Measuring the EUV-induced contamination rates of TiO_2-capped multilayer optics by anticipated production-environment organics

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This work supported in part by Intel Corporation

Outline

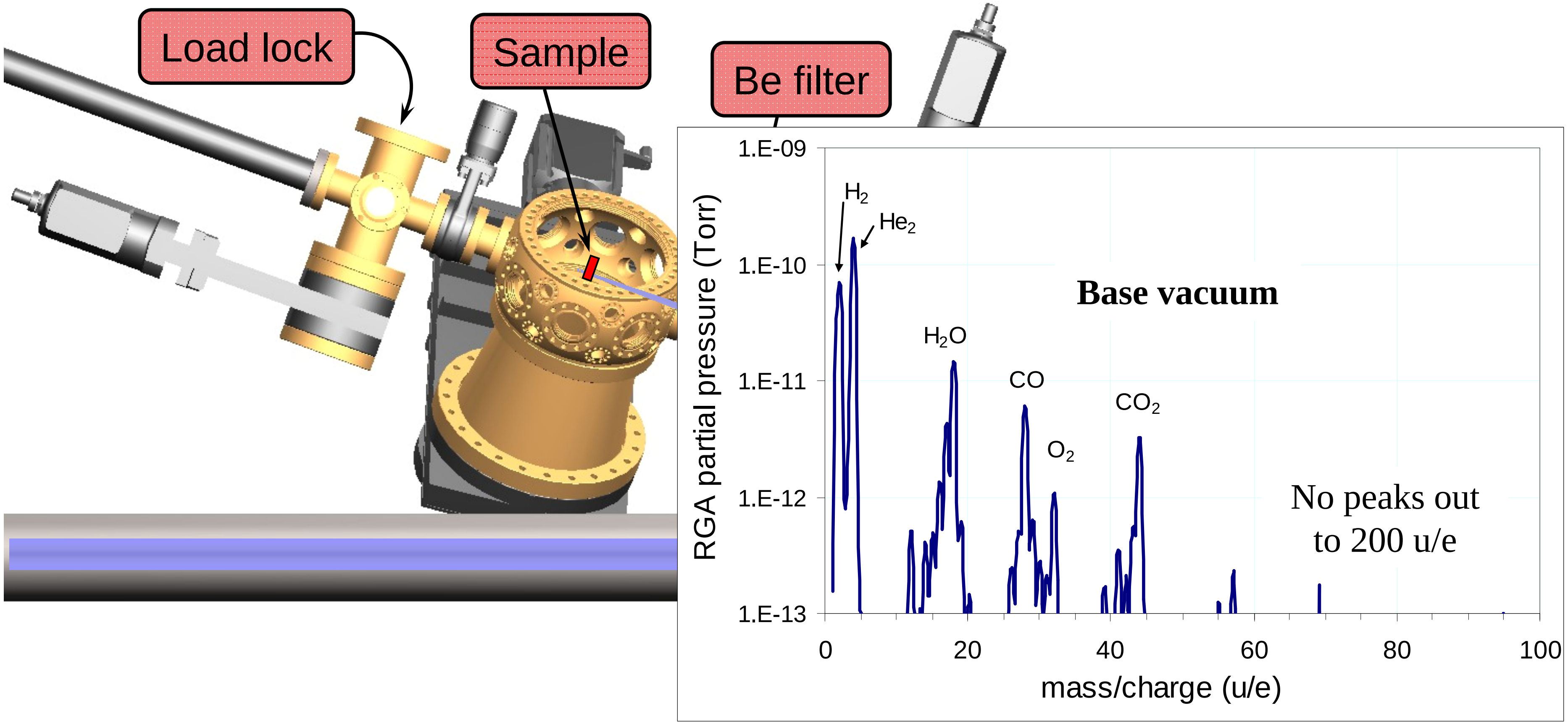
1) EUV-induced contamination rate measurements

2) Correlation with coverage measurements (Rutgers)

3) Scaling laws and extrapolation

4) Summary

NIST optics testing facility



- Average, in-band (13.1-13.6nm) intensity 4-8 mW/mm^2 at sample
- Expose in controlled partial pressure of admitted gases
- Bake to 150^o C
- Base pressure ~2×10^{-10} Torr

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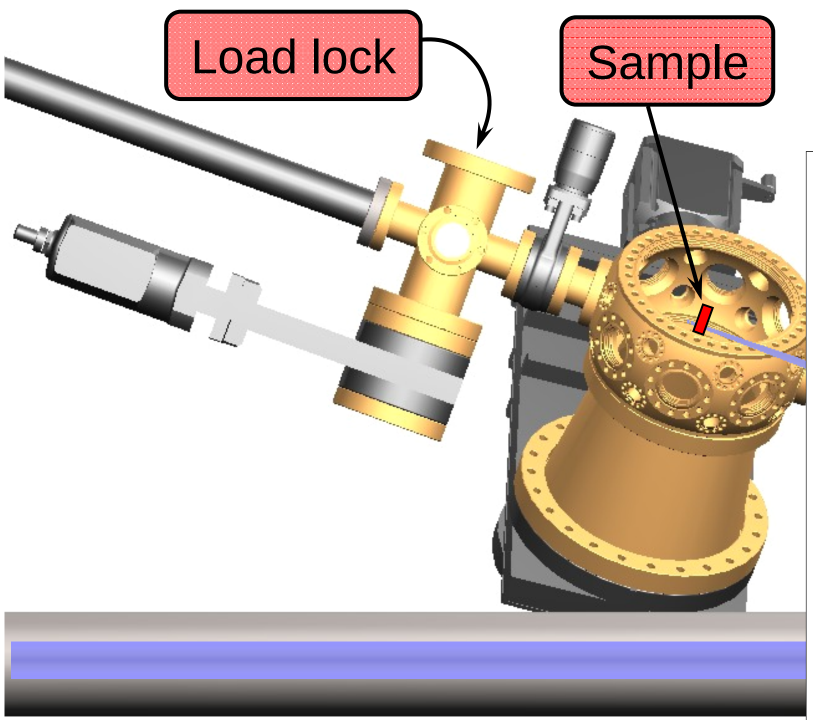

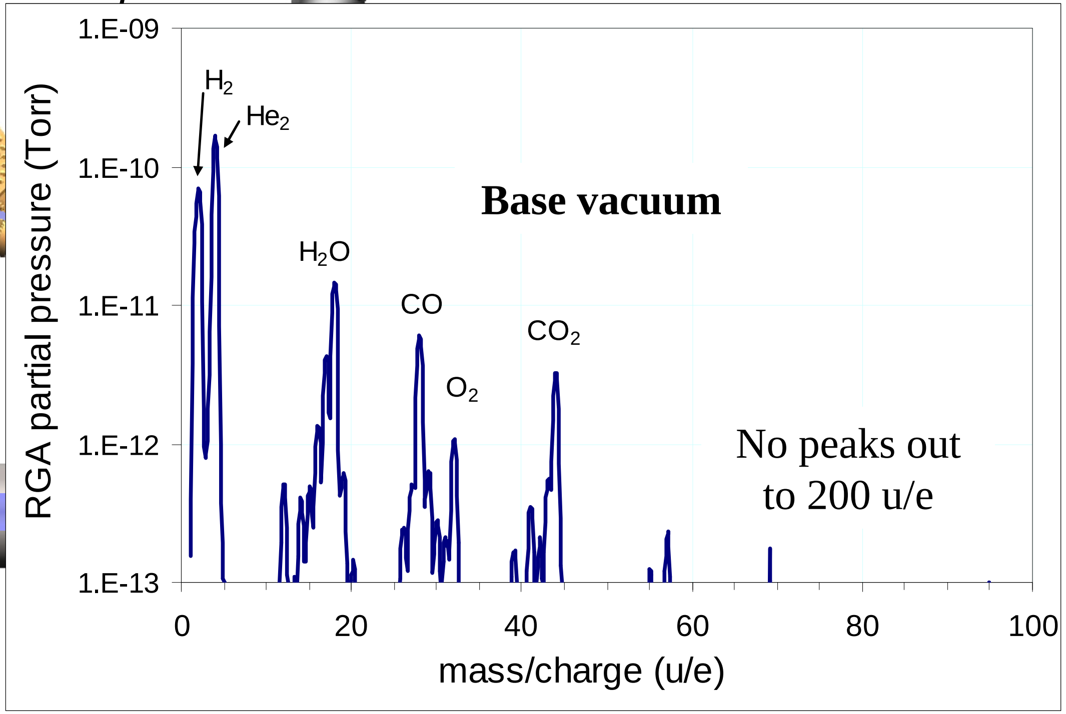

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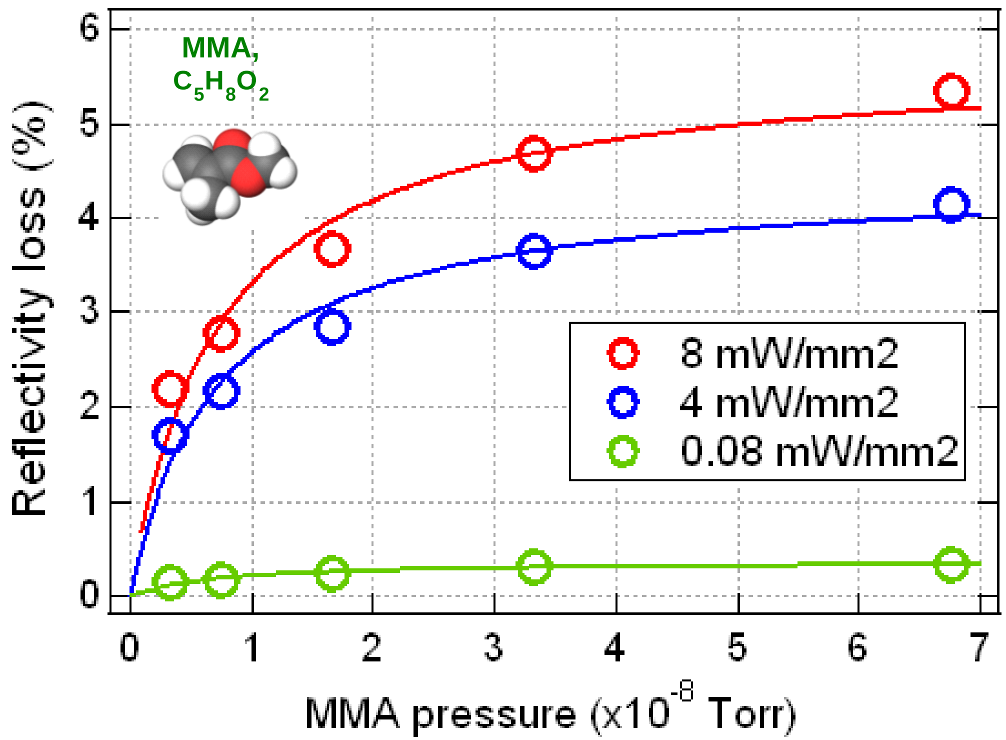
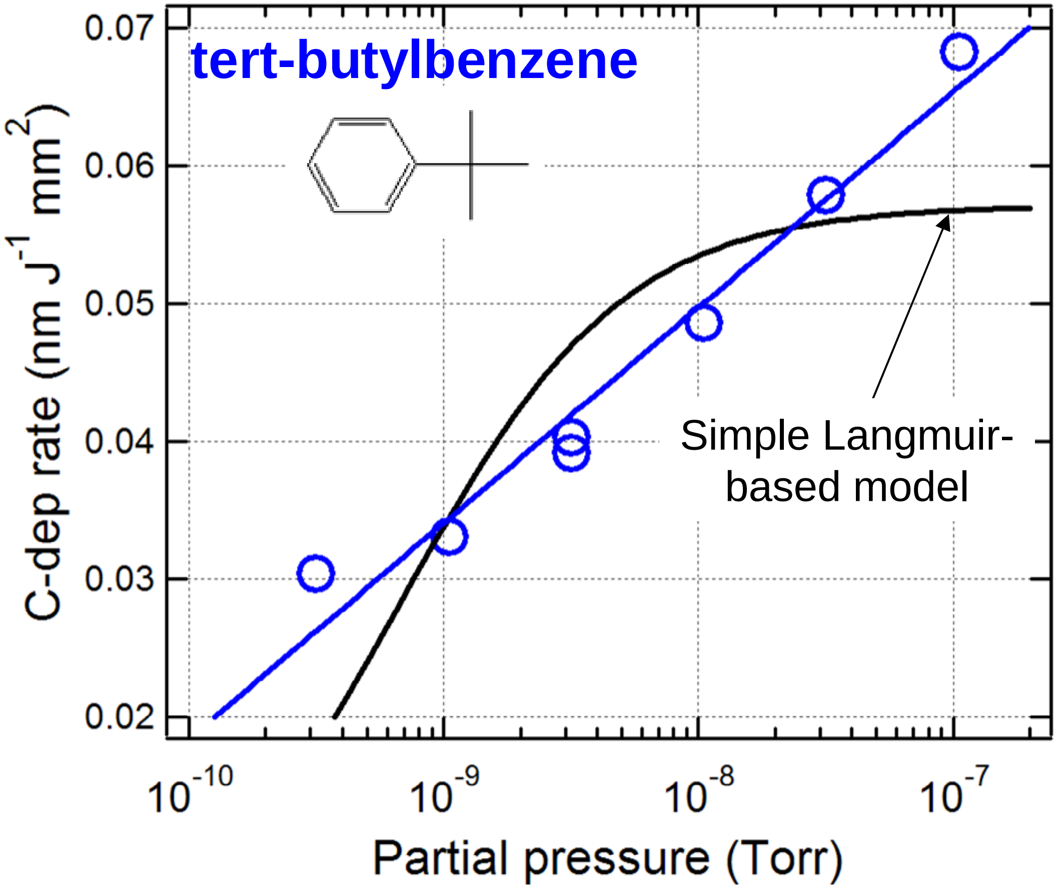
- C-deposition measured by XPS

Initial EUV-induced C-contamination studies



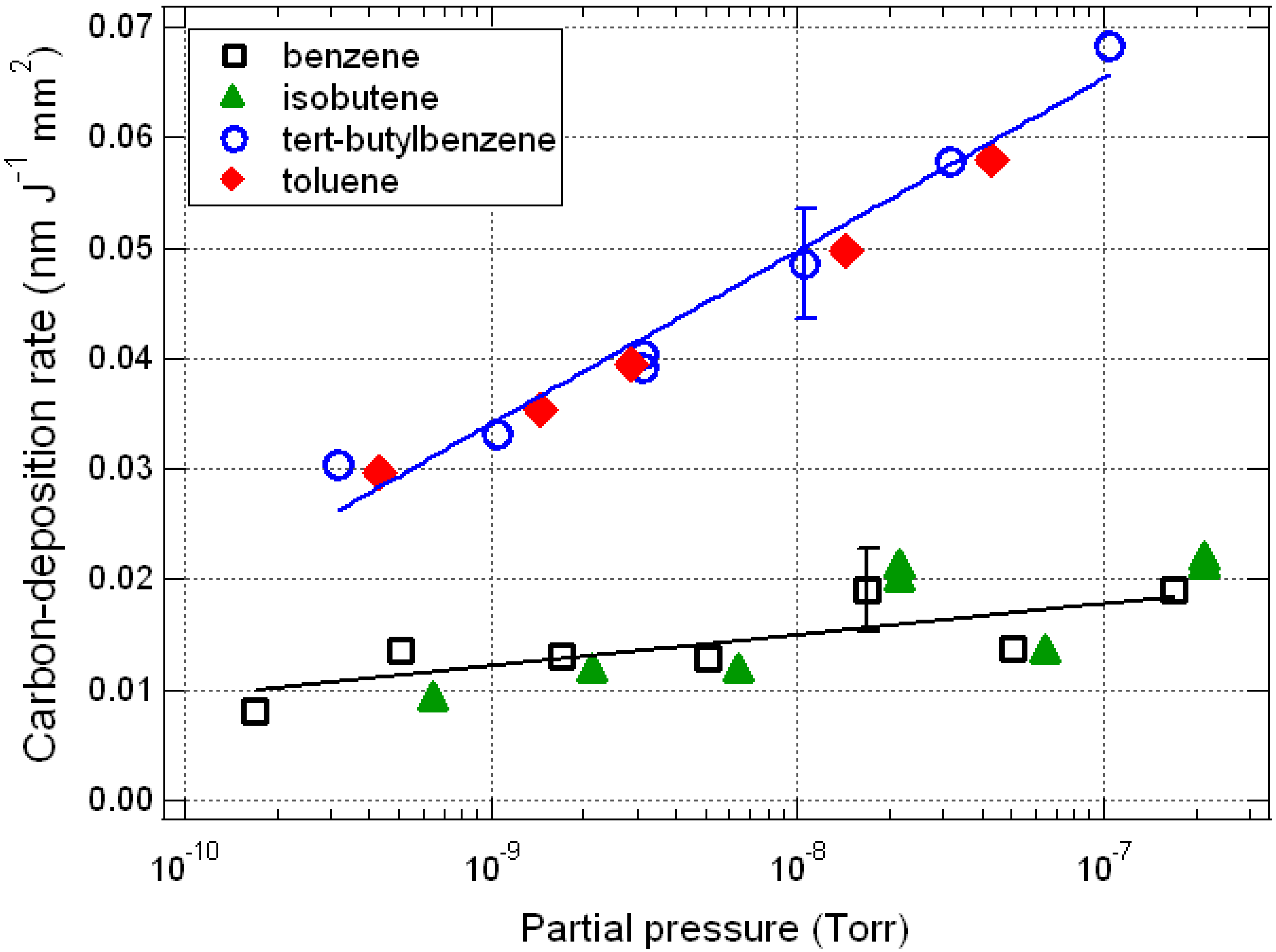
- Developed simple Langmuir model assuming:
  - Reversible adsorption/desorption
  - Finite density of identical adsorption sites
  - Desorption energy independent of coverage (i.e., constant residence time)
- Observed saturation ascribed to site competition
- BUT fit to data predicts unphysical parameters: NOT the whole story

Test model by expanding pressure range



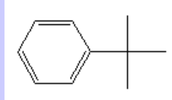
- Contamination rates appear to scale *logarithmically* with partial pressure
- Simple Langmuir-based model clearly inapplicable over larger pressure range
- Correct scaling law *critical* to span 3-6 orders of magnitude between testing and production environments.

Recent measurements of relevant contaminants



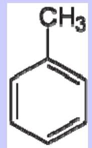
tert-butylbenzene

$C_{10}H_{14}$



toluene

C_7H_8

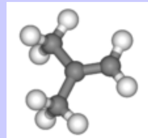


benzene

C_6H_6

isobutene (isobutylene)

C_4H_8



- Logarithmic scaling with pressure over 3 decades: $\sim A \cdot \log(p/p_0)$
- Number of C atoms not necessarily good indicator of contamination rate

Correlation with physical properties of organics

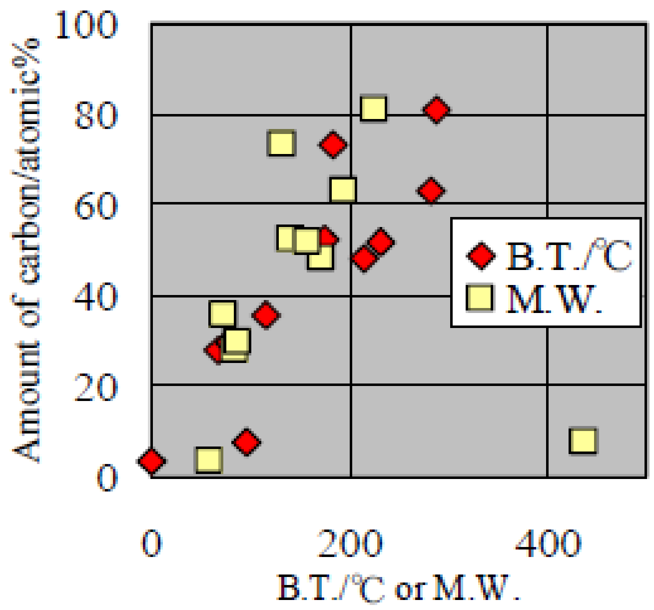
EUVA, Univ. Hyogo (Japan)

Carbon deposition on multi-layer mirrors by extreme ultra violet ray irradiation

S. Matsunari[*a], T. Aoki[a], K. Murakami[a], Y. Gomei[b],
S. Terashima[a], H. Takase[a], M. Tanabe[a], Y. Watanabe[a], Y. Kakutani[c], M. Niibe[c], Y. Fukuda[a]

Proc. SPIE, Vol. 6517, 65172X (2007)

Organic gas	B.T./°C	M.W.
Buthane	-1	58
Buthanol	117	74
Methyl propionate	79	88
Hexane	69	86
Perfluoro octane	97	438
Decane	174	142
Decanol	231	158
Methyl nonanoate	214	172
Diethyl benzene	183	134
Dimethyl phtalate	283.7	194
Hexadecane	287	226

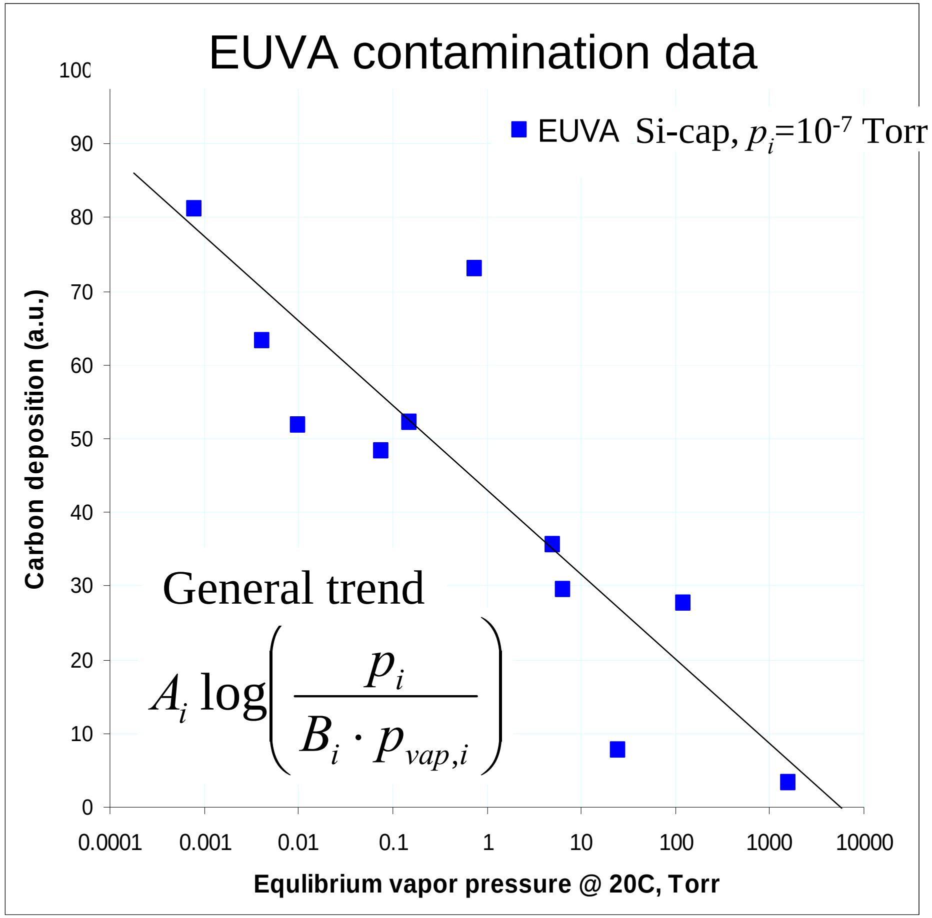


Correlation with vapor pressure (EUVA)

EUVA Measurements†

Species	Vapor pressure at 20C, Torr	Atomic % carbon
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)



Contamination rate for species *i* trends with the log of the ratio of ambient pressure, p_i, to vapor pressure, $p_{vap,i}$

Correlation with physical properties

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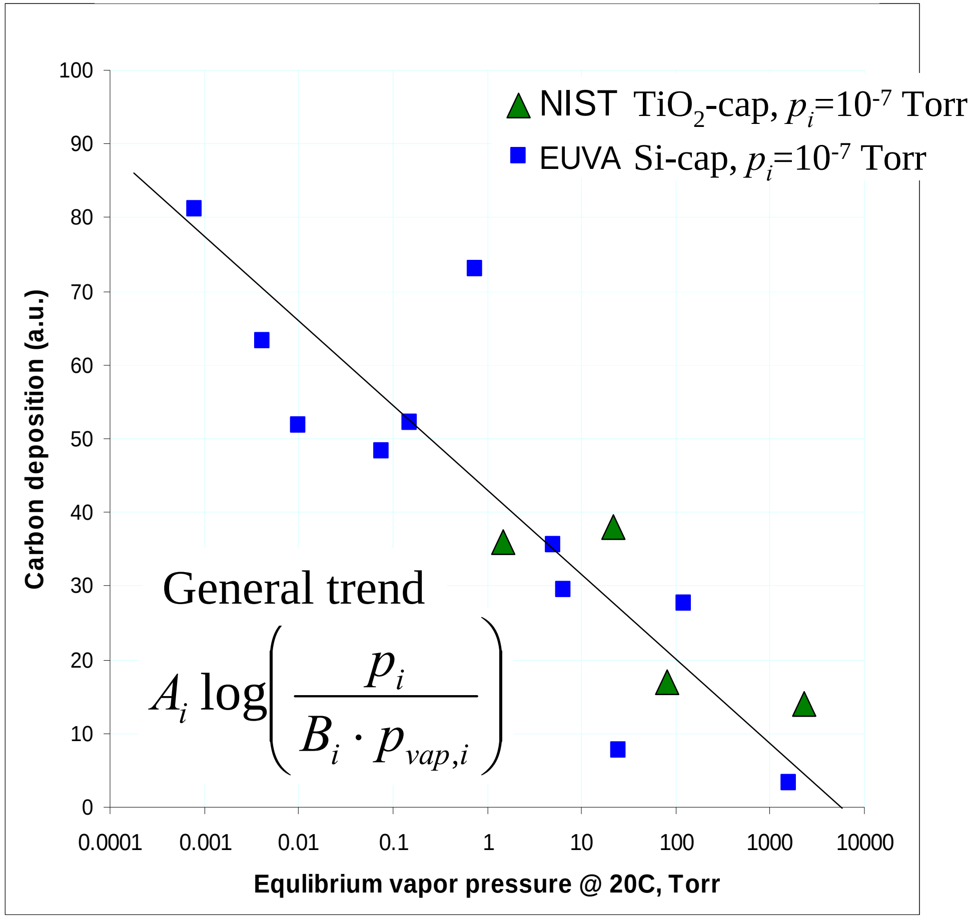
NIST Measurements (normalized)

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

Relative carbonization rates



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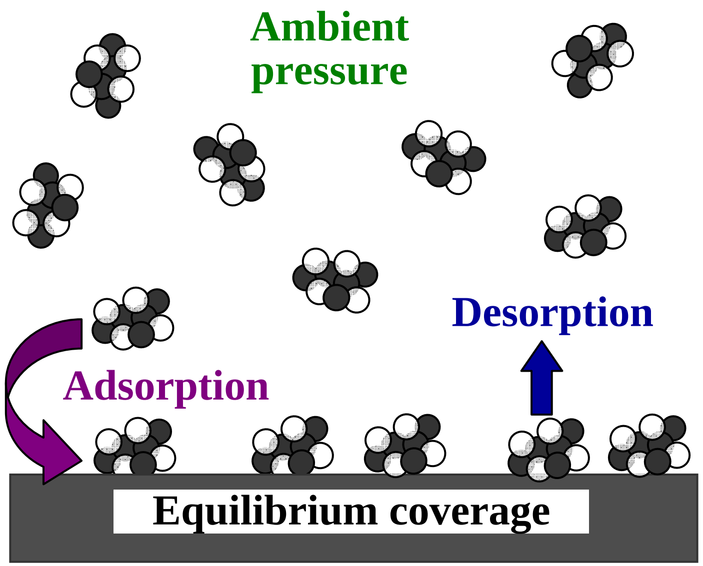
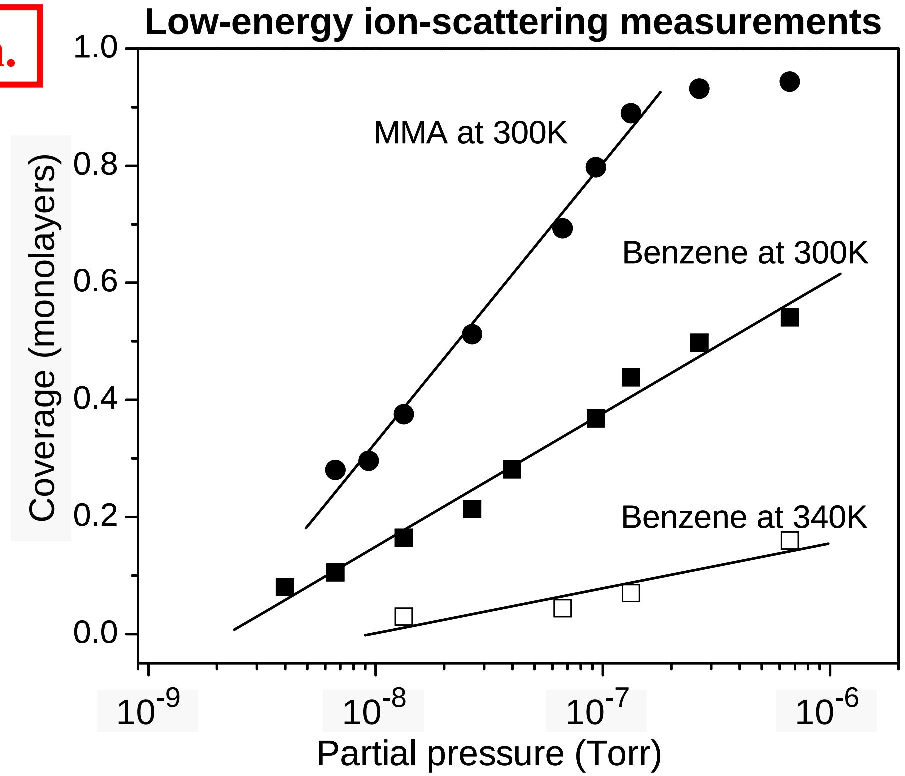
Coverage measurements at Rutgers University

Yakshinskiy, *et al*, Proc. SPIE 7271-36 (2009), *and* S. Zalkind, *et al*, J. Vac. Sci. Technol. B 26, p. 2241 (2008)

Molecular coverage. No EUV irradiation.



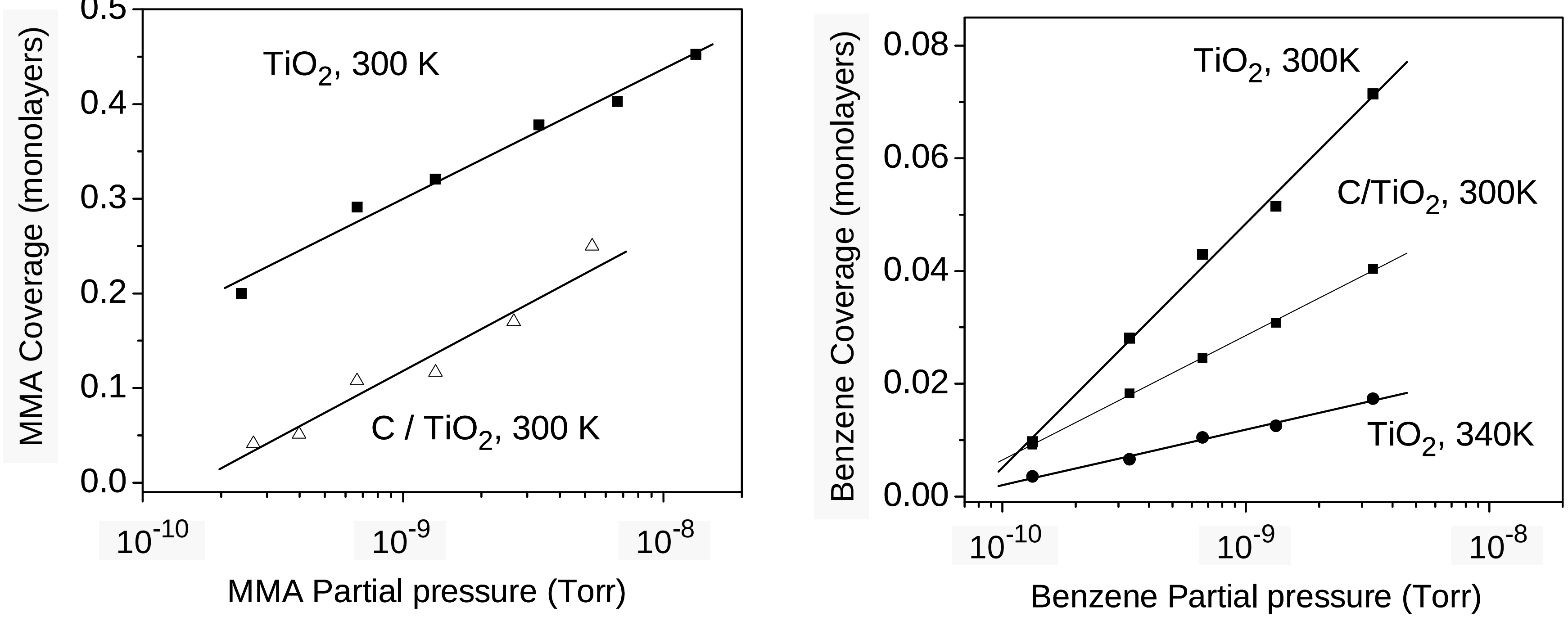


- Steady state coverage of organic molecules on clean TiO_2(011)
- Low-energy ion-scattering used for pressures >10^{-9} Torr
- Logarithmic pressure dependence over 2-3 orders of magnitude
- Consistent with EUV-contamination rate proportional to coverage

Coverage measurements at Rutgers University

Yakshinskiy, *et al*, Proc. SPIE 7271-36 (2009), *and* S. Zalkind, *et al*, J. Vac. Sci. Technol. B 26, p. 2241 (2008)

Temperature-programmed desorption measurements



- Steady state coverage of molecules on clean *and C-covered* $TiO_2(011)$
- Same behavior on C surface suggests scaling not specific to TiO_2
- Logarithmic pressure dependence continues down to 10^{-10} Torr

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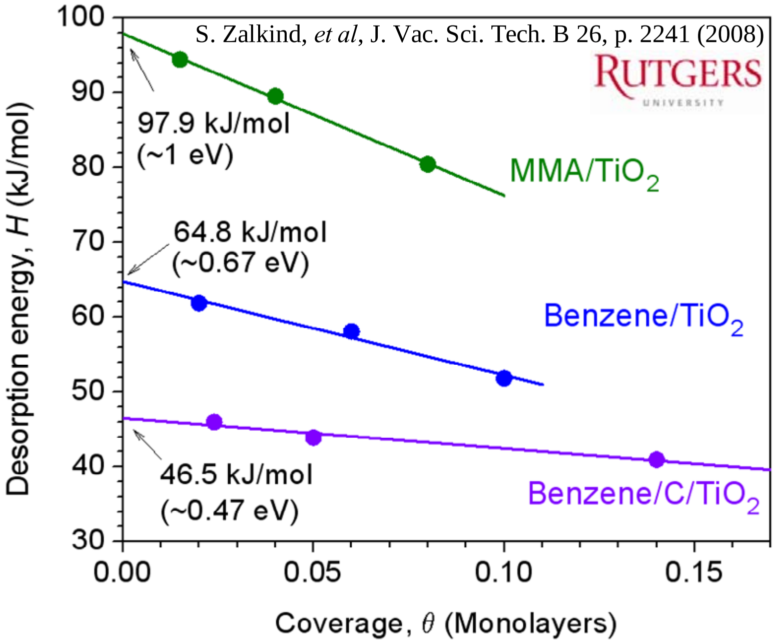
Possible origins of logarithmic scaling: Temkin models

- Molecular interactions: **desorption energy, *H***, decreases linearly with **coverage, θ**



$$(Residence\ time) \sim e^{\frac{H}{kT}} = e^{\frac{H_0 - \alpha \cdot \theta}{kT}}$$

Modification of Langmuir: Temkin isotherm

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

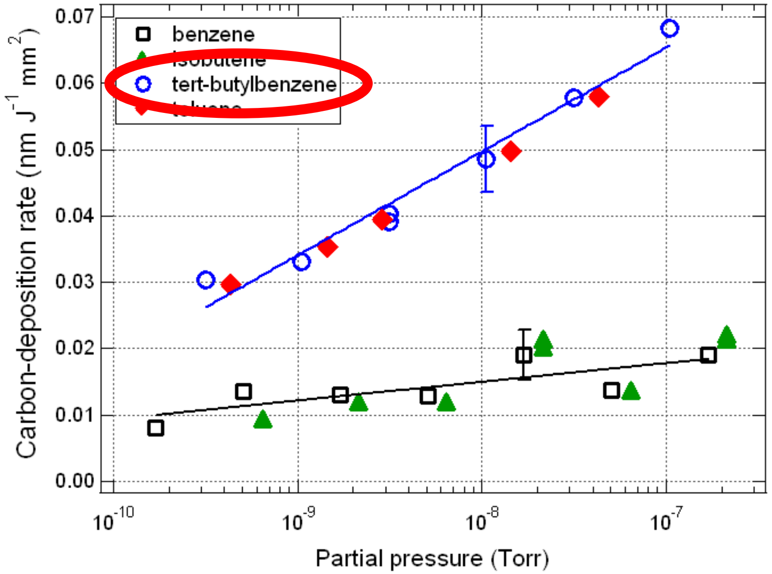
$$\Rightarrow \theta \approx \begin{cases} 1\ \text{ML}, \text{ for } p >> p_0 \\ \boxed{\frac{1}{\beta} \cdot \log\left(\frac{p}{p_0}\right)} \\ \frac{p}{p_0}, \text{ for } p << p_0 \end{cases}$$

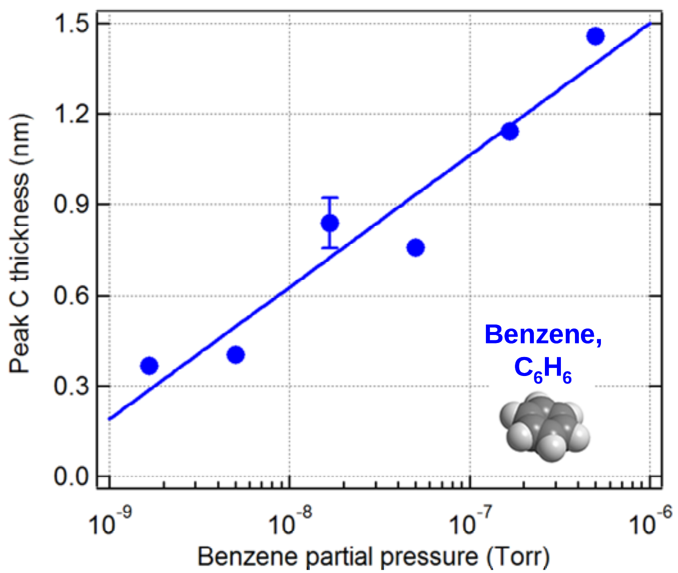
- Surface defects: distribution of adsorption energies $\Rightarrow \boxed{\theta = \log\left(\frac{1 + a \cdot p}{1 + b \cdot p}\right)}$

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

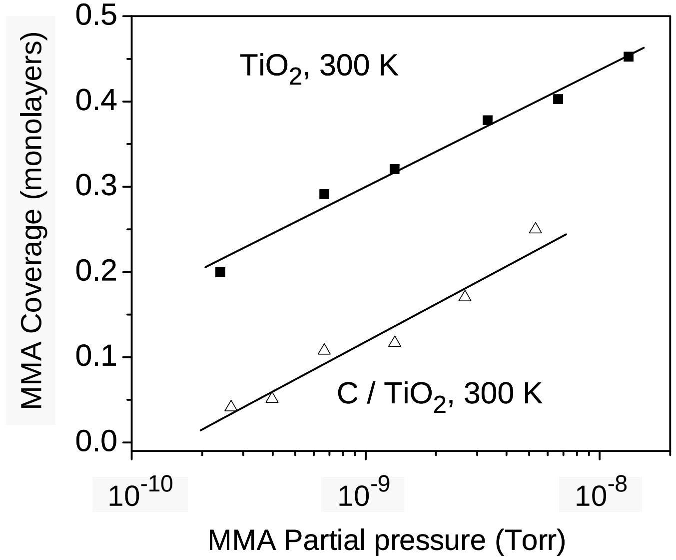
log(*p*) scaling persistent at lowest measured pressures

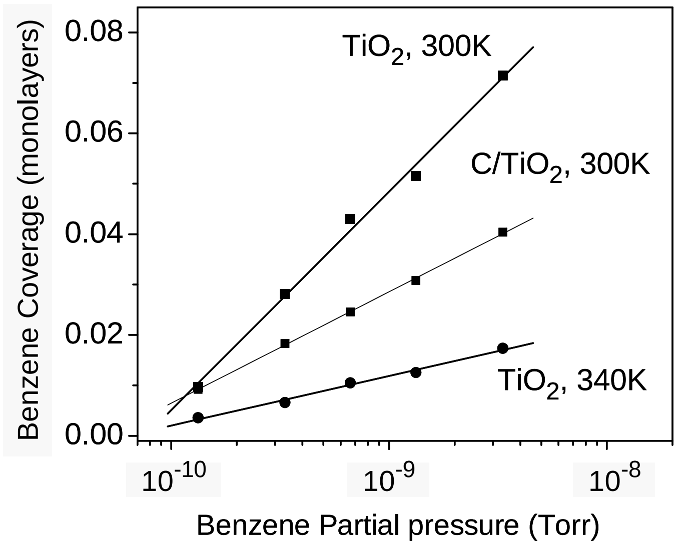
NIST contamination measurements



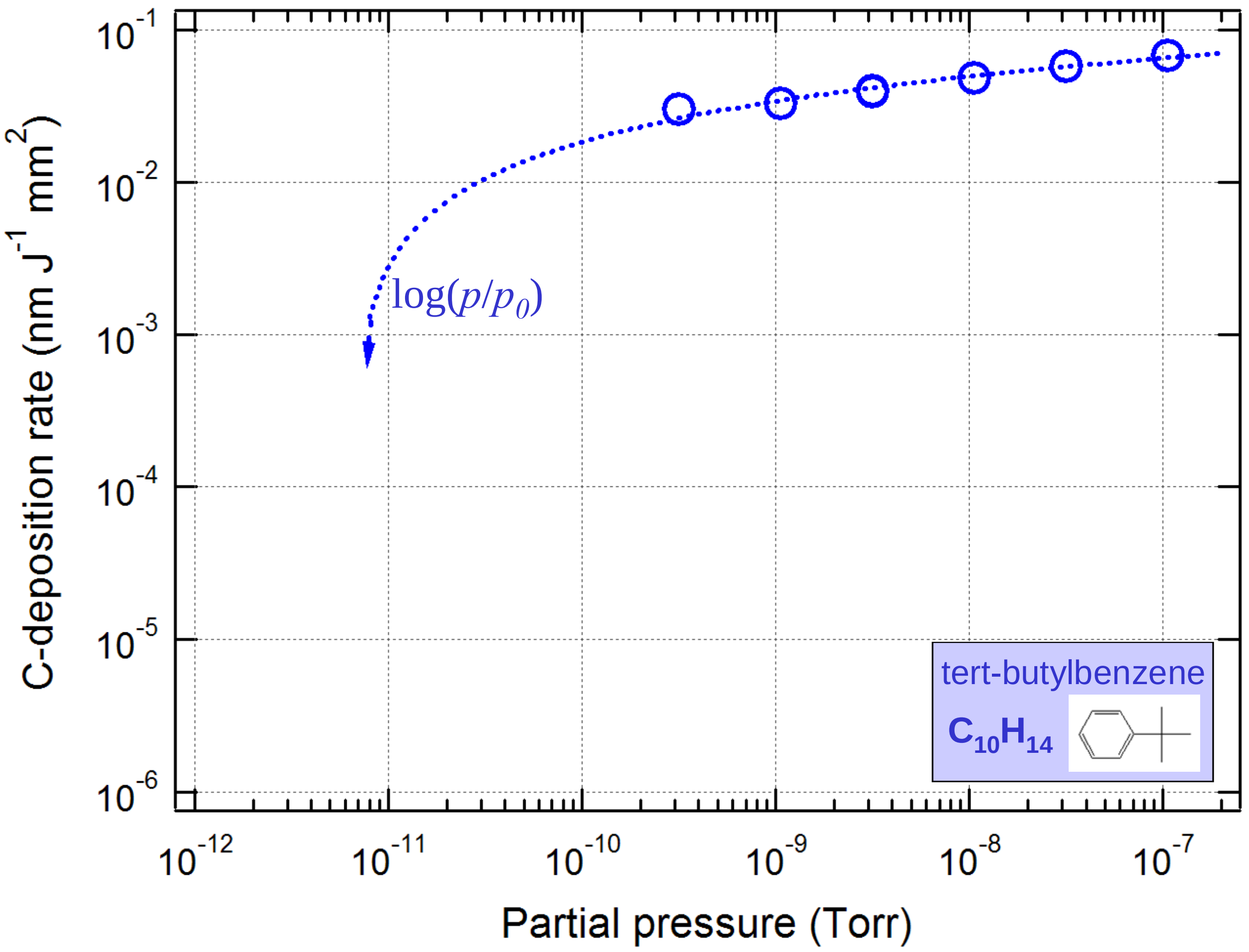


Rutgers coverage measurements

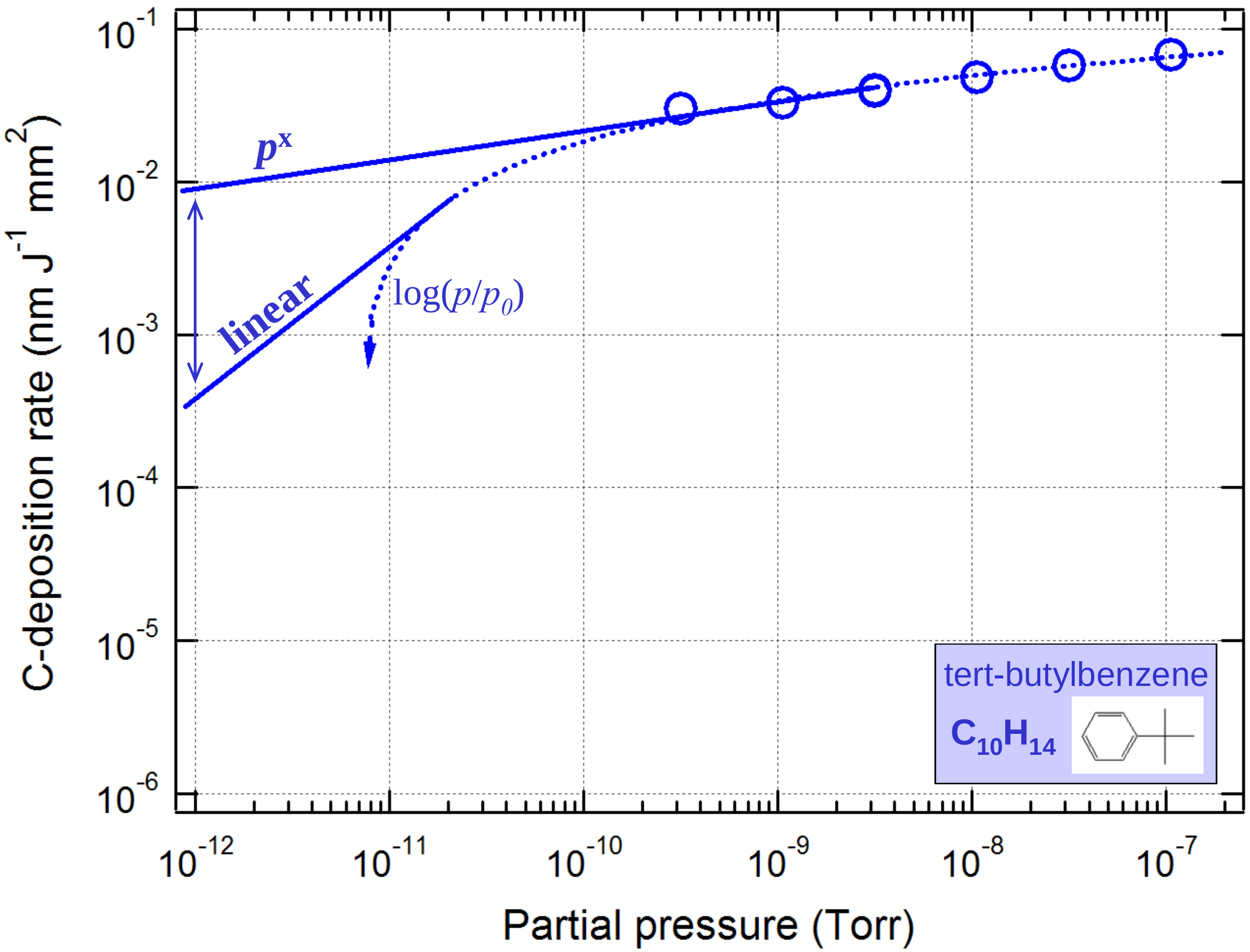




Extrapolation to lower pressures

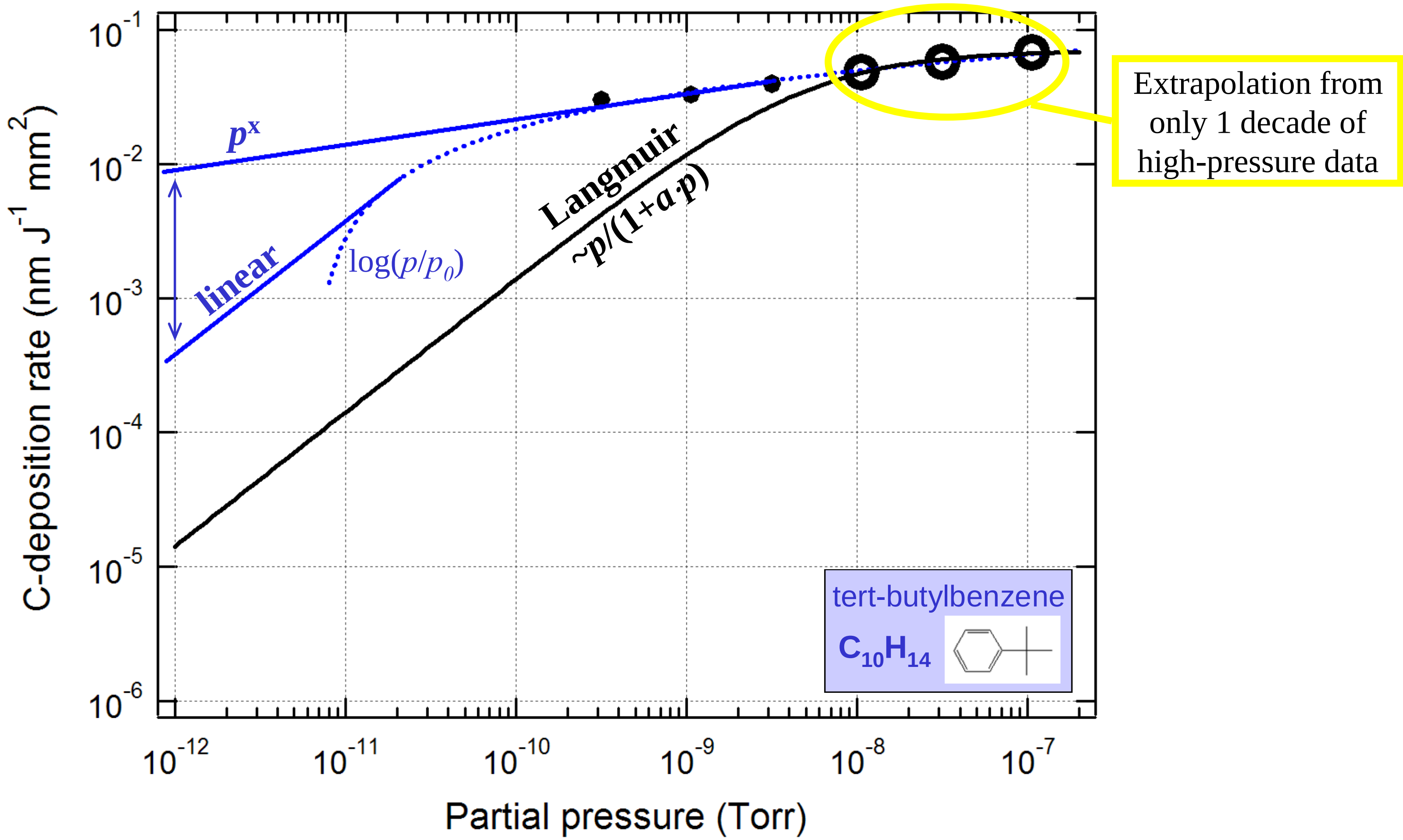


Extrapolation to lower pressures: estimated limits



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

Extrapolation to lower pressures: potential errors



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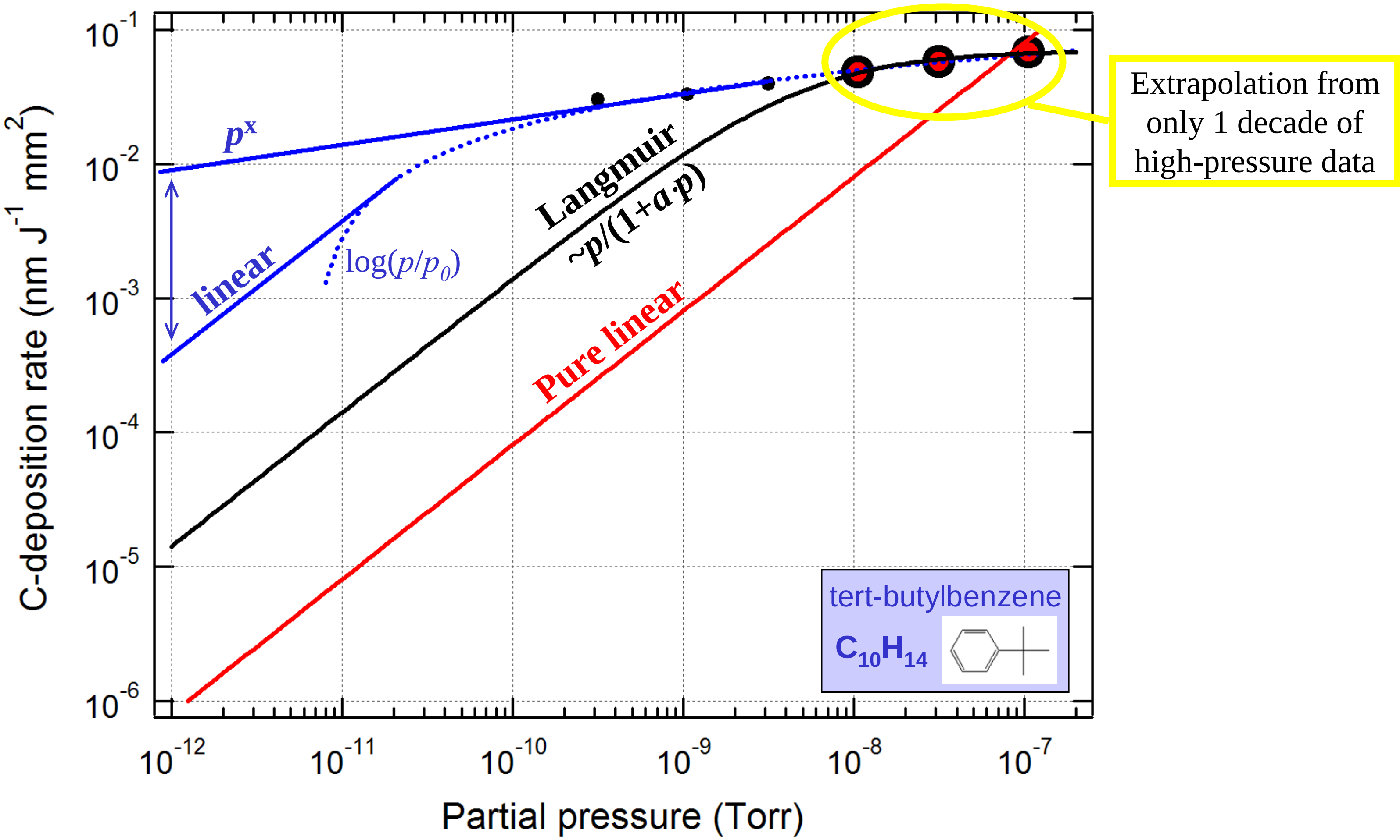

- Transition from log(p) not observed: estimate upper & lower extrapolation limits
- Linear extrapolation of a few high-pressure measurements will *underestimate* rates at lower pressures by multiple orders of magnitude.

Summary

- Both EUV-contamination (NIST) and non-irradiated coverage (Rutgers) measurements show pressure scaling much closer to logarithmic than linear.

- Such behavior predicted by models with coverage-dependent surface binding energy (e.g., Temkin)

- Contamination rates in tool environment can be *severely* underestimated by extrapolation with purely linear or quasi-linear (Langmuir) models.

- **Accurate extrapolation of low-pressure rates requires measurement over a large range of pressures extending as low as possible**.

- Plan to look for transition to linear scaling at very low pressures.