# Surface Analysis for EUV Lithography Thermal Outgassing Studies

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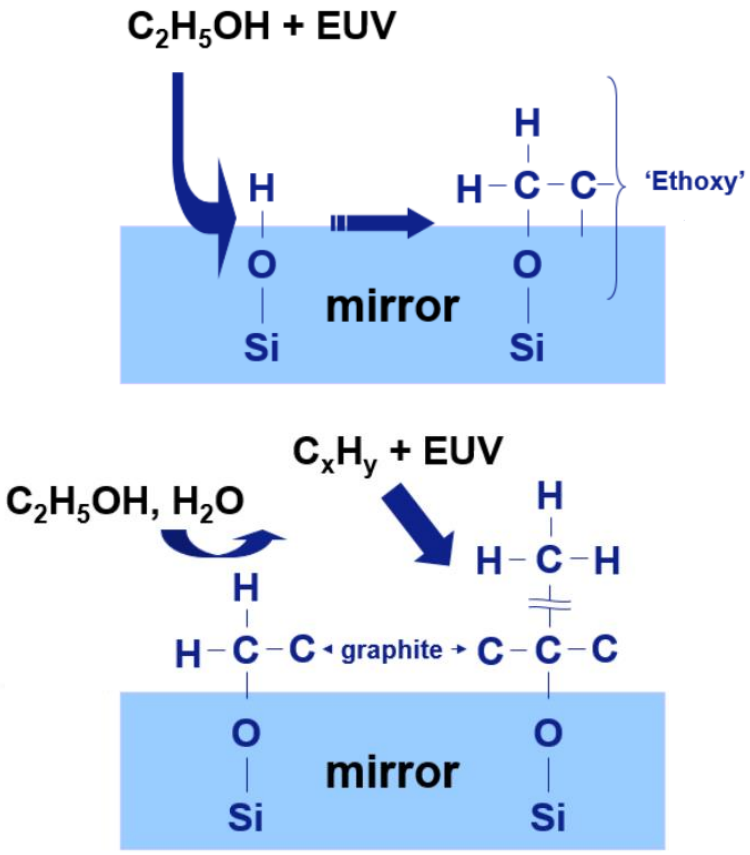
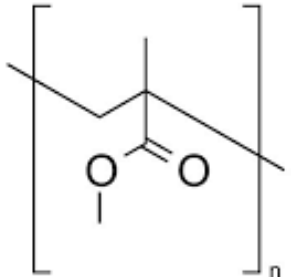
# Introduction

- Extreme ultraviolet (EUV) lithography is a key enabling technology for the sub-10 nm process technology node.
- A major challenge for EUV lithography components and materials is the requirement for high cleanliness, particularly with regard to outgassed organic contamination.
- Volatile organic contaminants can foul EUV optics.
- A common source of organic outgassing is the photoresist. Due to their high absorptivity in the EUV, component heating may occur, resulting in thermal outgassing (*Proc. SPIE*, Vol. 8322, 83222X, 2012)
- To study temperature-dependent outgassing phenomena, we investigate the surface chemistry of a model photoresist formulation containing poly(methyl methacrylate) (PMMA) and the photosensitizer Irgacure 907 (IG907) under thermal vacuum conditions.



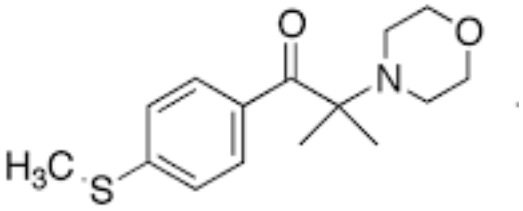
# Experimental Design

- PMMA is a commonly used model photoresist for DUV and EUV lithography.
  - First EUV use demonstrated in the 80's (Namioka, *Revue Phys. Appl*. 1998, 23, 1711-1726)
  - Frequently used to demonstrate ultimate resolution in lithography research




PMMA

- IG907 is a commonly used organic UV photoinitiator with high solubility in common solvents

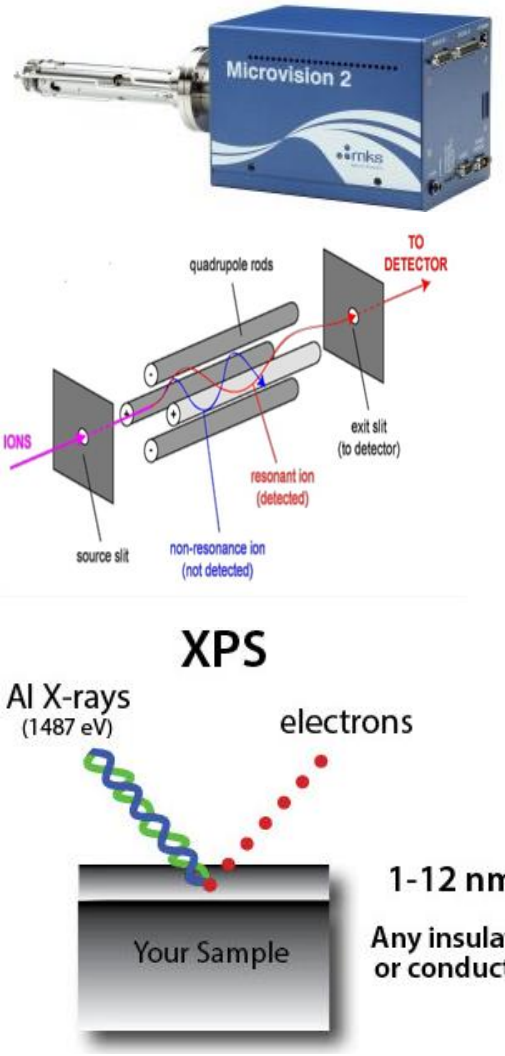



Irgacure 907

- Mixture of PMMA/IG907 as a model photoresist formulation to investigate thermal outgassing of small molecule photoinitiators in polymer matrix

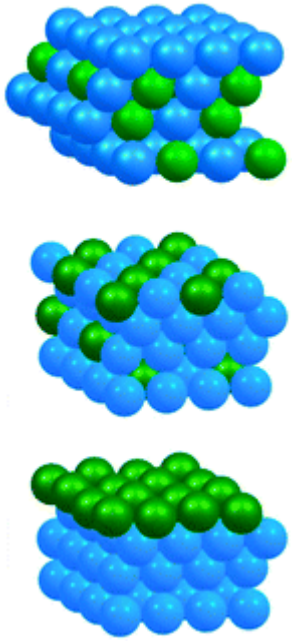
# Analytical Methods

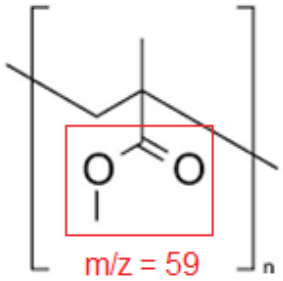
- X-ray photoelectron spectroscopy (XPS) uses photoelectric effect to obtain elemental and chemical information of a surface
  - Ejects core electrons with elemental-unique binding energy
  - Only top 1-12 nm electrons escape without scatter
- Residual gas analyzers (RGA) measures the vacuum outgassing of solid materials
  - Quadrupole mass spectrometry in UHV
  - Electron impact ionization
- Thermal desorption spectroscopy (TDS) uses temperature to separate gases for RGA mass spectrometry analysis

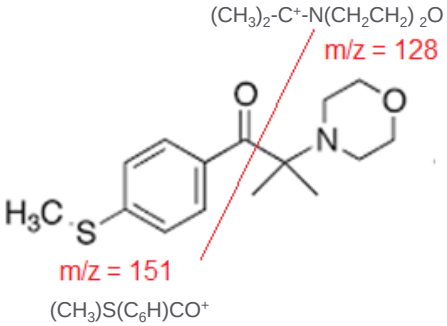


# Analytical Methods

- RGA/TDS used to identify IG907 and PMMA chain scission product partial pressure as a function of temperature
  - Fragmentation patterns used to identify gas phase composition
  - Desorption temperature depends on strength of **chemical** forces between the gas molecule and the substrate
- XPS produces surface chemistry information
  - Ratio of IG907:PMMA on surface
  - Chemical environment of each atom
  - Pre- and post- heating measurements

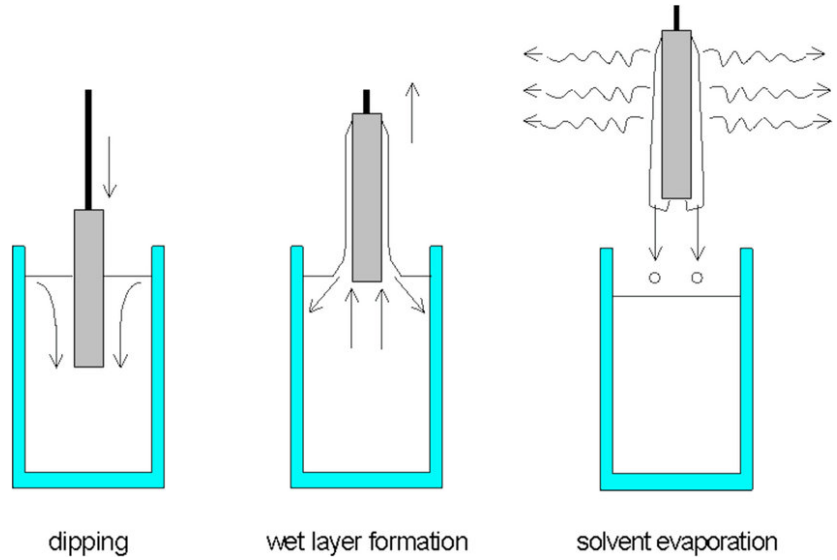




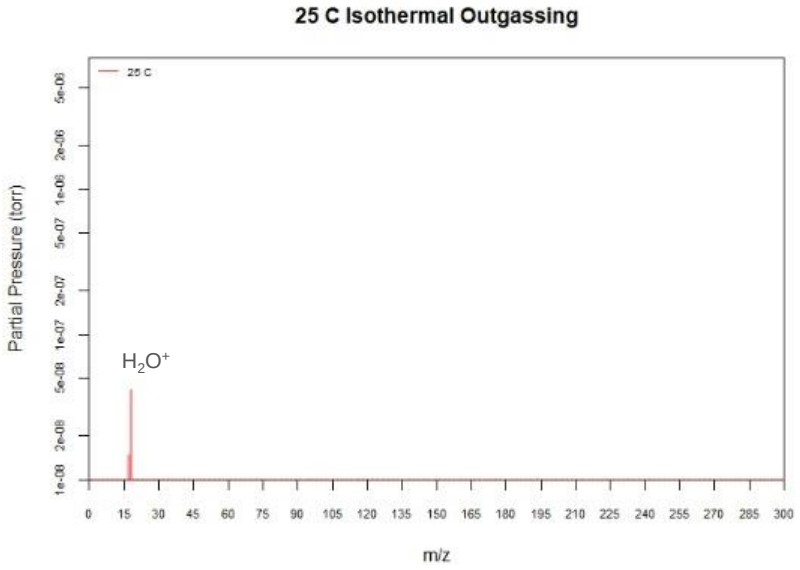



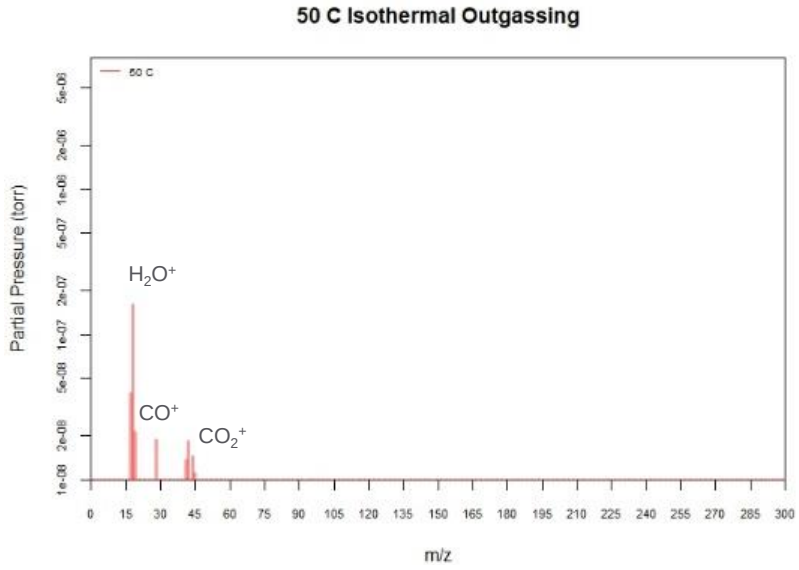
# Sample Preparation

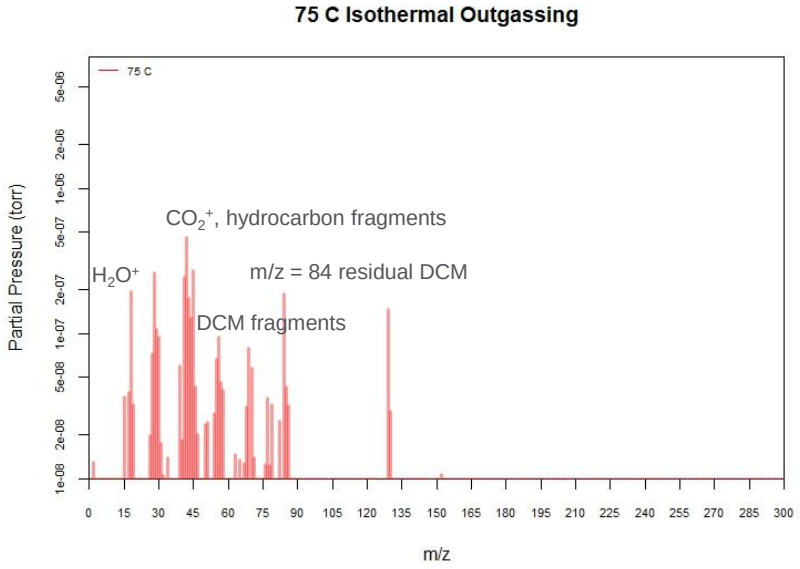
- Poly(methyl methacrylate) (PMMA, 99%, average $M_w$ = 120 kDa) and Irgacure 907 (98%) were obtained from Sigma-Aldrich and used without further purification.
- 0.5% PMMA was dissolved in analytical grade dichloromethane at room temperature. Equal weight percent IG907 was separately dissolved in equal volume of dichloromethane at room temperature.
- 25 ml of each solution was then mixed in a third container to form a 1:1 mixed PMMA/IG907 solution.
- 1x1 cm Si (100) wafer fragments were immersed in the mixed solution to form a PMMA-IG907 photoresist formulation film.

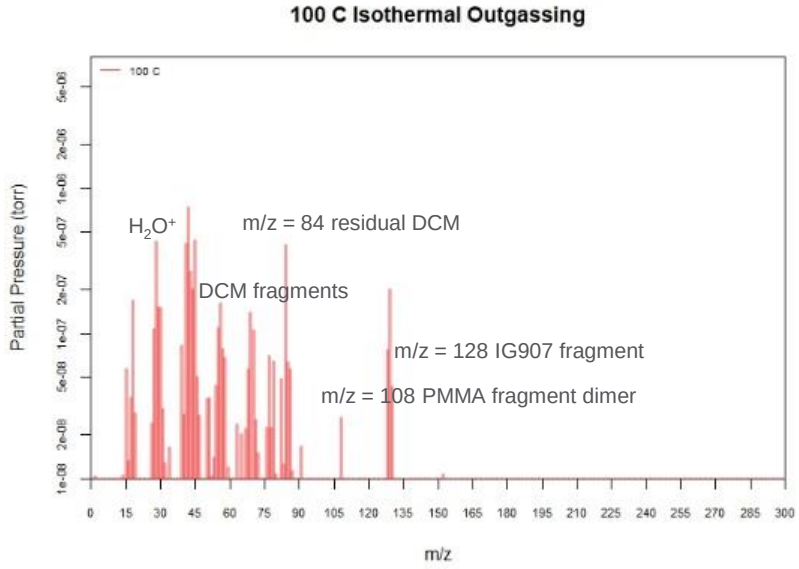


# Results: RGA/TDS



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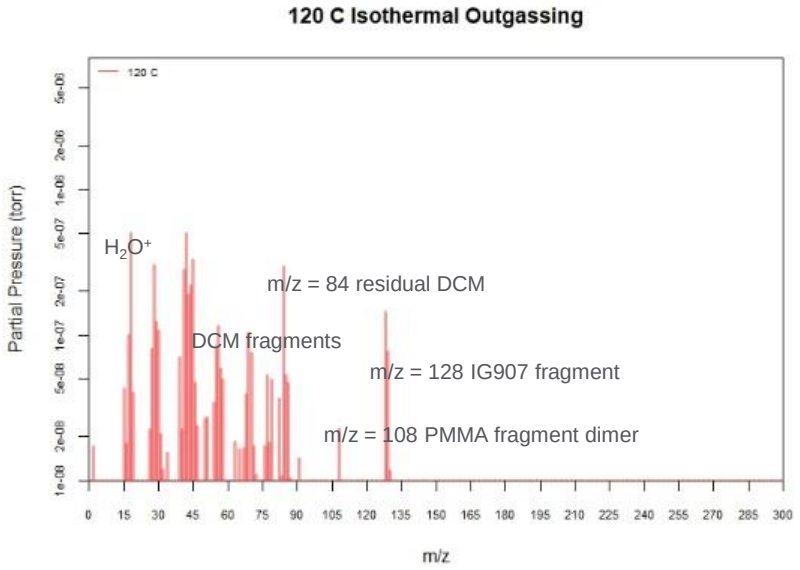
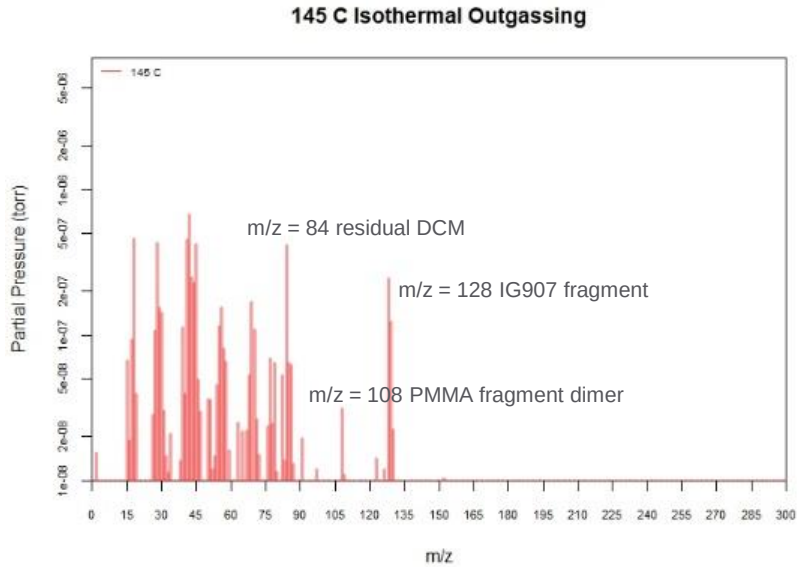
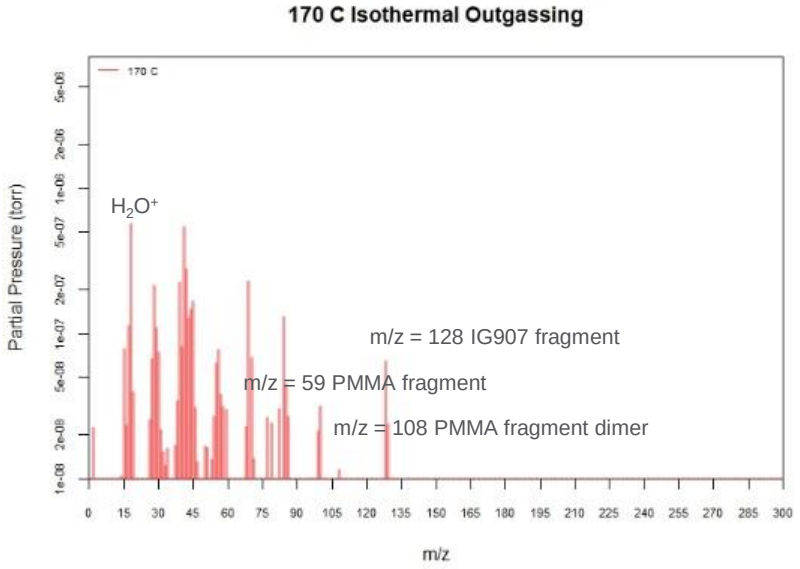
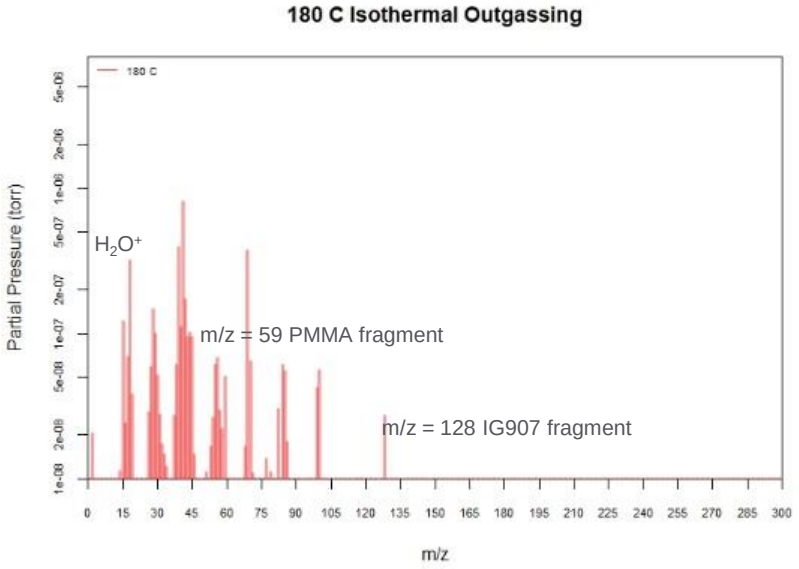


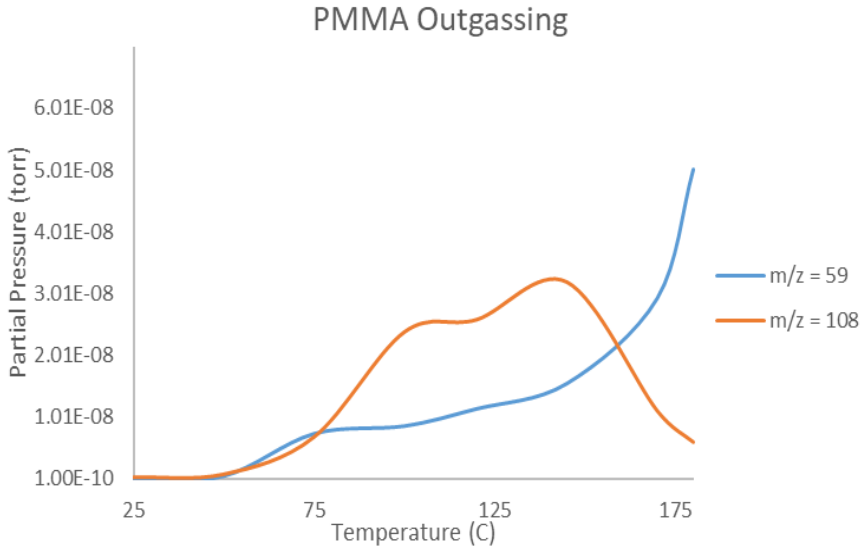



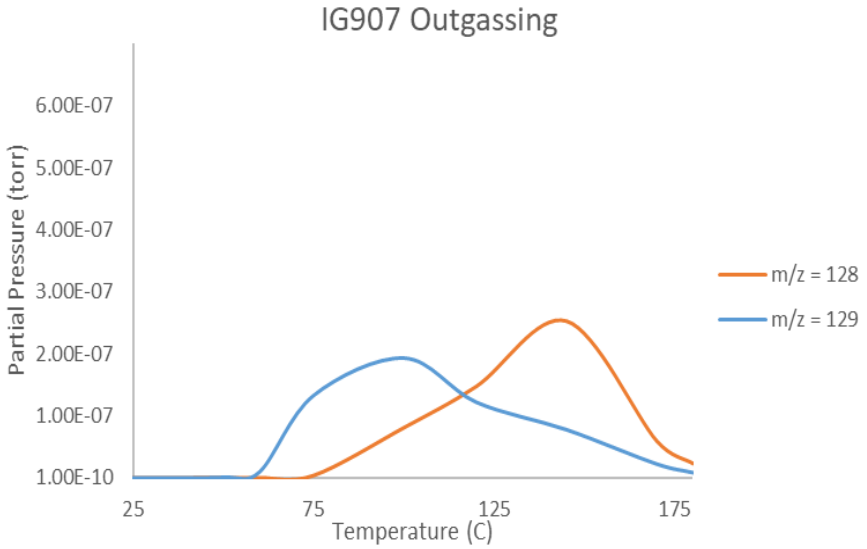



# Results: RGA/TDS

- PMMA decomposition begins as low as 75°C
  - Decomposition starts dominated by sidechain dimer outgassing
  - At high temperatures (>160°C) outgassing dominated by monomer
  - Monomer outgassing continues to increase with temperature while dimer outgassing declines

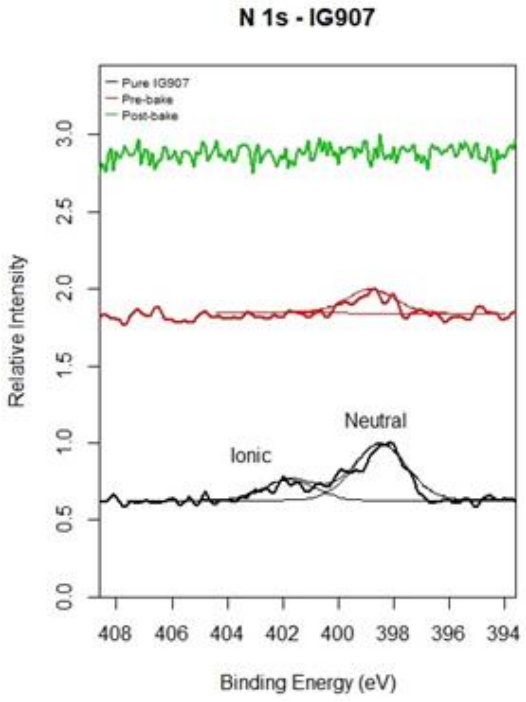


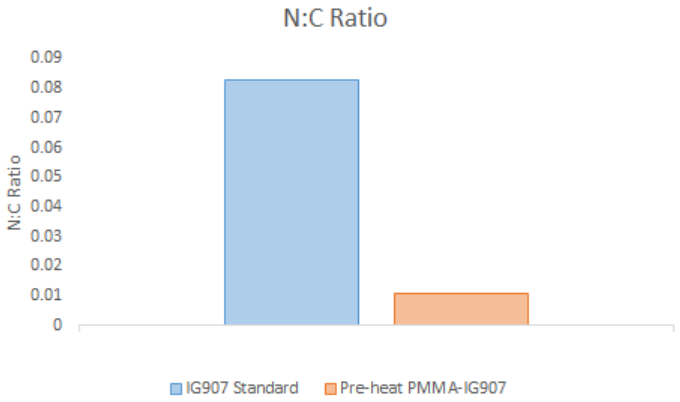

- IG907 outgassing began at 75°C and peaked at ~140°C
  - IG907 is a tertiary amine and may form stable salt with addition of water in ambient atmosphere
  - Loss of hydrated salt form and conversion to neutral form at high temperature



# Results: XPS

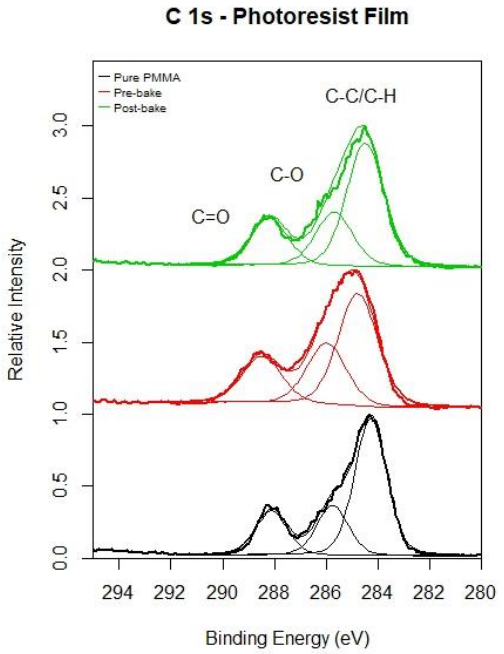
- XPS detects surface chemistry
  - N:S ratio in IG907 maintained at 1:1 for both pre-heat and post-heated films
  - No thermal decomposition
- IG907 highly diluted at surface of PMMA formulation
  - N:C ratio of the PMMA-IG907 mixture is 7x lower than N:C ratio of IG907
  - After vacuum heating, IG907 is completely removed from mixture
- N 1s spectra differentiates between basic and neutral forms of IG907
  - Pure IG907 is in a mixed neutral and ionic form
  - After processing into a mixed PMMA-IG907 film, IG907 is in neutral form
  - Ionic form outgasses first from RGA

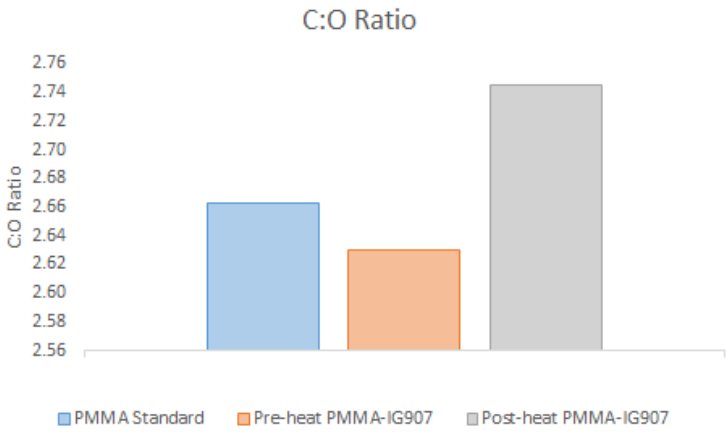


# Results: XPS

- PMMA/IG907 films are visually smooth and free of macroscopic porosity
  - Unaffected by thermal processing
  - No Si signal observed
- Post-heating films show signs of thermal degradation near melting point
  - C:O ratio in PMMA-IG907 increases after heating, consistent with side chain loss
  - C 1s spectra shows little compositional change before and after heating



# Conclusions

- Room temperature outgassing measurements may not accurately represent process conditions
  - Outgassing easily detected using mass spectrometry but only at elevated temperatures
  - No outgassing at room temperature – current standardized tests insufficient for detection of real outgassing during processing!
  - Complete loss of photoinitiator with only slight polymer degradation
- Alternative reaction paths of photoresist formulation components are important to consider
  - Hydration and moisture uptake during processing creates new acid/base chemistry
  - Different volatility of ionic and neutral forms
  - Implications for resist formulations to ensure correct function and reduce outgassing
- **Complex surface and gas phase chemistry occurs during any real process!**

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- Volatile organic contaminants can foul EUV optics.
  - A common source of organic outgassing is the photoresist. Due to their high absorptivity in the EUV, component heating is likely to occur, resulting in thermal outgassing (*Proc. SPIE*, Vol. 8322, 83222X, 2012)
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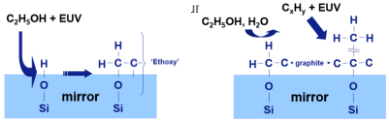


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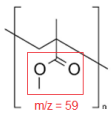
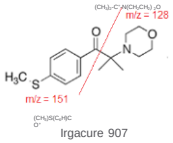
  - Frequently used to demonstrate ultimate resolution in lithography research
- IG907 is a commonly used organic UV photoinitiator with high solubility in common solvents
- Mixture of PMMA/IG907 as a model photoresist formulation to investigate thermal outgassing of small molecule photoinitiators in polymer matrix
  - X-ray photoelectron spectroscopy (XPS) and residual gas analysis/thermal desorption spectroscopy (RGA/TDS) measures surface chemistry changes




PMMA




Irgacure 907

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- 25 ml of each solution was mixed in a third container to form a 1:1 mixed PMMA/IG907 solution.
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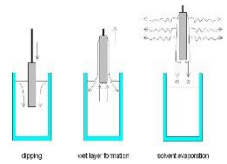
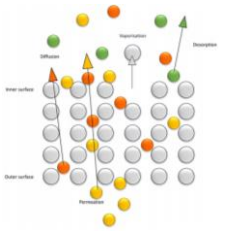
- Samples heated in vacuum chamber for thermal outgassing



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  - Ejects core electrons with elemental-unique binding energy
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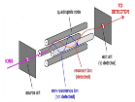
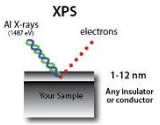
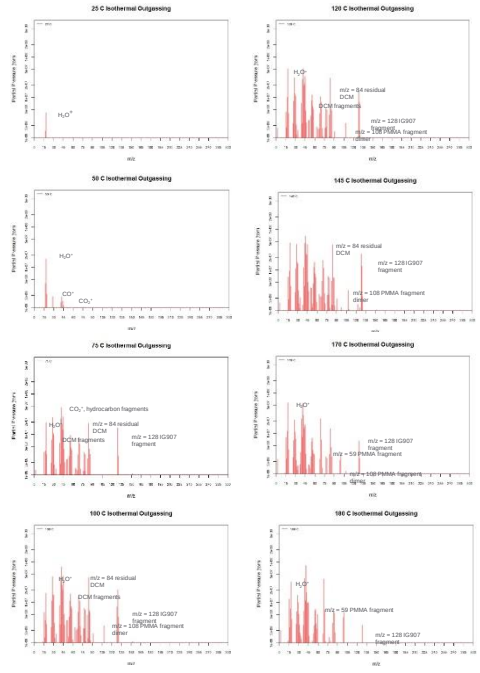
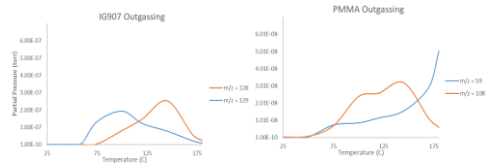
  - XPS produces information about the sample surface including:
    - Ratio of IG907:PMMA on surface
    - Pre/post-heating surface chemistry
- Residual gas analyzers (RGA) measures the vacuum outgassing of solid materials
  - Quadrupole mass spectrometry in UHV
  - Electron impact ionization
- TDS uses temperature to separate gases for RGA mass spectrometry analysis
  - Desorption temperature depends on **chemical** forces between gas molecule and substrate
  - RGA/TDS used to identify IG907 and PMMA outgassing product partial pressure as a function of temperature






## Results

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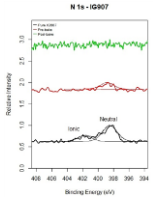


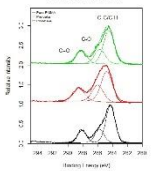



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  - Hydration and moisture uptake during processing creates new acid/base chemistry
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