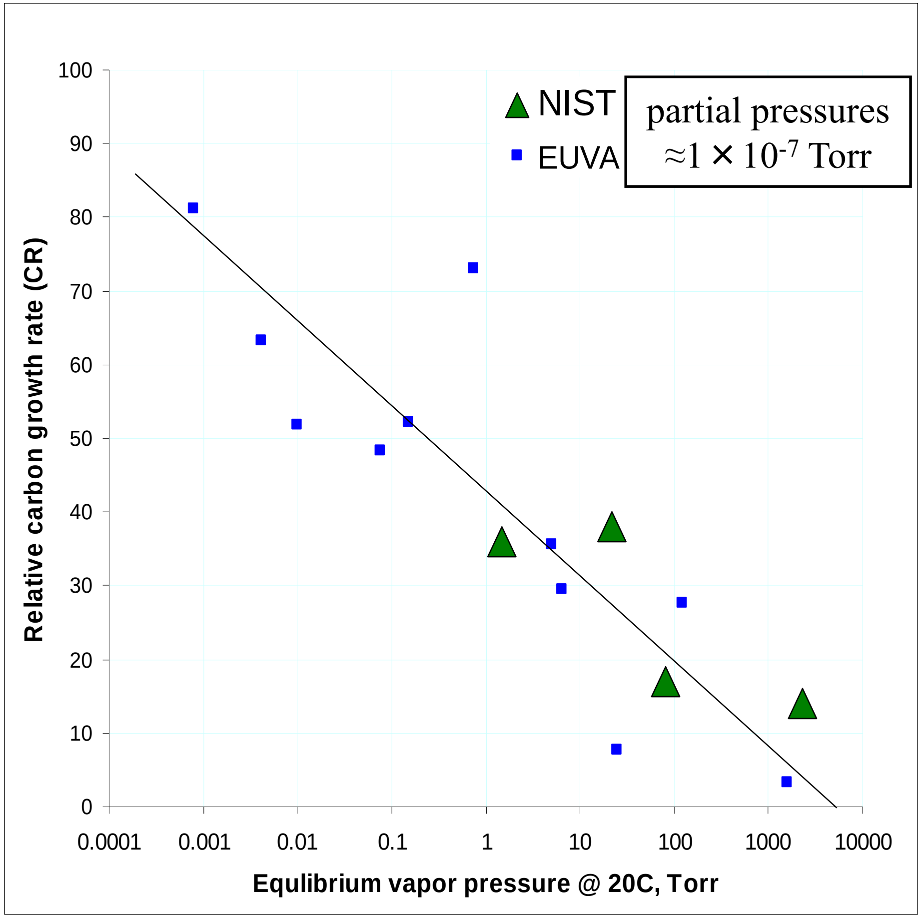
† Hill, *et al*, Proc. SPIE, Vol. 7271, 727113 (2009)

EUVA (Japan) Measurements *

Butane	1556.54	3.3
Hexane	121.26	27.7
Methyl propionate	6.38	29.6
Polyfluorooctane	25	7.8
Butanol	5.02	35.7
Decane	0.15	52.2
Diethyl benzene	0.75	73
Methyl nonanoate	0.075	48.4
Decanol	0.01	51.8
Dimethyl phthalate	0.00417	63.3
Hexadecane	0.0008	81.1

* Matsunari, *et al*, SPIE Vol. 6517, 65172X, (2007)

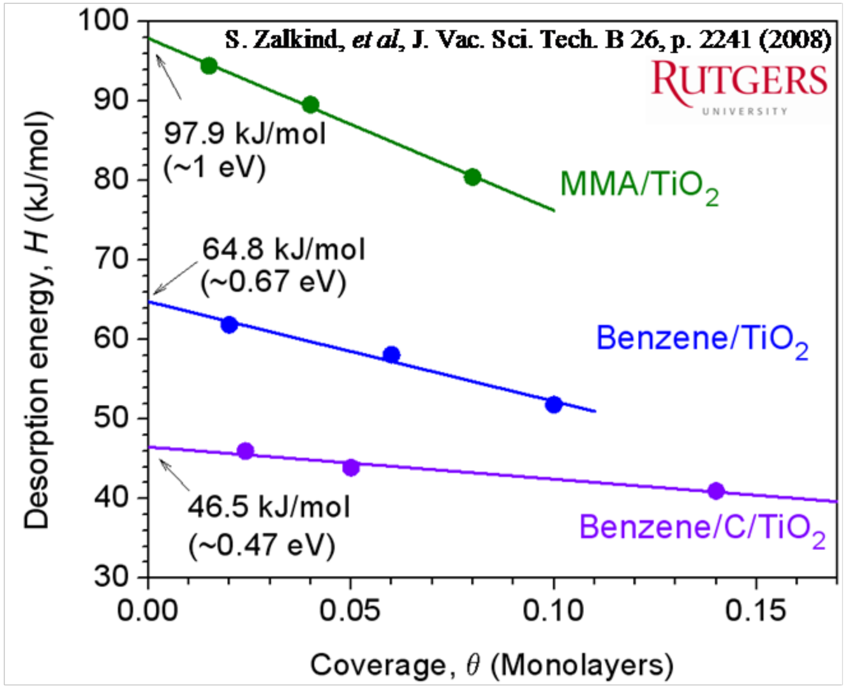
Relative carbon growth rates



Note: C-growth rate trends with log of the inverse of equilibrium vapor pressure

Possible origins of logarithmic scaling: Temkin models

- Molecular interactions: desorption energy, E_d, decreases linearly with coverage



$$(Residence\ time) \sim e^{\frac{E_d}{kT}} = e^{\frac{E_0 - \alpha\cdot\theta}{kT}}$$

Modification of Langmuir: Temkin isotherm

$$\Rightarrow \log\left(\frac{p}{p_0}\right) = \beta\cdot\theta + \log\left(\frac{\theta}{1-\theta}\right)$$

$$\Rightarrow \theta \approx \begin{cases} 1\ \text{ML, for } p >> p_0 \\ \boxed{\frac{1}{\beta}\cdot\log\left(\frac{p}{p_0}\right)} \\ \frac{p}{p_0}\text{, for } p << p_0 \end{cases}$$

- Surface defects: distribution of desorption energies $\Rightarrow \boxed{\theta = \log\left(\frac{1+a\cdot p}{1+b\cdot p}\right)}$

- Temkin and Langmuir models become linear in pressure as $p \rightarrow 0$

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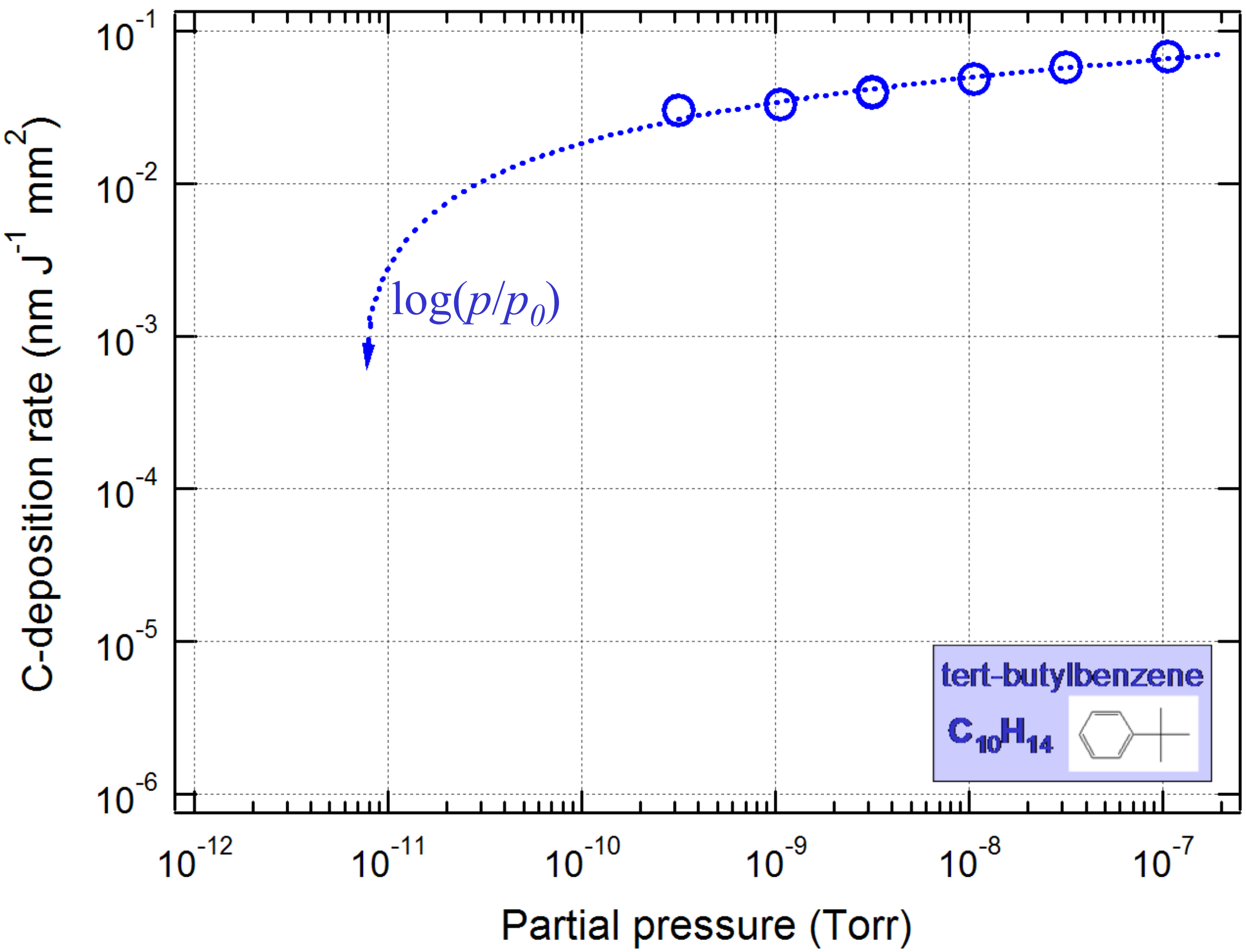
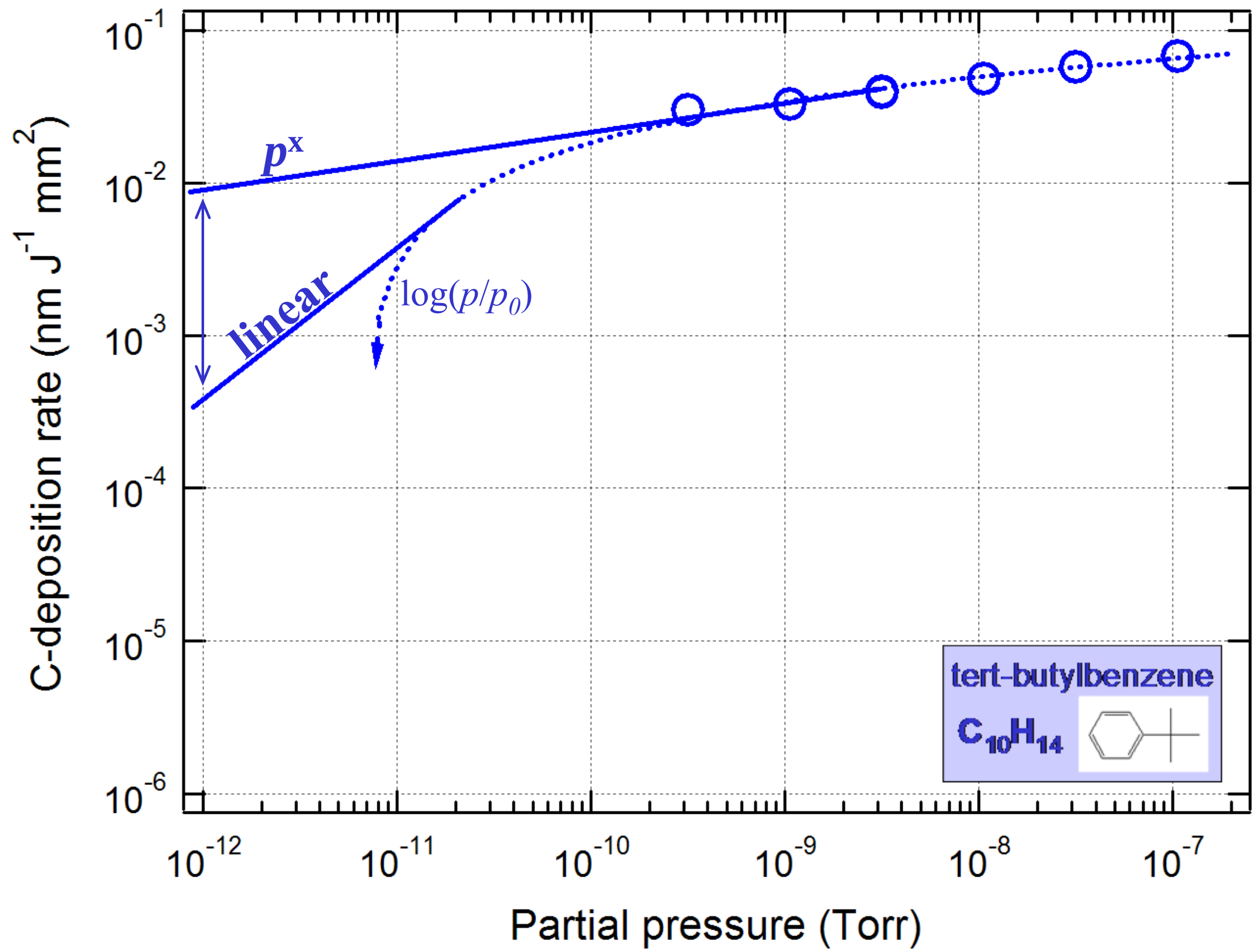
Extrapolation to lower pressures

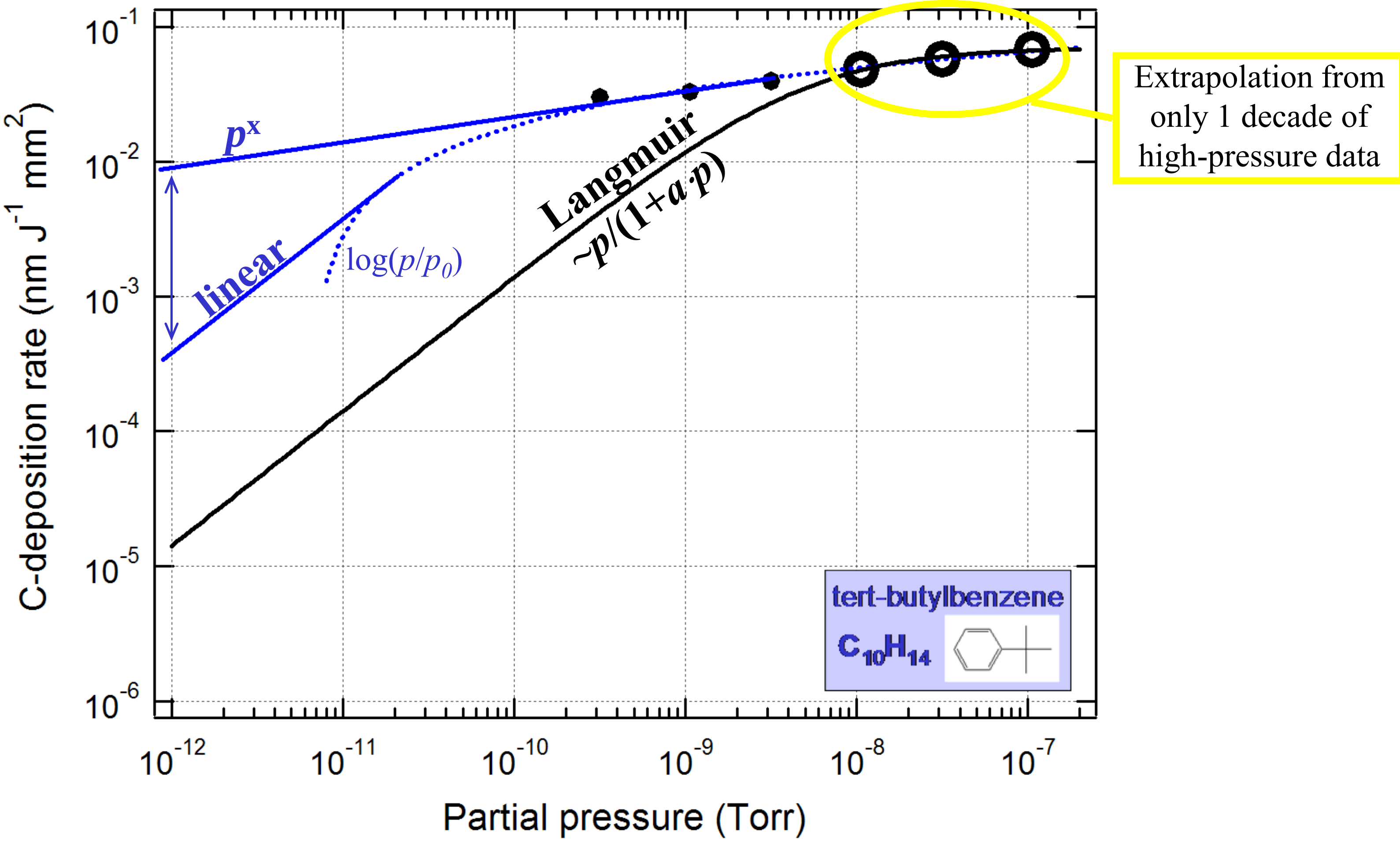


Extrapolation to lower pressures: estimated limits



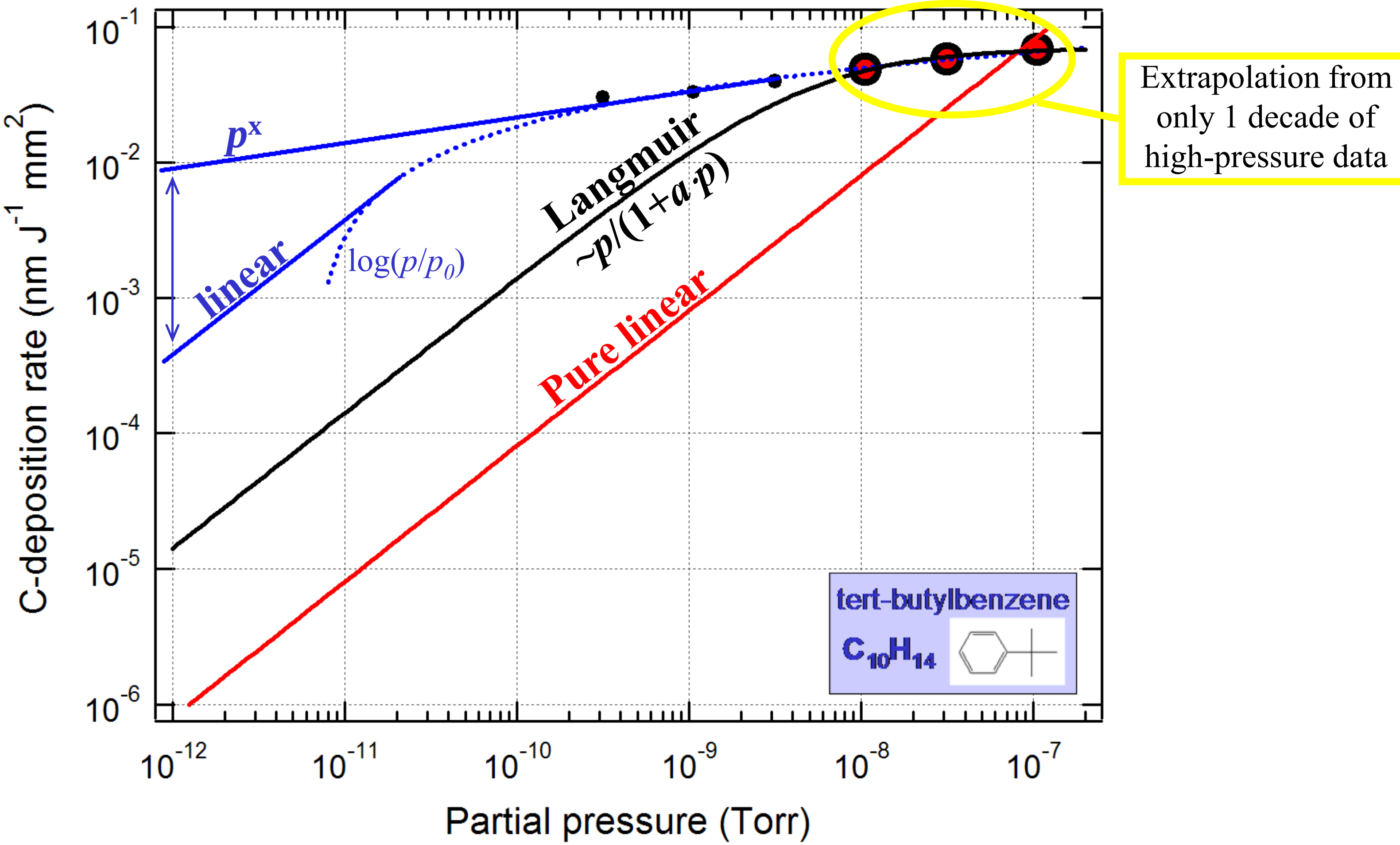
- Transition from log(p) not observed: estimate upper & lower extrapolation limits

Extrapolation to lower pressures: potential errors



- Transition from $\log(p)$ not observed: estimate upper & lower extrapolation limits

Extrapolation to lower pressures: potential errors



- Transition from log(p) not observed: estimate upper & lower extrapolation limits
- Linear extrapolation of a few high-pressure measurements will *underestimate* rates at lower pressures by multiple orders of magnitude.

Summary

We propose to rank the relative contamination risk of a resist by correctly scaling and summing the contamination and outgassing rates of the individual components.

Several critical issues require further investigation:

- Extrapolation of contamination rates below 10^{-10} Torr
- Establishing scaling laws for intensity
- Determining the effects of water vapor

Recommendations and plans:

- Require collaboration with surface science community to understand and model ultra-low-pressure adsorption physics
- Interim ranking of resist components using contamination rates measured at lowest pressures (no scaling)
- Qualitatively combine outgas rate with interim ranking to give a tentative quality rating to the resist
- Compare all ranking methods to witness-plate testing protocols