UNIVERSITY AT ALBANY
State University of New York

Quantitative Measurement of EUV Resist Outgassing

Gregory Denbeaux, Rashi Garg, Justin Waterman, Yu-Jen Fan, Robert Brainard, Chimaobi Mbanaso, Kim Dean*

College of Nanoscale Science and Engineering
University at Albany
*SEMATECH, Austin, TX

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gdenbeaux@uamail.albany.edu

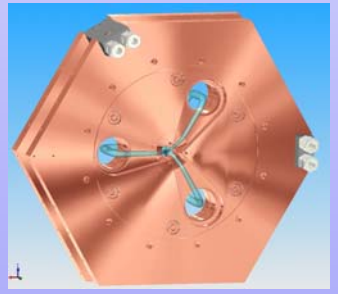
Outline

- **Why measure outgassing?**
  - EUV radiation will cause contamination of projection optics in EUV exposure tools
  - Controlling the vacuum environment near the optics by careful choice of resists will help improve the lifetime of the optics
- **Accurate measurement of both species and number of molecules leaving resists has been a challenge**
- **This project uses four techniques to measure the outgassing to ensure accurate calibration**
  - Quadrupole mass spectrometer
  - Pressure rise from ion gauge
  - Mass loss from quartz crystal microbalance
  - Accumulation of outgassed species in thermal desorption tube
- **Summary of these methods and results**

Compact EUV Source from Energetiq

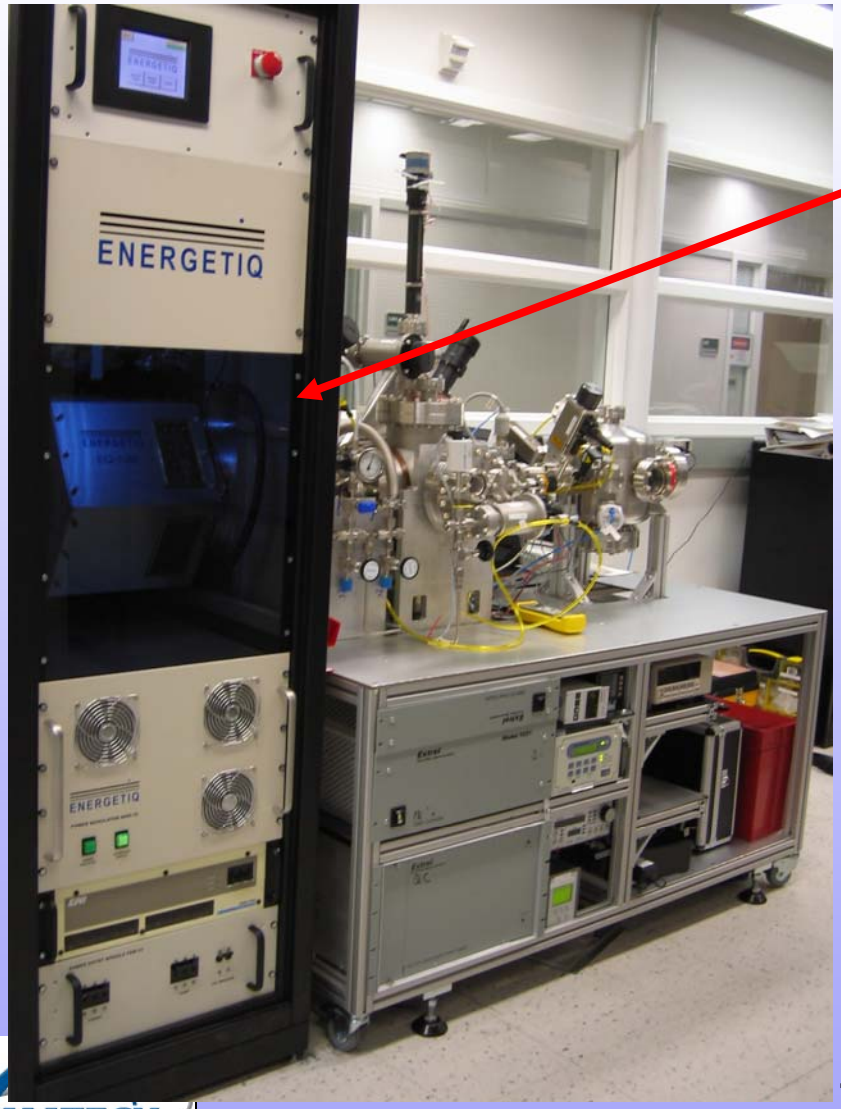
10W DPP Xe source

It has been in use for over a year in Albany



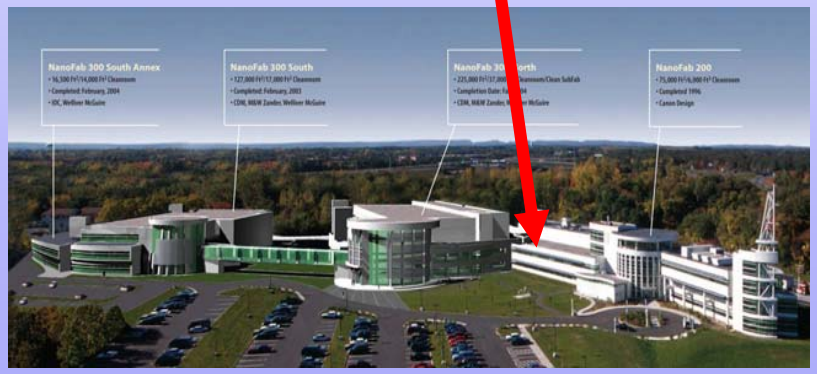
EUV ROX system Is in Operation

(EUV Resist Outgassing and eXposure)



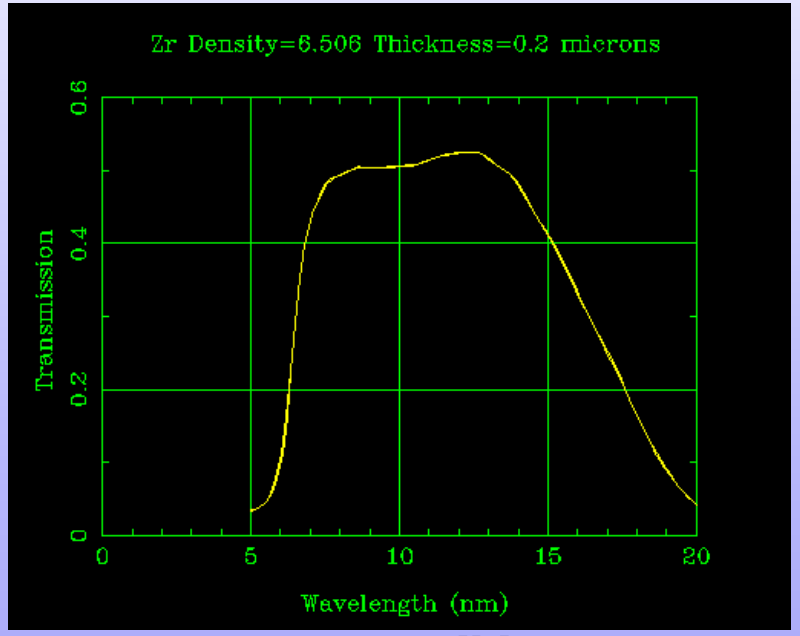
10W electrodeless Xe source from Energetiq

- **It is on the 2nd floor of the CESTM building in this complex**



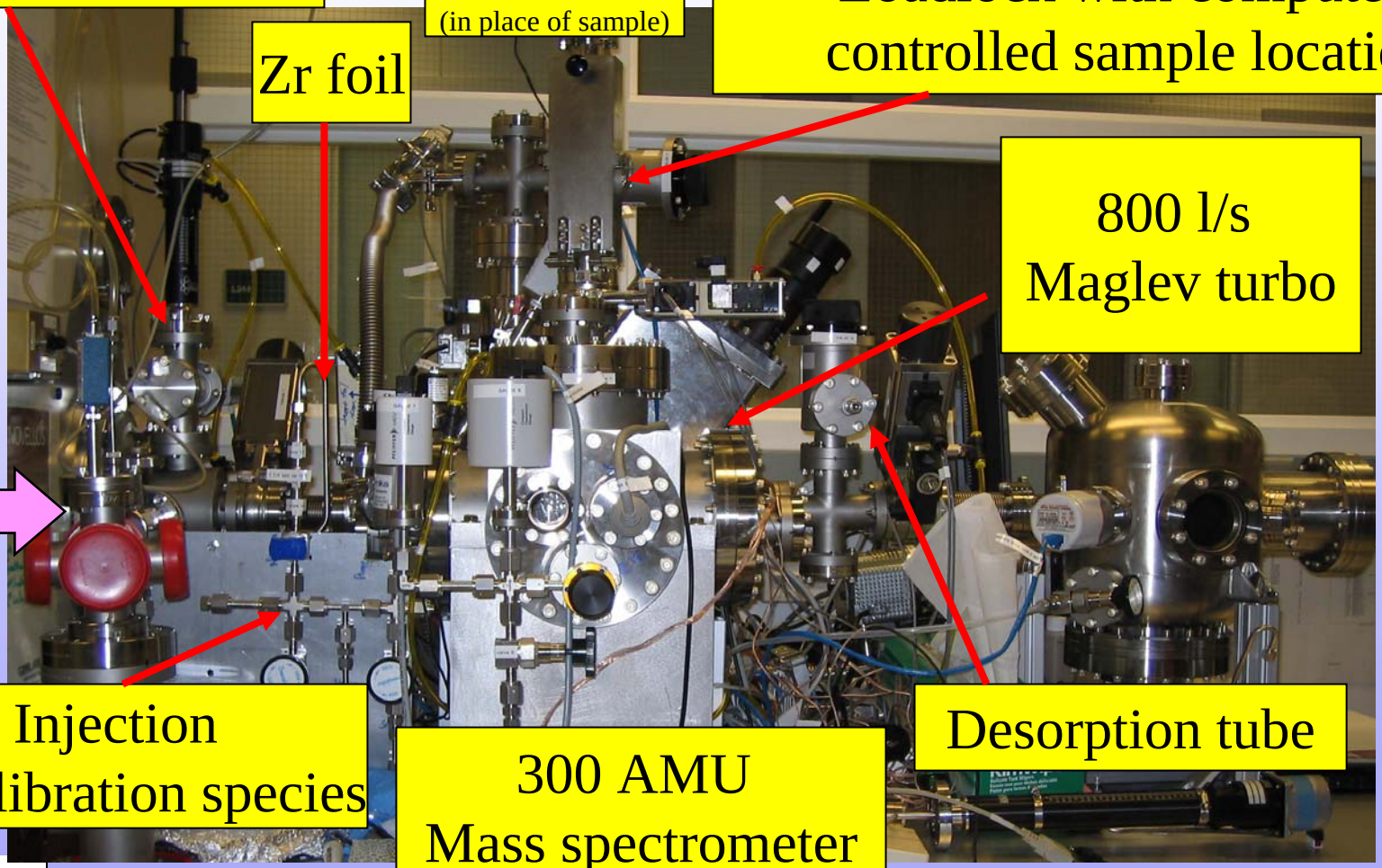
Source Spectrum

- Xe spectra has most energy within 10.5 to 15.5 nm
- Zr filter transmission from CXRO shows transmission between about 7 to 17 nm and negligible DUV and visible transmission
- Net spectra during exposure likely between 10.5 nm to 15.5 nm with little long wavelength out-of-band radiation
- Power on resist can be varied between 0.9 to 3.6 mW/cm^2 in a 4 cm^2 area

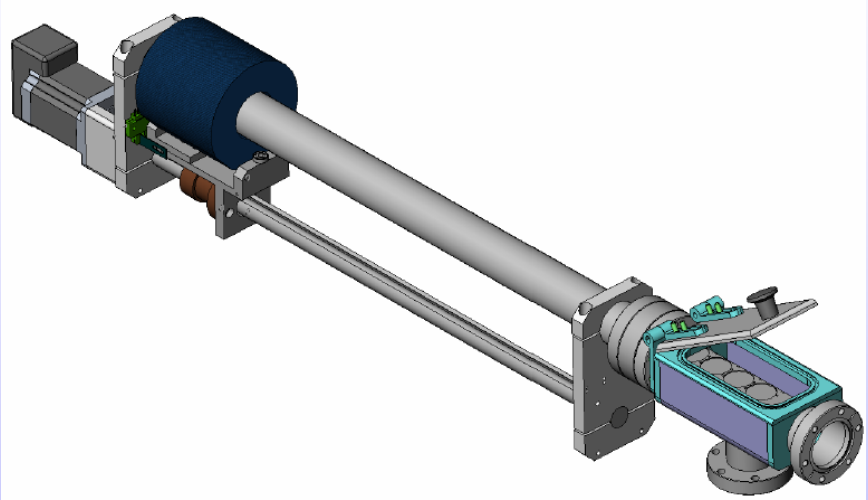


From www.cxro.lbl.gov

EUV-ROX System Details



Loadlock for Quick Sample Transfer



- UHV loadlock with magnetic coupling and computer control of motor
- Samples are pieces of wafers, 2 cm x 15 cm
- Exposure is 2 cm x 2 cm area circle or 3 mm strips 2 cm wide
- Motorized stage moves sample through EUV illumination for continuous exposure during outgassing tests
- Motorized stage moves sample in steps for individual exposures for resist sensitivity and contrast tests

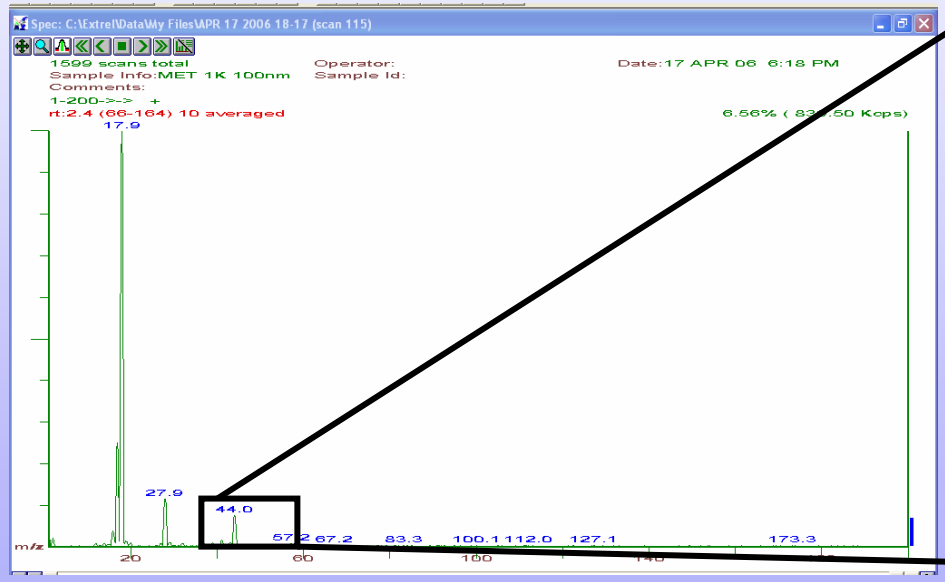
Mass Spectrometer

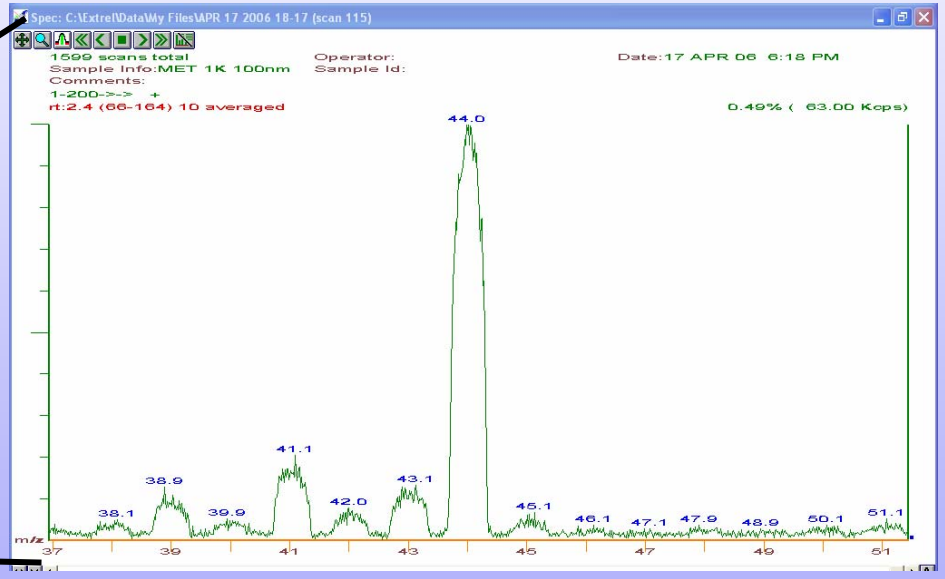
Extrel MAX300

- **1-300 AMU mass range**
- **Partial pressure detectability of 3 x 10^-15 Torr**
- **Positive or negative ion detection**
- **Cross beam Ionizer**
- **19 mm diameter rods**

Chamber Background

- **The chamber pumps down routinely to 1 x 10^{-8} Torr**





Dominant peaks are H_2O (18), CO (28), CO_2 (44), nothing noticeable beyond there

Closer view of some peaks show clearly defined peaks without tails between them

Calibration of Mass Spectrometer

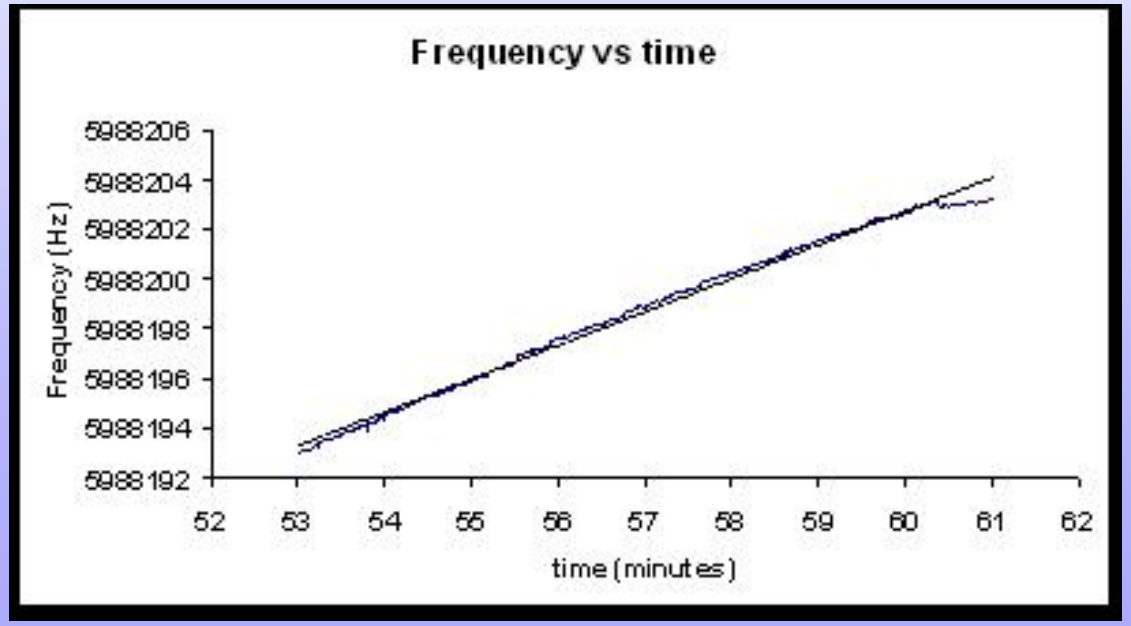
- **Species with known cracking patterns and high masses (SF_6) are used to calibrate the mass range of the mass spectrometer**
- **Injection of known species (methanol, isobutylene, PGMEA, …) are used to determine the specific "signature" of each species in this mass spectrometer**
  - Outside resources (NIST) are available, but each instrument will cause slightly different fragmentation patterns
- **Sensitivity of mass spectrometer is used with ion gauge calibrated for nitrogen and a variable nitrogen leak into the chamber**
- **Actual pumping speed is measured to determine residence time of outgassed molecules**
- **Finally, the results are compared to quartz crystal microbalance, pressure rise, and thermal desorption tube experiments on the same resists**

QCM Calibration

- Resist is spun onto quartz crystal and exposed
- Frequency change represents mass loss in resist film due to outgassing
- Experiment is performed while simultaneously measuring species detected by mass spectrometer
- Results show about ~2x fewer molecules lost by QCM than detected by mass spectrometer

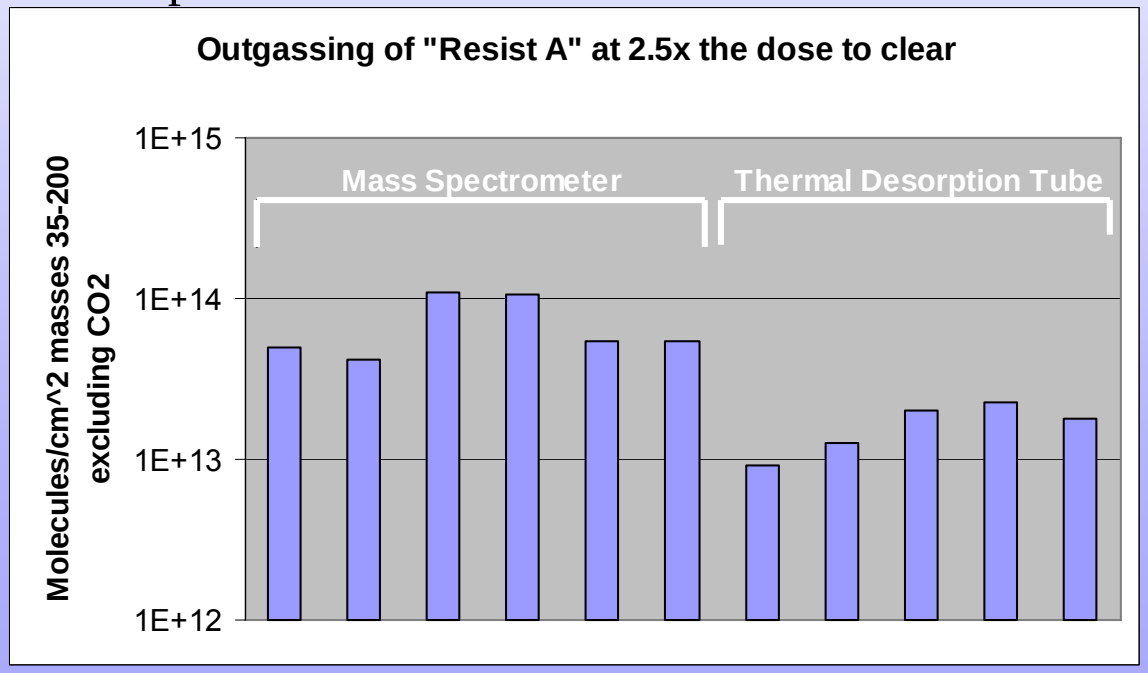
$$MassLoss = \frac{N_q D_q A_{crystal}}{\pi F_c Z} \arctan\left[Z \tan\left(\frac{\pi (F_q - F_c)}{F_q} \right) \right]$$

Where,
N_q = 1.668e13 Hz/m^{-10}
D_q = 2.648 gm/cc
Z ~ 1 (z-factor)
F_q: start frequency
F_c: end frequency



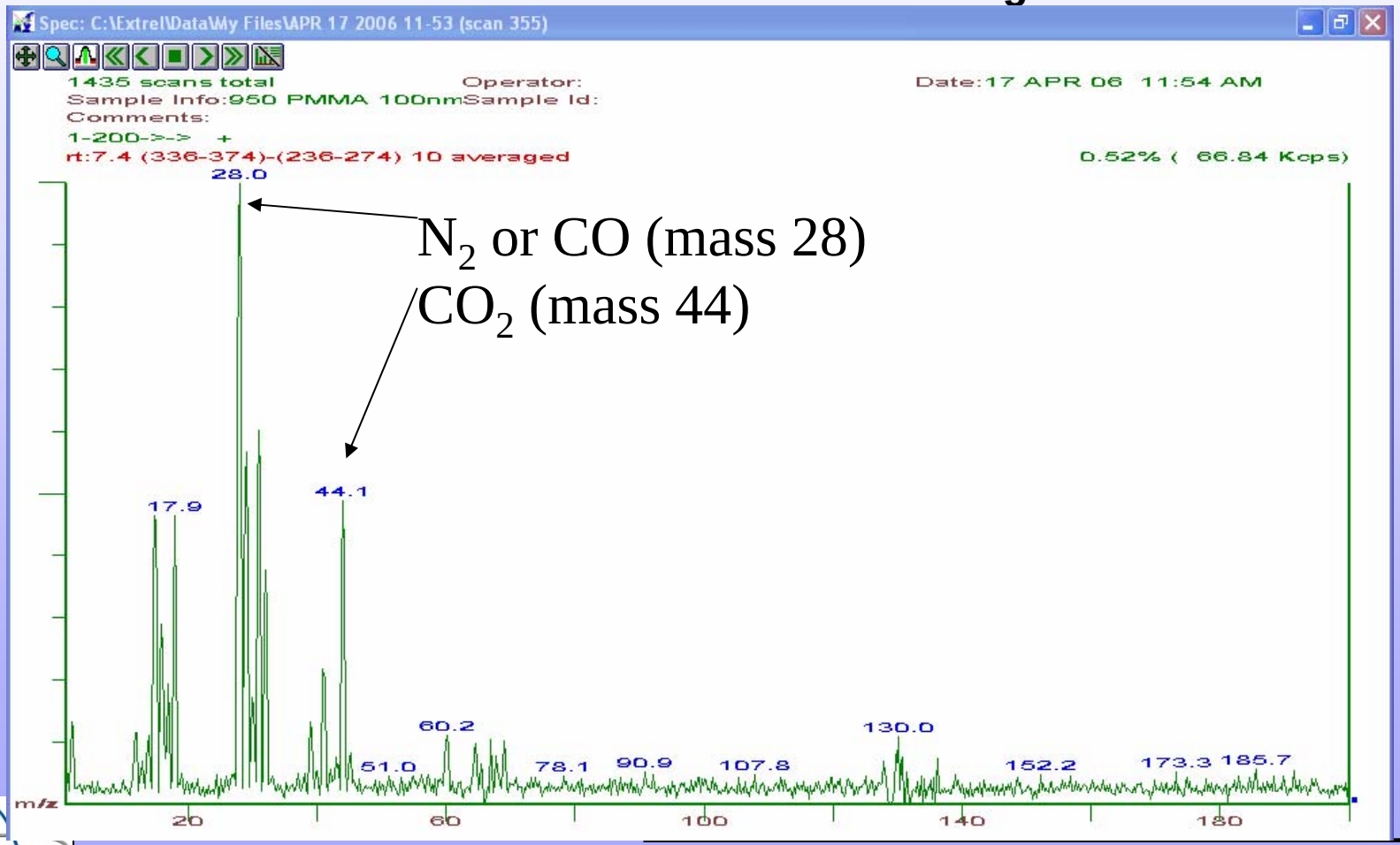
Comparison Between Mass Spectrometer and Thermal Desorption Tube Results

- Thermal desorption tube measurement is performed in sealed chamber with exposure and subsequent purging of molecules through the trap for external GC/MS analysis
- Results show ~4x fewer molecules detected by Thermal Desorption Tube compared to Mass Spectrometer
  - This could be due to losses by molecules that stick to the chamber wall, or pass through the desorption tube

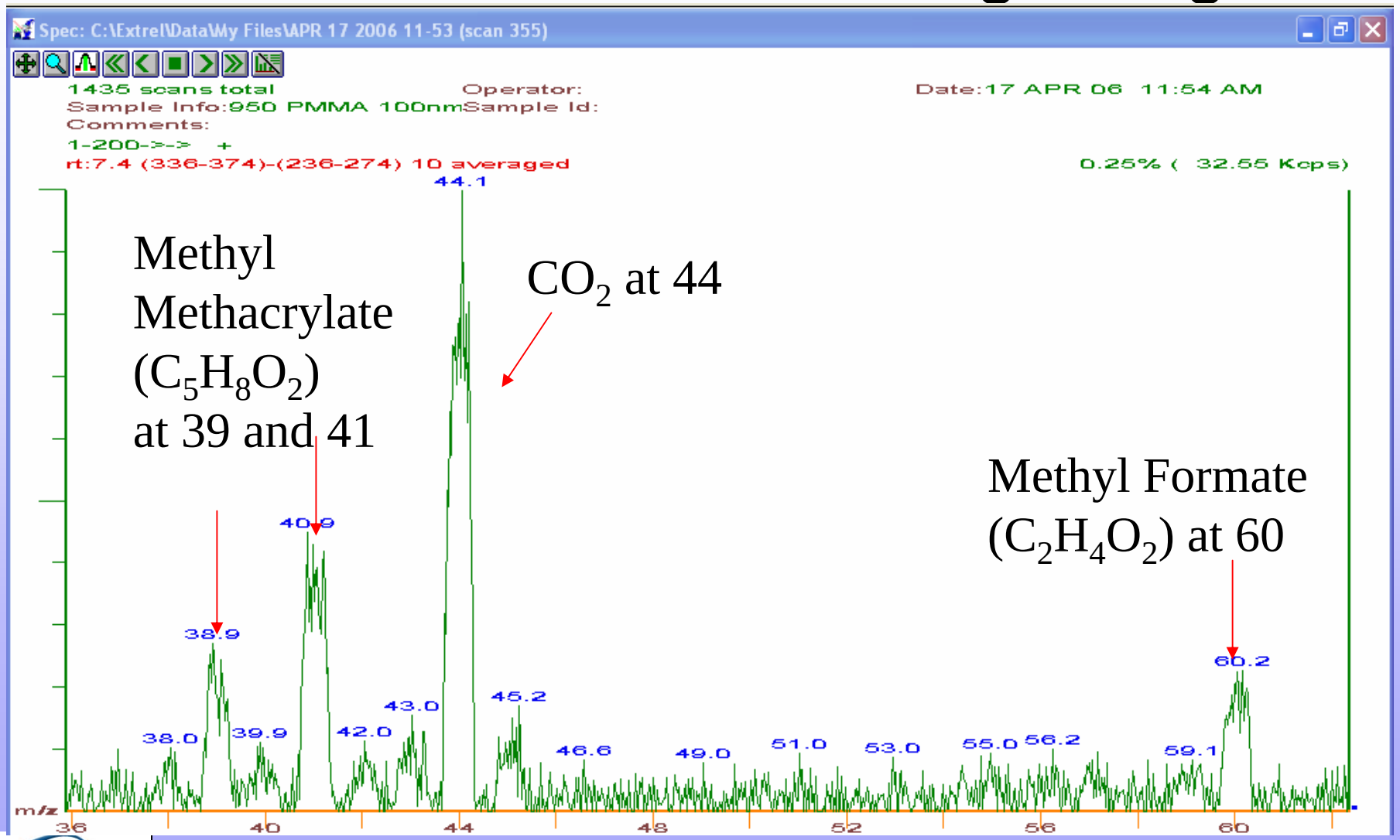


PMMA Outgassing

- **Expose at a rate of approximately 1 mW/cm^2 for a total dose of approximately 15 mJ/cm^2**
- **Scans shown are after subtraction of chamber background**



Local Detail of PMMA Outgassing



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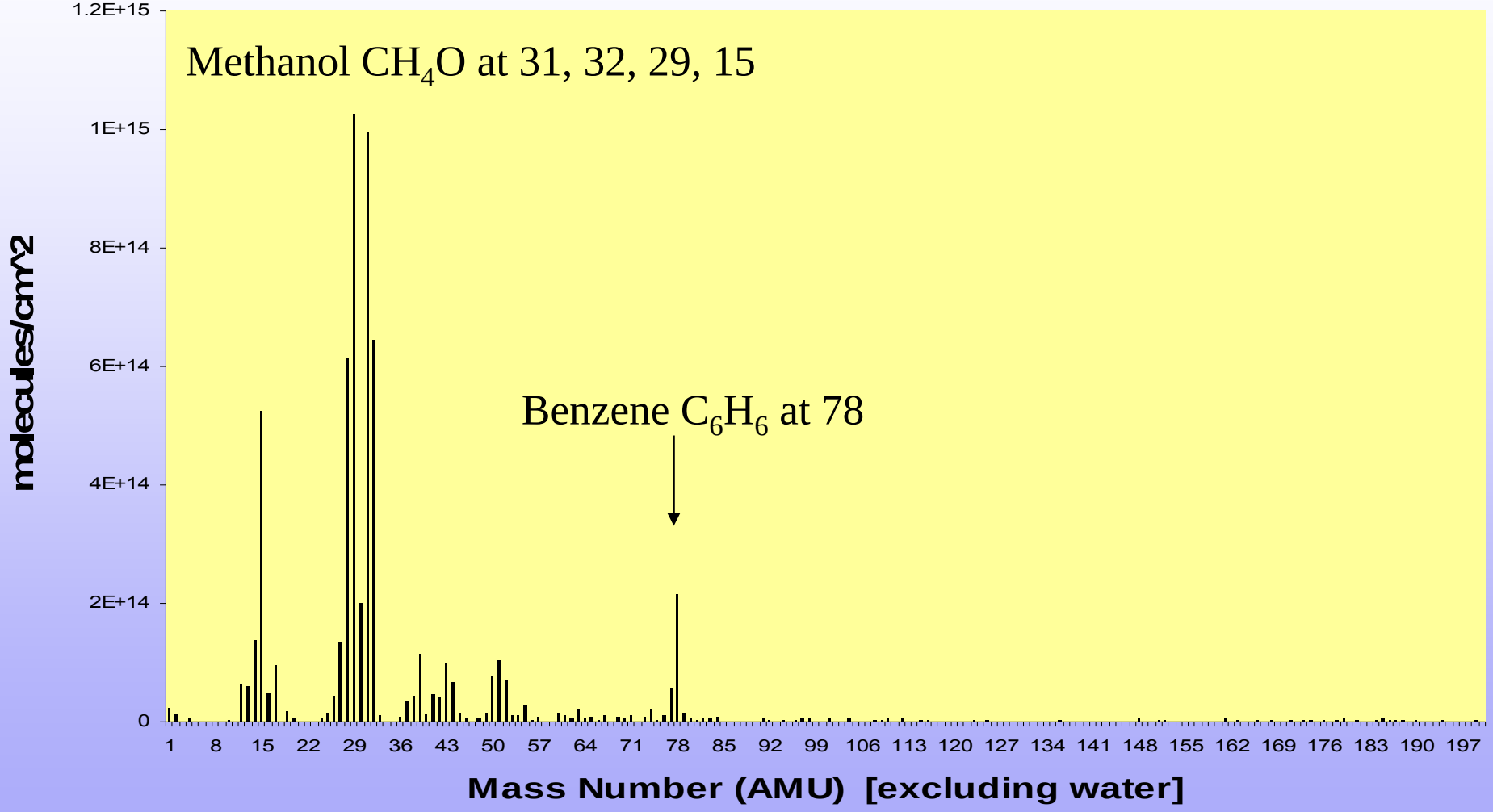
Sample outgassing result

(a KRS resist)



(Sample courtesy of Robert Allen, Greg Wallraff, Ann Fornoff, Carl Larson, Huo Trong, IBM)

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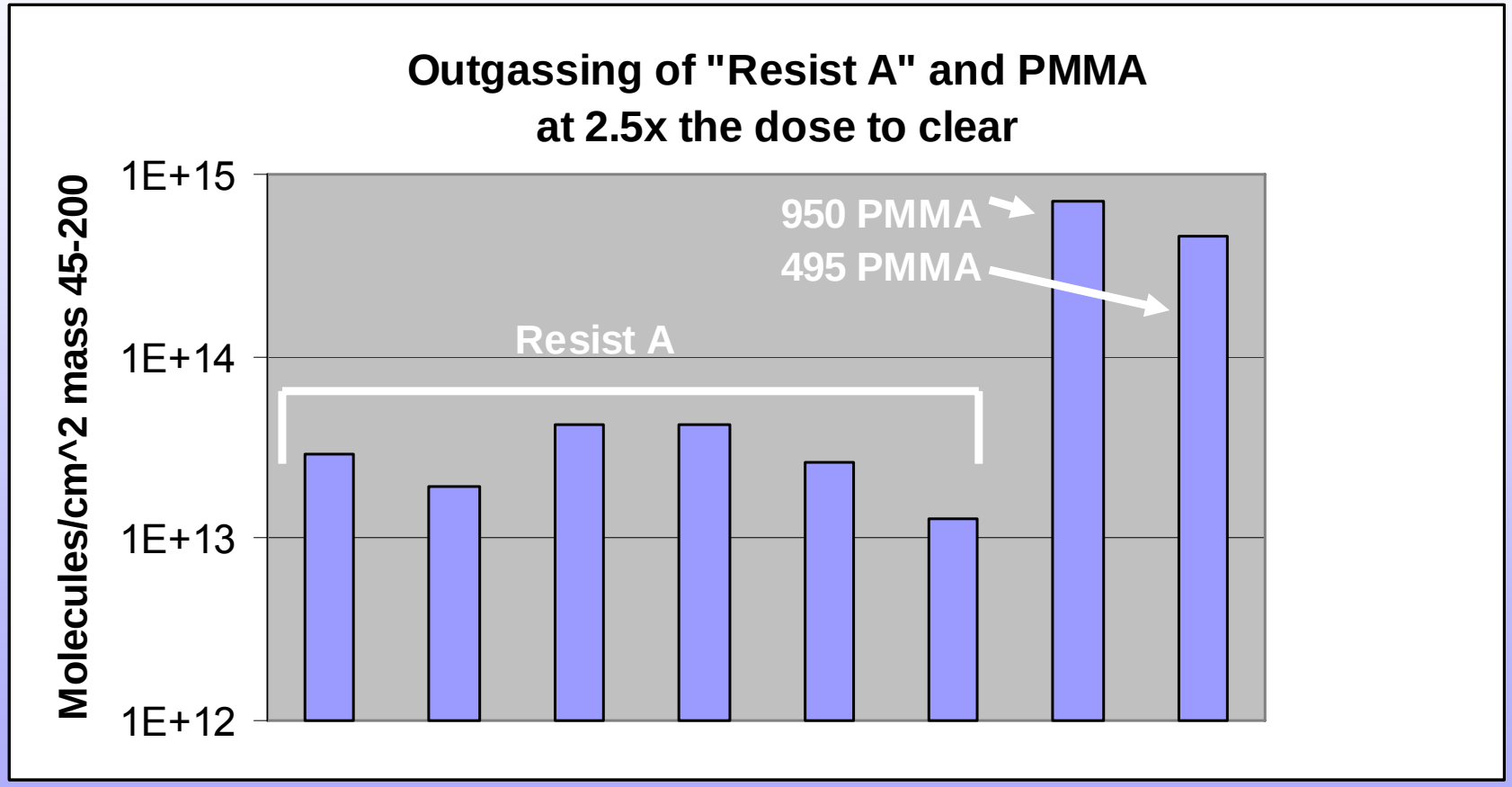
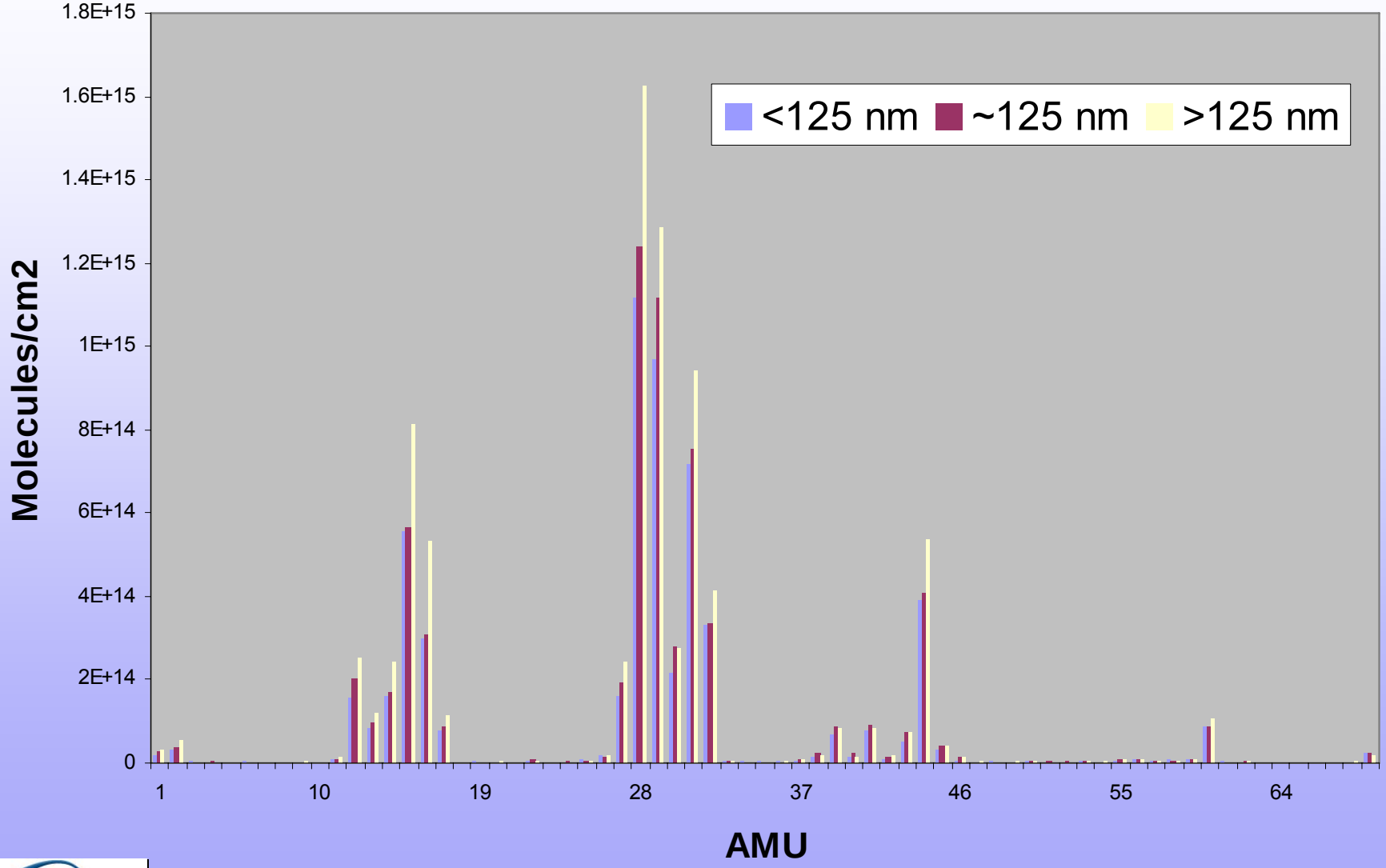
Outgassing Tests with Dose to Clear Measurements Completed Routinely

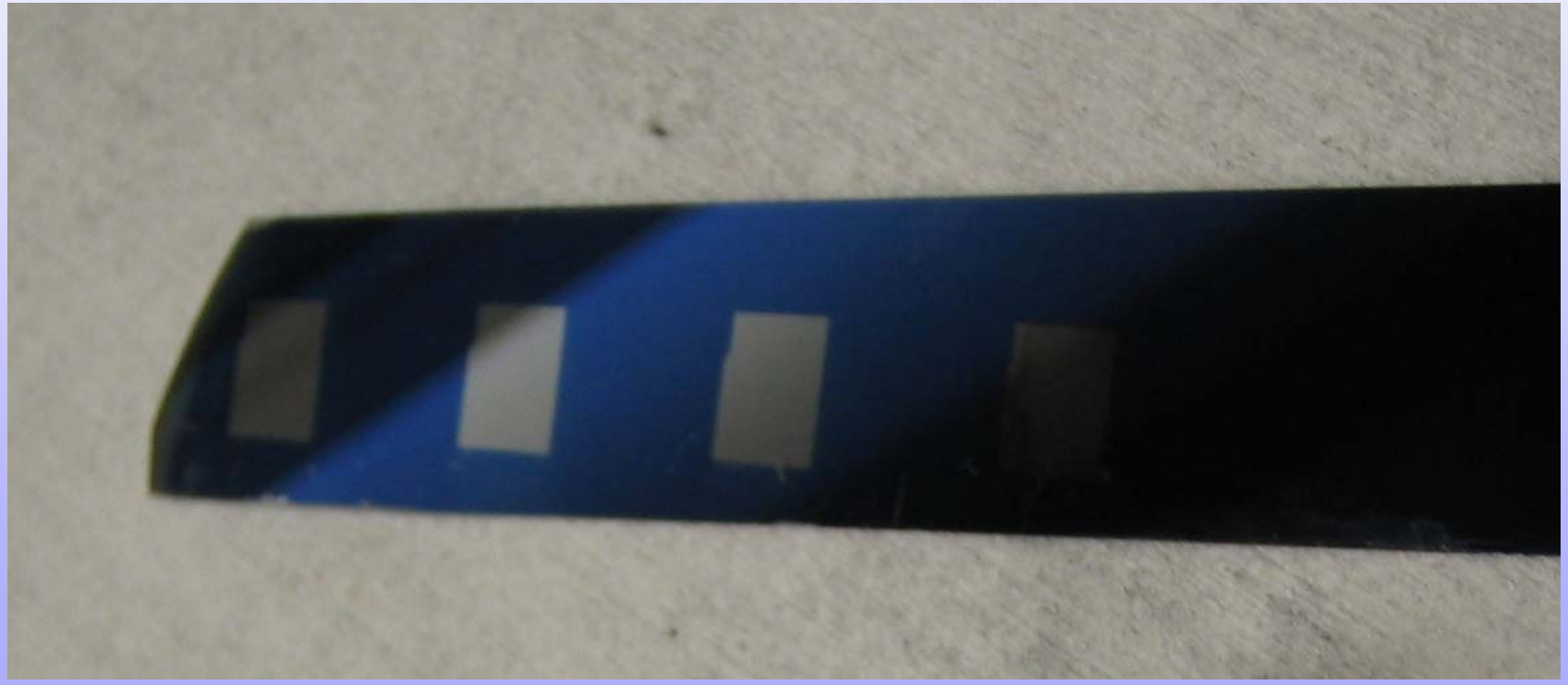


Outgassing vs. Thickness for PMMA



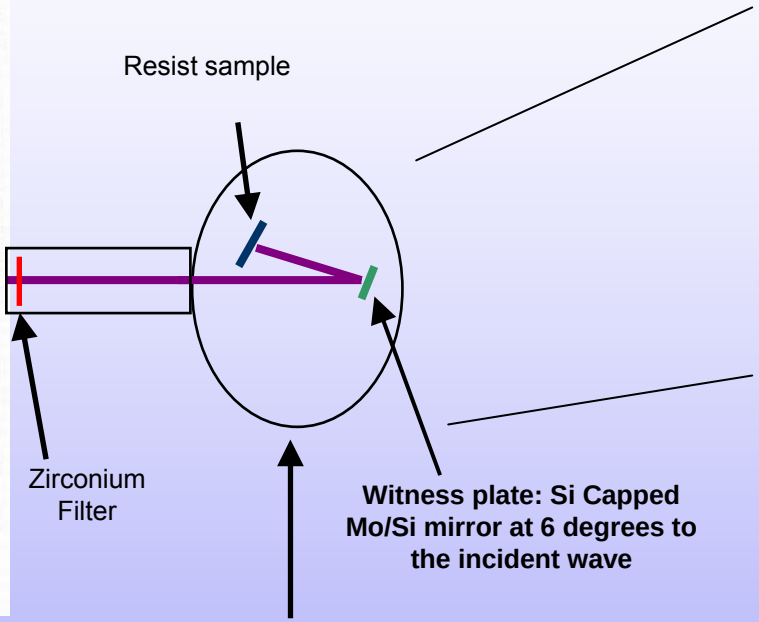
Dose to Clear and Contrast Curves

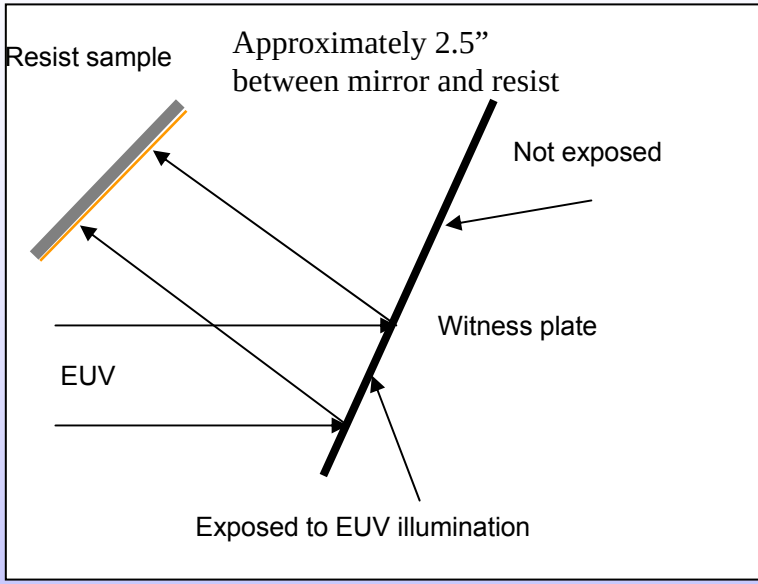
- **Dose to clear completed routinely for outgassing measurments and contrast curves are also available**



Witness Plate Experimental Configuration for Resist Testing

Energetiq Xenon Plasma EUV Source





- ASML proposed test to expose 300 mm wafer worth of resist
  - If reflectivity loss is ≤ 2%, the resist is safe for use

For latest results and discussion of future plans come to the combined session of the Resist TWG and Optics Lifetime Workshop on Thursday

Conclusions

- **Based on multiple methods (mass spectrometer, thermal desorption tube, pressure rise and quartz crystal microbalance), we have confidence in the calibration of this system to count number and species of molecules outgassed by EUV resists**
  - The Mass Spectrometer has a fast measurement time and measures the species
- **Using witness plate tests, we will work toward a more meaningful counting molecule specification for EUV resist outgassing**

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