Effect of Substrate Temperature for Plasma-Enhanced Chemical Vapor Deposition of Poly(methylmethacrylate) as a Sacrificial Material for Air Gap Fabrication

NSF/SRC ERB for Environmentally Benign Semiconductor Manufacturing

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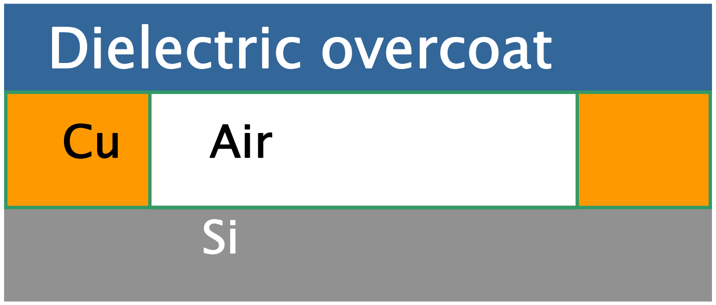
Thrust A2: Solventless Low-k Dielectrics

- **Why investigate air gaps?**
  - **Dense solutions are approaching the limit for OSG materials**
  - **Integration of porous materials is an integration nightmare**
  - **Leap forward in performance increase as opposed to incremental improvements that face difficult challenges**
- **Semiconductor International – January 1, 2005**

  Senior Editor, Laura Peters
  - ***Argues for air gaps as a low-k alternative needed at this time***
  - ***“Porous dielectrics have too many problems — at least as many as their dense counterparts — and the overall benefit they deliver, represented as the effective k value, may be small given the integration, yield and reliability challenges they pose and the costs required to surmount them.”***

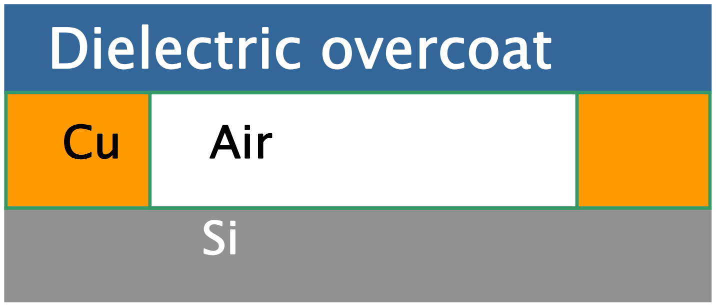
Why Air Gaps: Low-κ Solution

- **Air has lowest dielectric constant**
  - Faster Integrated Circuits
  - Decrease power consumption
  - Reduce cross-talk
  - Leads to fewer levels of interconnect
- **Air has lowest refractive index**
  - Use in optical filters/reflectors/refractors
- **Closed cavity air gap**
  - Additional applications in microfluidic devices



Anatomy of an Air Gap

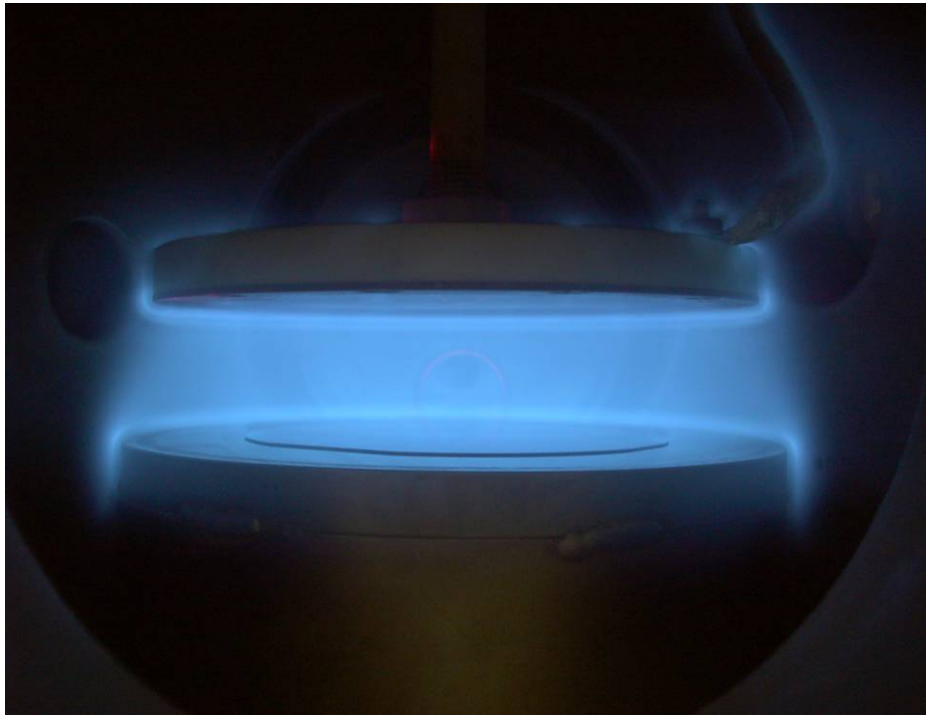
- Overlying Dielectric
  - Organosilicate Glass (OSG)
  - Remains as bridge layer
- Metal Lines and Barrier Layers
- Sacrificial Material
  - Poly(methylmethacrylate) (PMMA)
  - Cleanly removed to form air gap

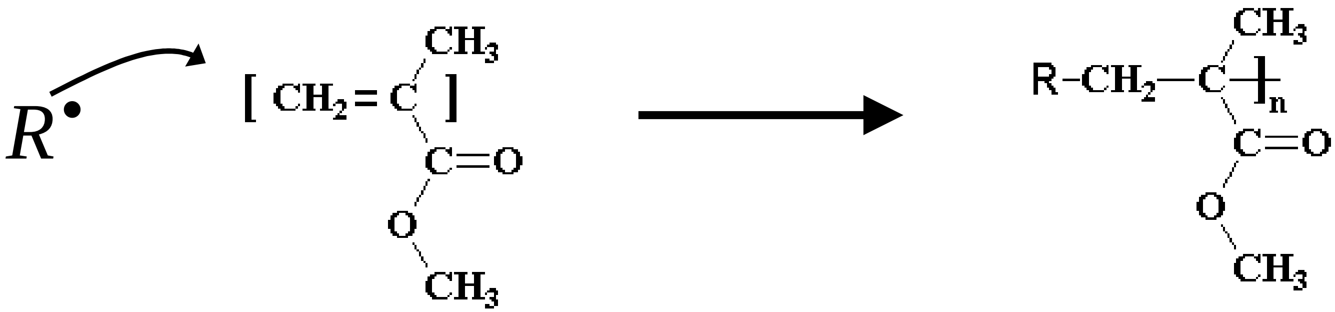


Criteria for Sacrificial Materials

- Ease of synthesis
- Decomposition in the absence of oxygen
- Desirable temperature range for decomposition
- Short decomposition time (small degradation fragments)
- Negligible residue
- Does not affect ILD and metal during deposition and removal
- Ability to be patterned
- Good mechanical properties & adhesion
- Survives aqueous and solution rinses

PECVD of Poly(methyl methacrylate) (PMMA)

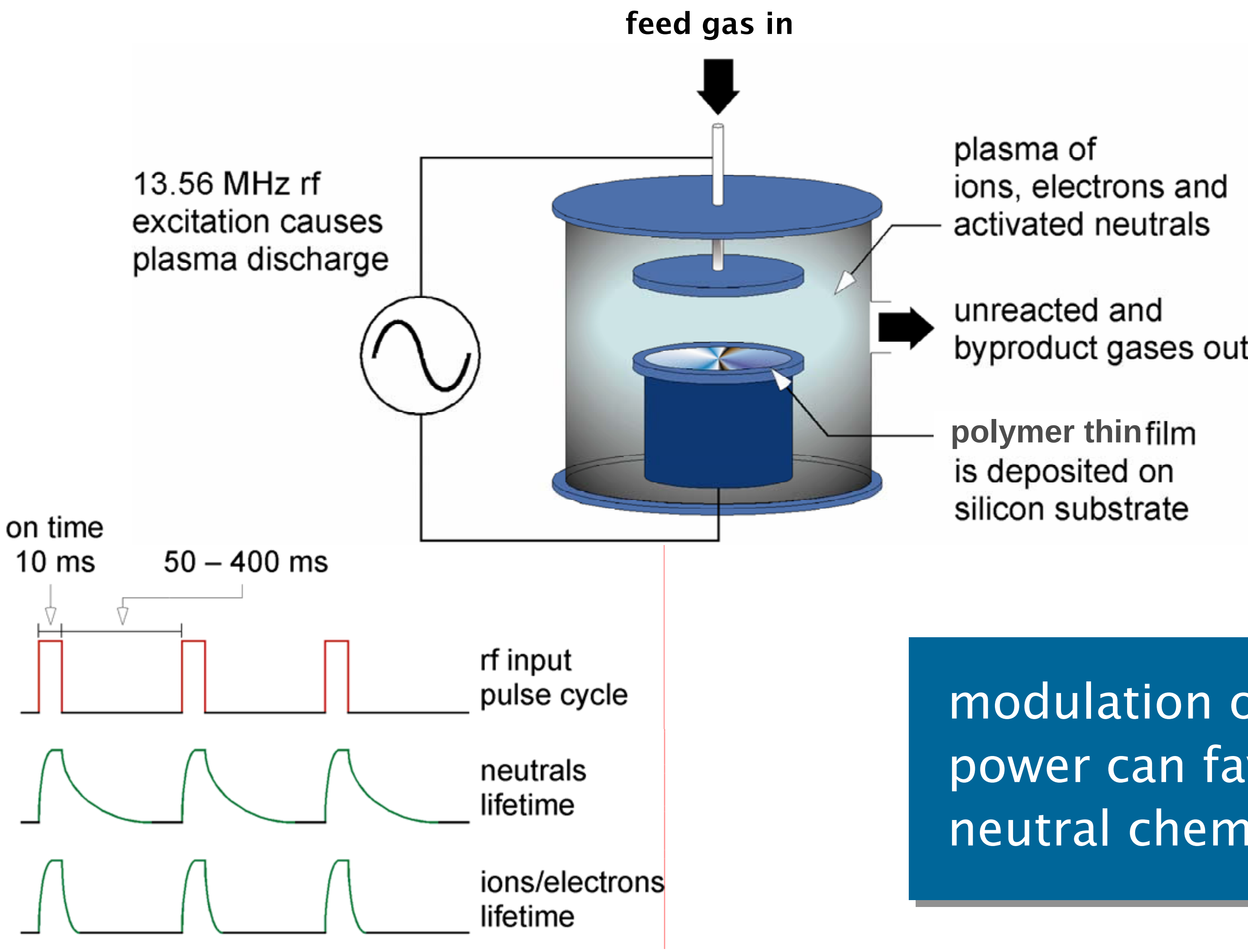




MMA

Free radical polymerization of MMA gas to form PMMA solid

Pulsed Plasma-Enhanced CVD (PPECVD)

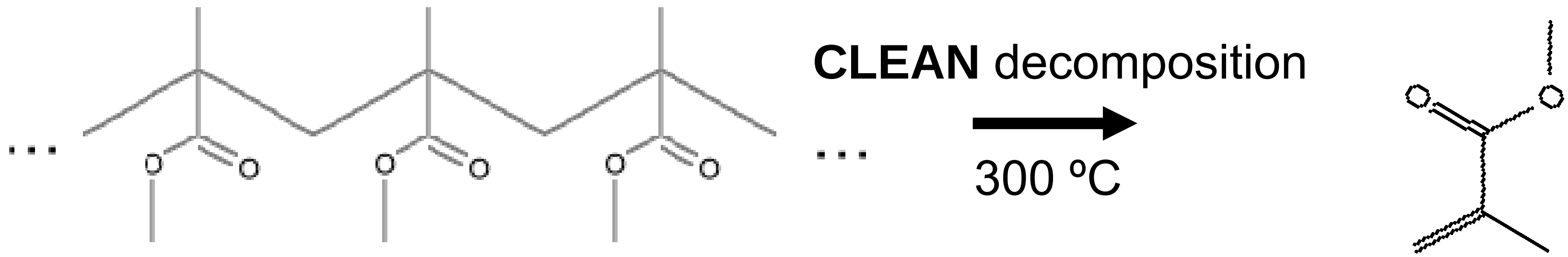


modulation of power can favor neutral chemistry

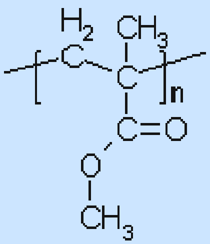
Process variables

- Substrate T: 50 to 130°C
- Power conditions: 10W CW *v.* 100W 10/90 Pulsed
- Pressure: 0.5 to 3 Torr

Poly(methyl methacrylate) (PMMA)



PMMA



Methyl Methacrylate

$CH_2{=}C(CH_3)COOCH_3$

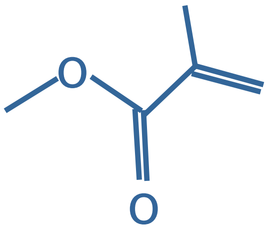
Bulk PMMA is insoluble in water and IPA at room temperature.

As a bulk polymer, PMMA is known for it outstanding mechanical properties.

Applications

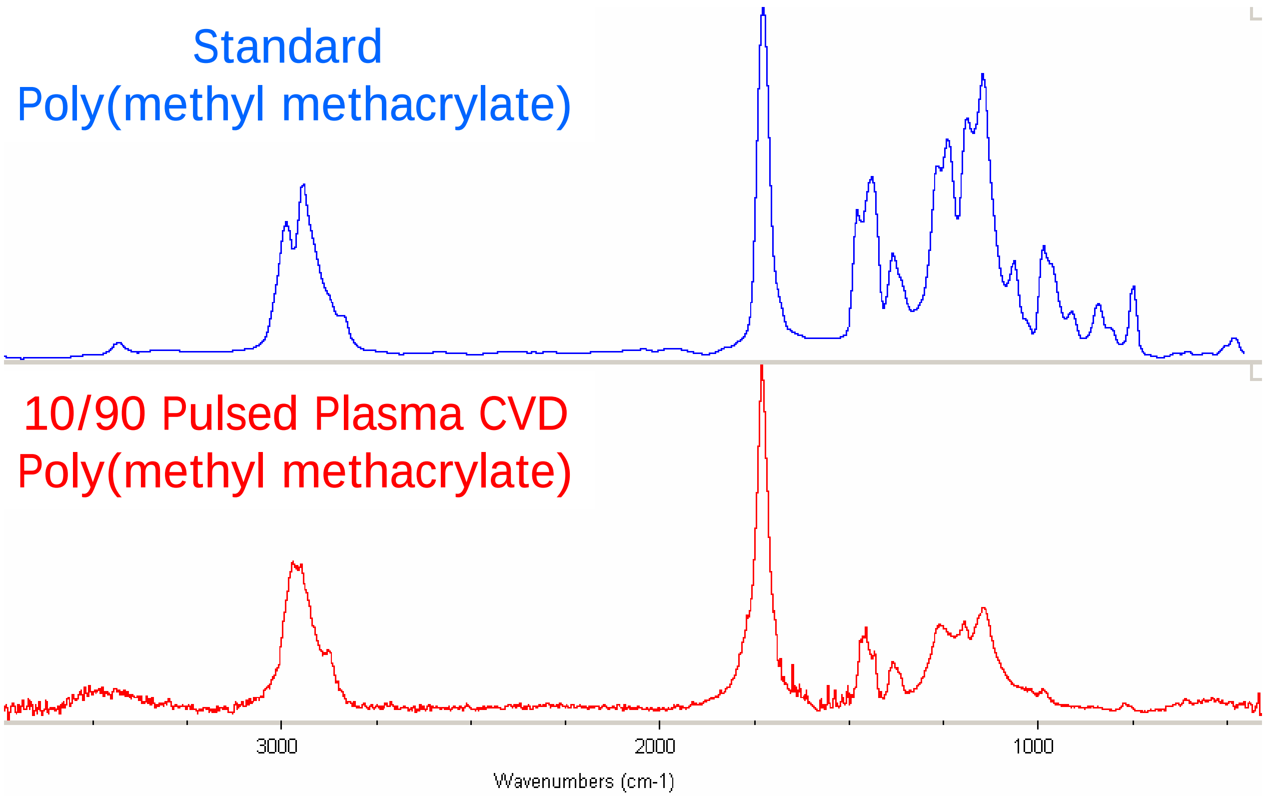
- Used in orthopedic surgery
  - Fix prosthetic components
  - Bone graft template
  - Femoral window plug in total hip replacement
- Used in various plastics, floor polish, glues, and packaging

PMMA Deposition and Characterization

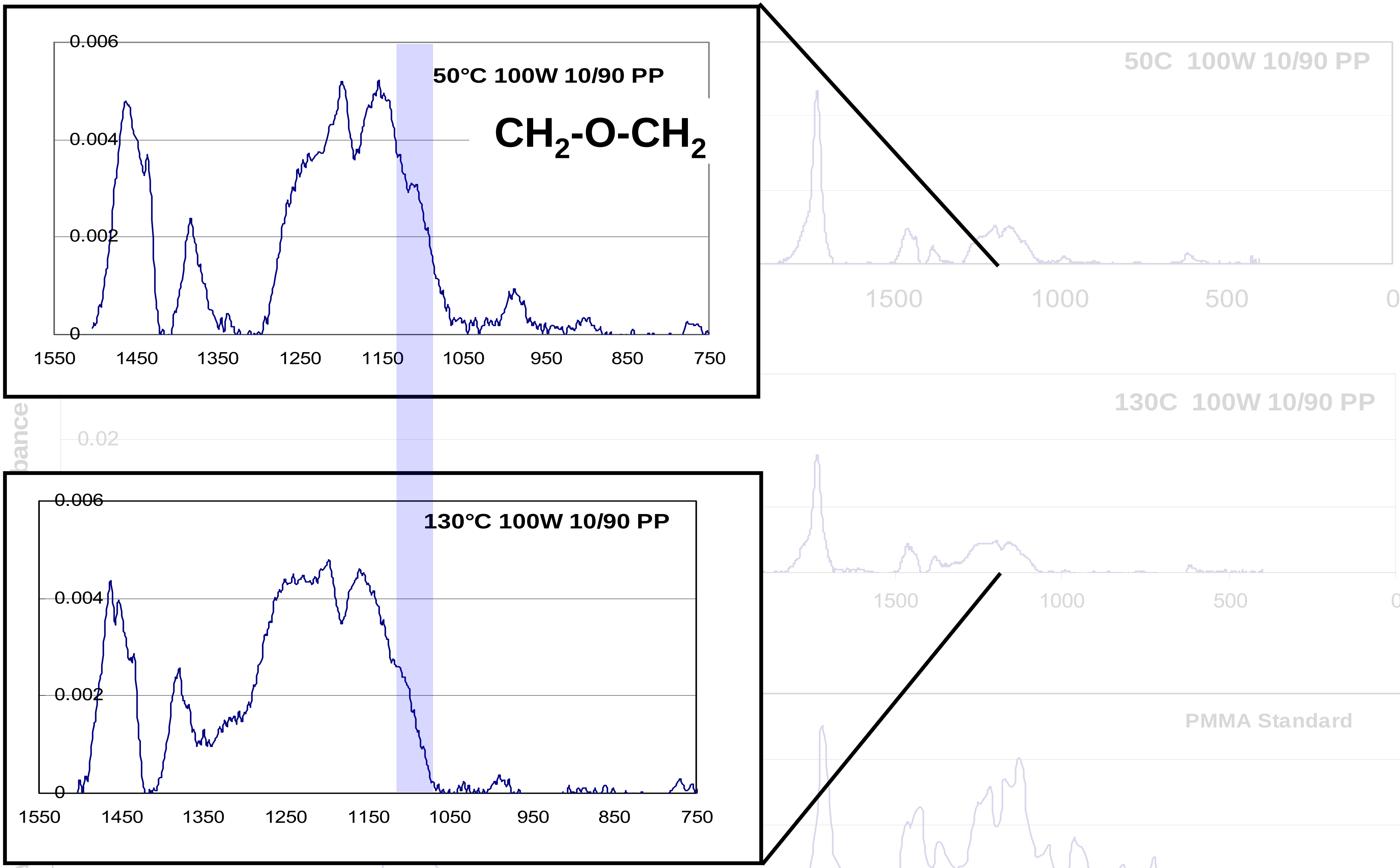


Methyl Methacrylate

- Polymerizes via vinyl bond to Poly(methyl methacrylate) (PMMA)
- Low duty cycle PPECVD retains much of PMMA funcitonality
- Thermally decomposes in the absence of oxygen to monomer form below 350°C

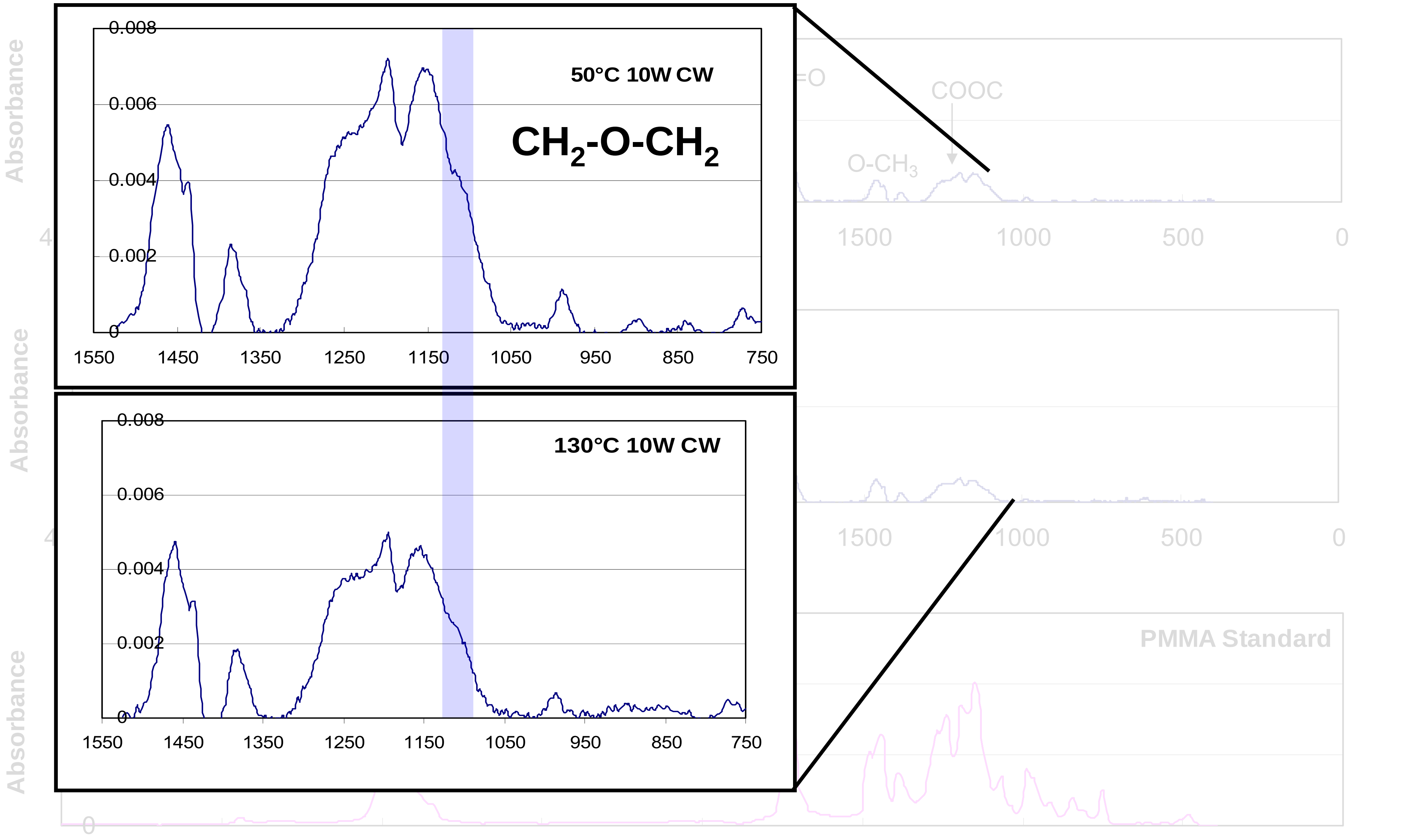


FTIR of Pulsed PECVD PMMA – 100W 10/90



Increased substrate temperature decreases oxygen incorporation into polymer backbone
Improves the thermal stability requiring a higher temperature for onset of decomposition

FTIR of PECVD PMMA – 10W Continuous Plasma



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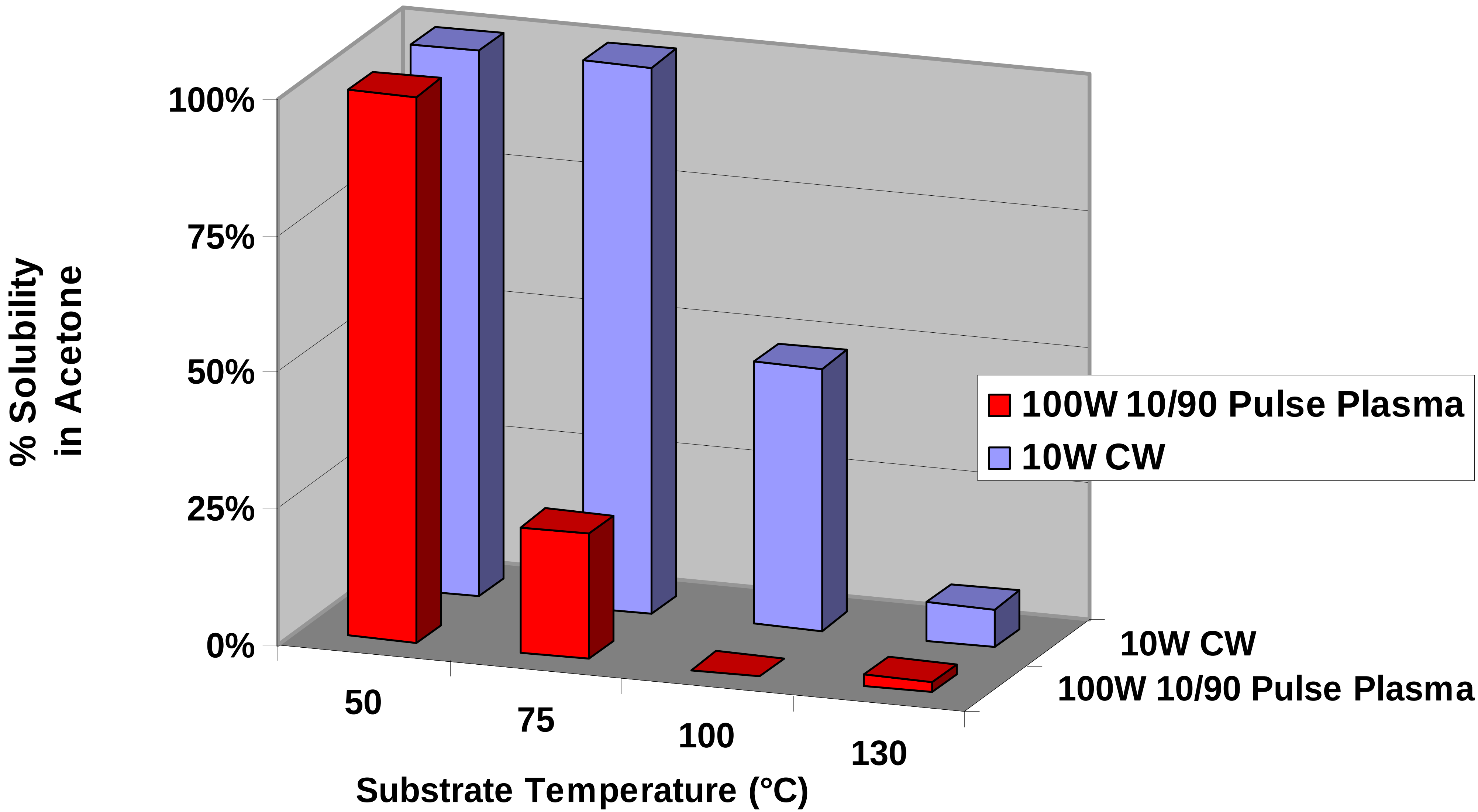
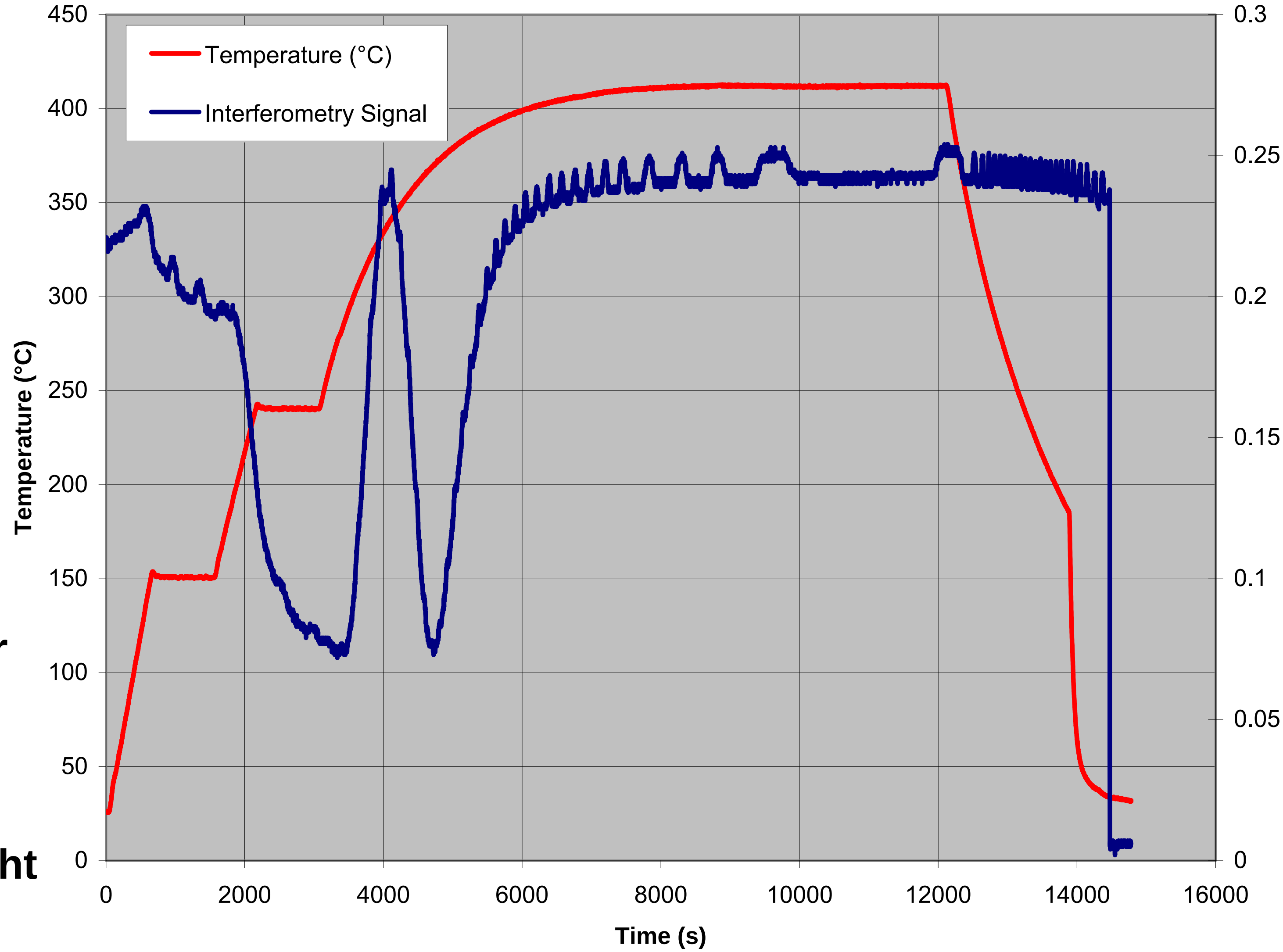
Solubility in Acetone *v*. Substrate Temperature



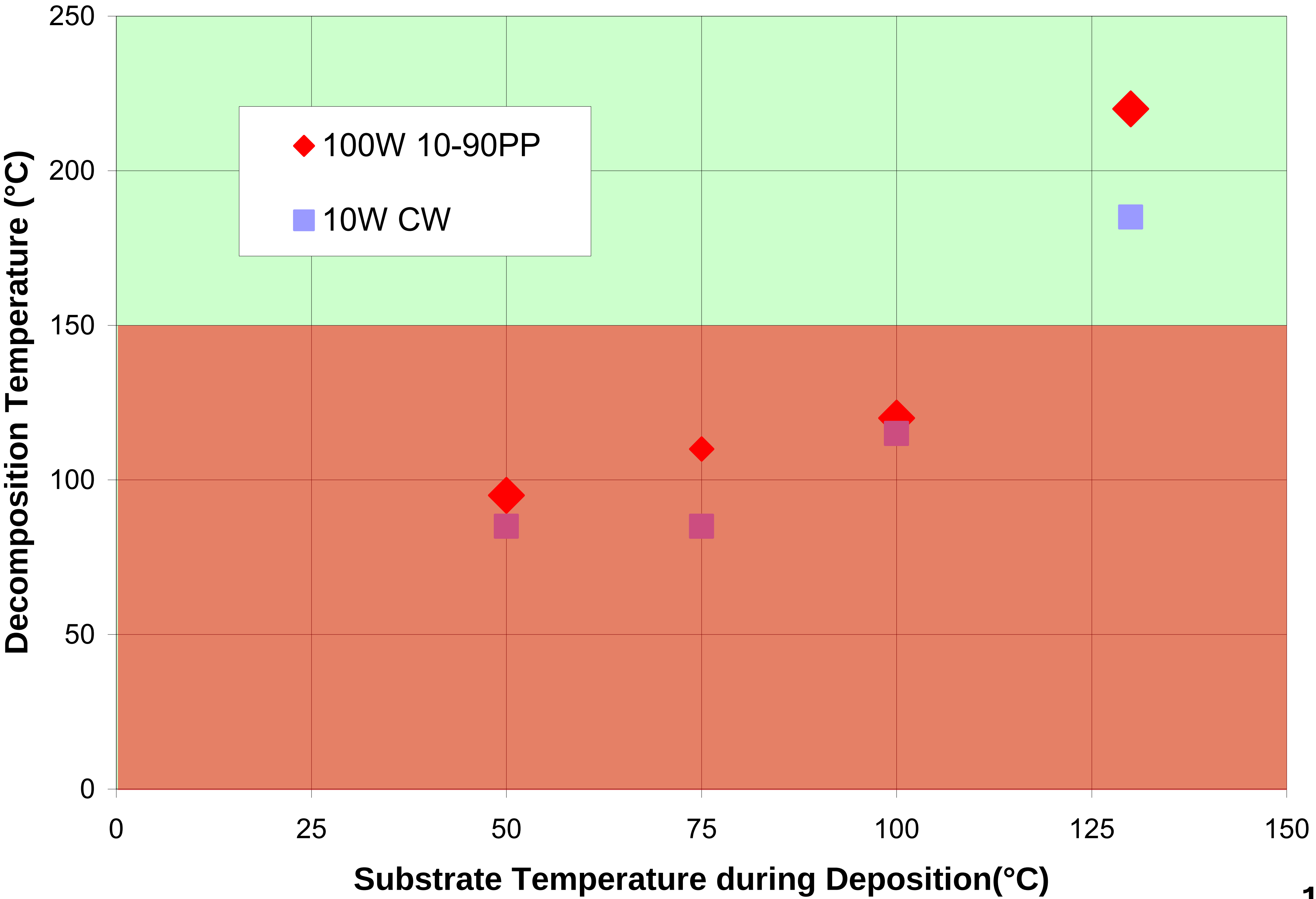
Interferometry for Thermal Stability (ITS)

- Nitrogen purged annealing chamber
- Ramp to 150°C
- Hold for 30 min
- Ramp to 240°C
- Hold for 30 min
- Ramp to 410°C
- Hold for 1 hour
- Cool

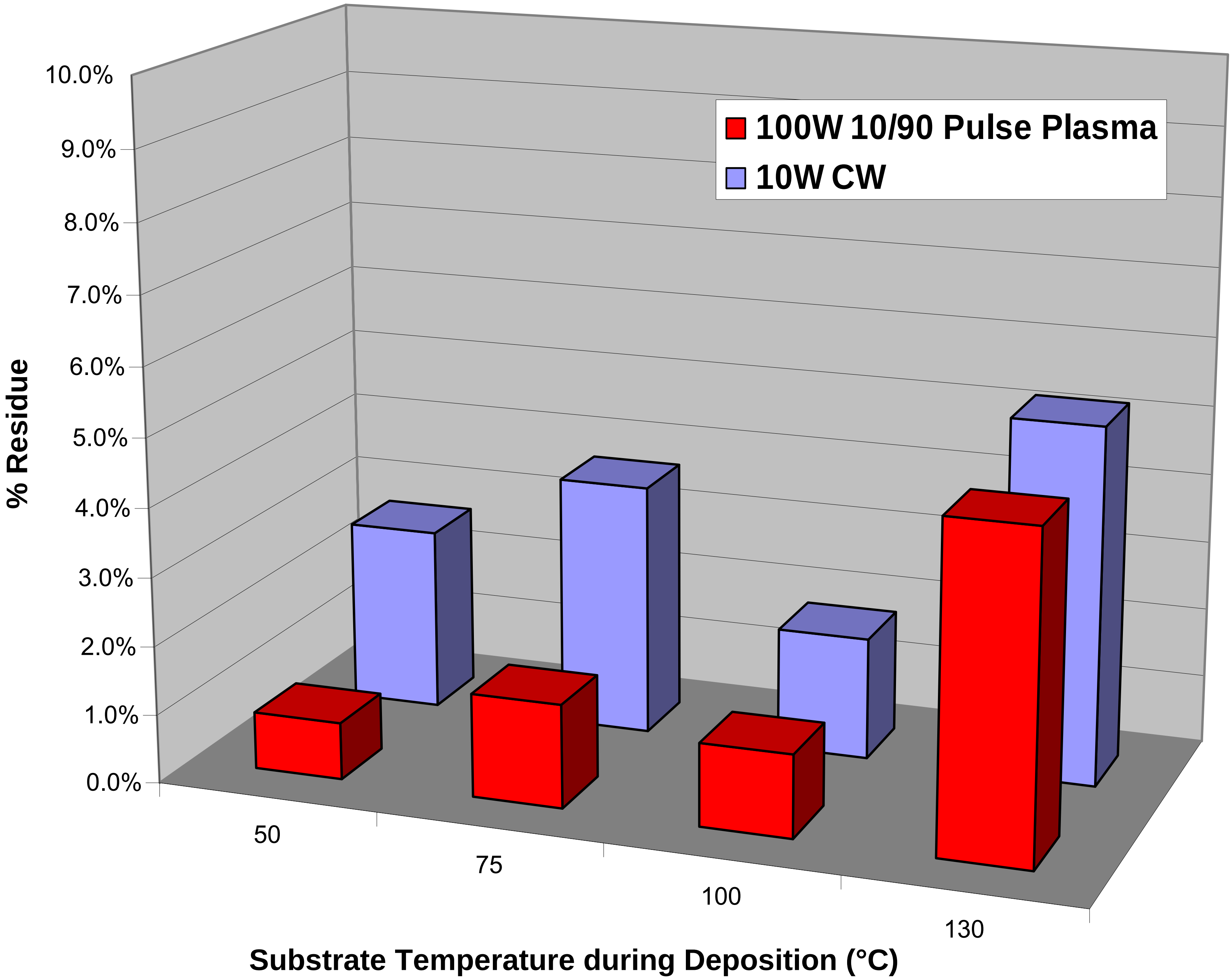


- Example ITS scan for 10W CW sample deposited at 100°C
  - Film swelling
  - Low molecular weight and weak bond breaking
  - Macro decomposition

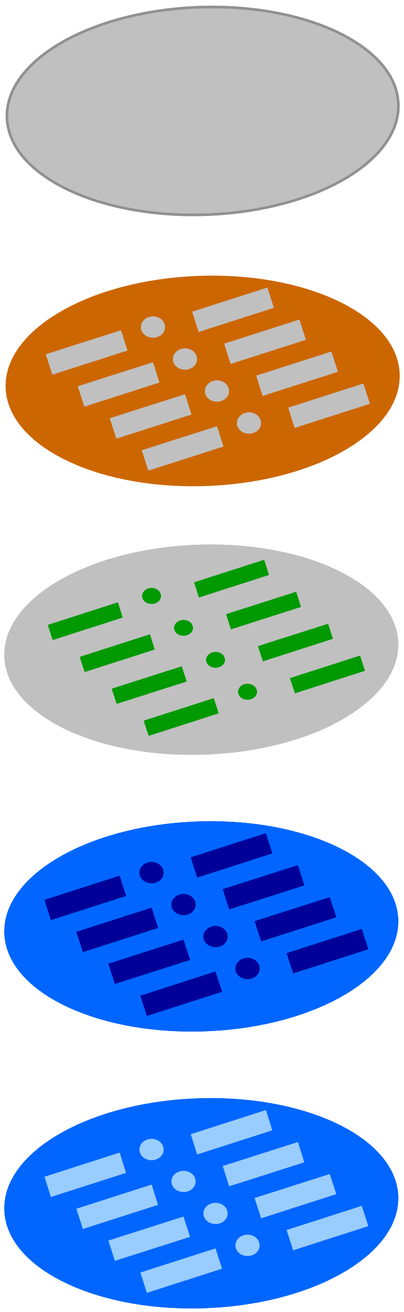
Onset of Thermal Decomposition *v.* Substrate Temperature



Residue after ITS anneal ramp to 410°C



Fabrication of Enclosed Void utilizing PMMA



Si Wafer

↓

Cover with contact mask

↓

Selectively deposit PMMA

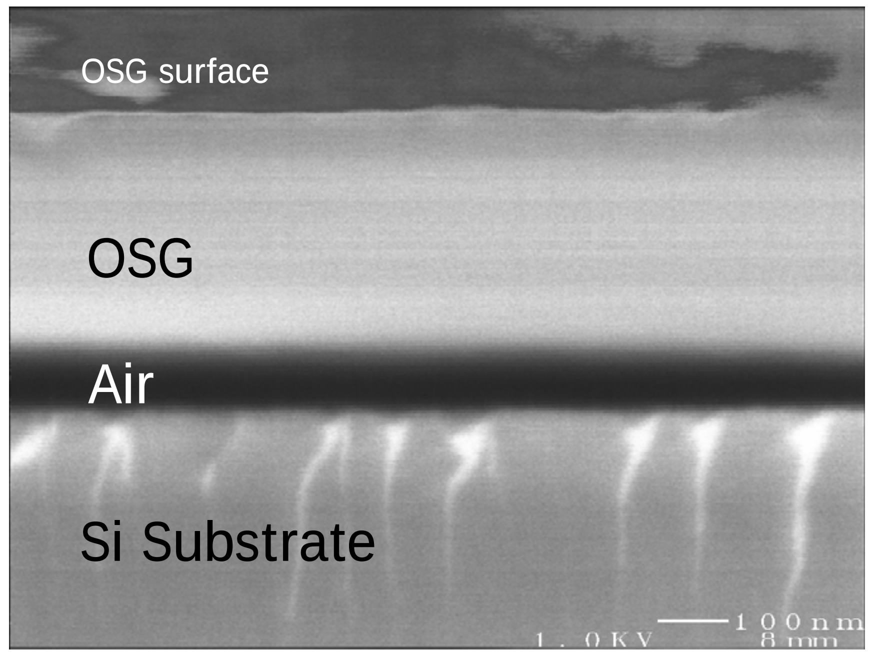
↓

Deposit OSG blanket film

↓

Anneal to remove PMMA creating air gap

- **Proof of Concept**
  - **Large scale features created by depositing sacrificial layer using a contact mask**



SEM of Air Gap from PMMA
~4000Å OSG deposited over ~1000Å PMMA
Anneal at 350°C creates ~1000Å Air Gap

Microscale Air-Gap Fabrication

No Hard Mask Required

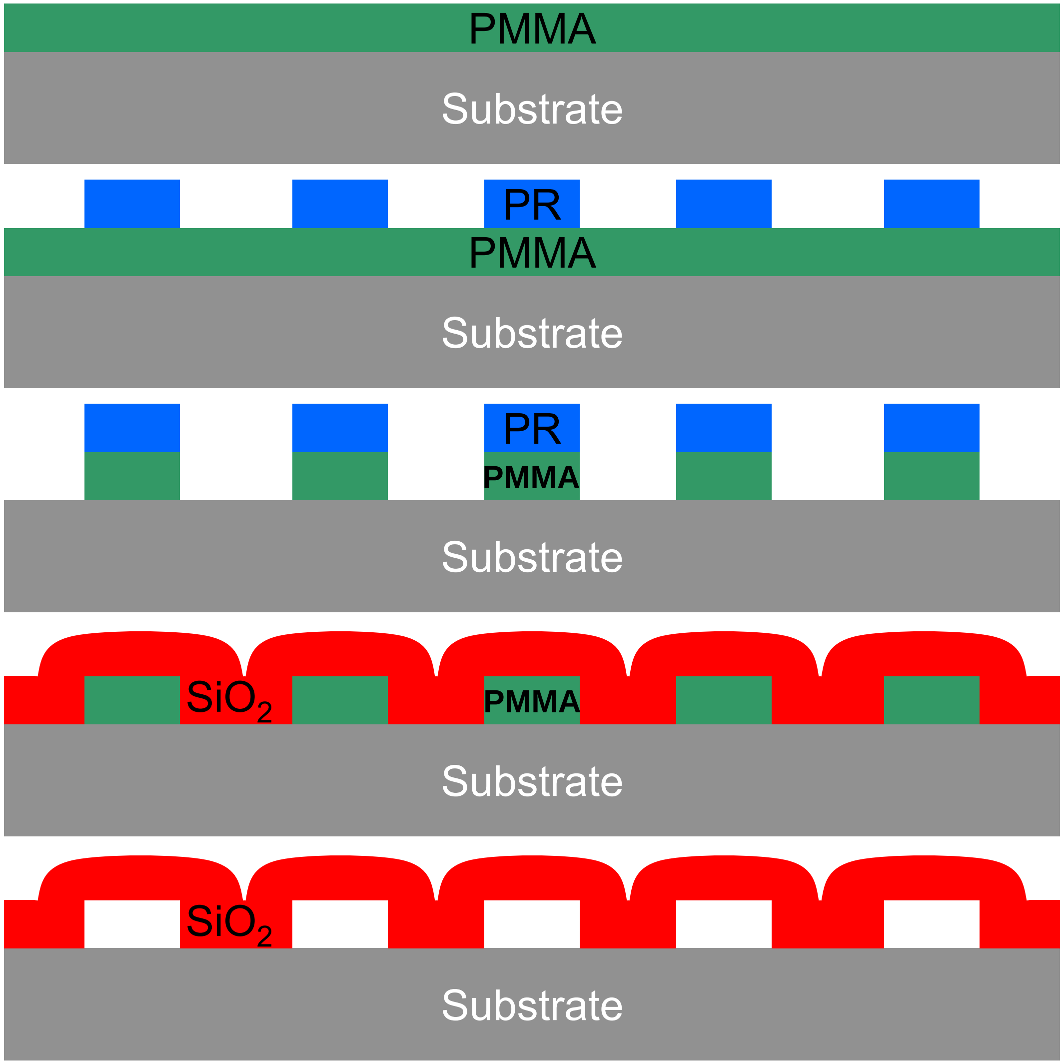
PMMA Deposition

Photolithography

O_2 Plasma Etching of PMMA

Photoresist Acetone Strip
SiO_2 Deposition

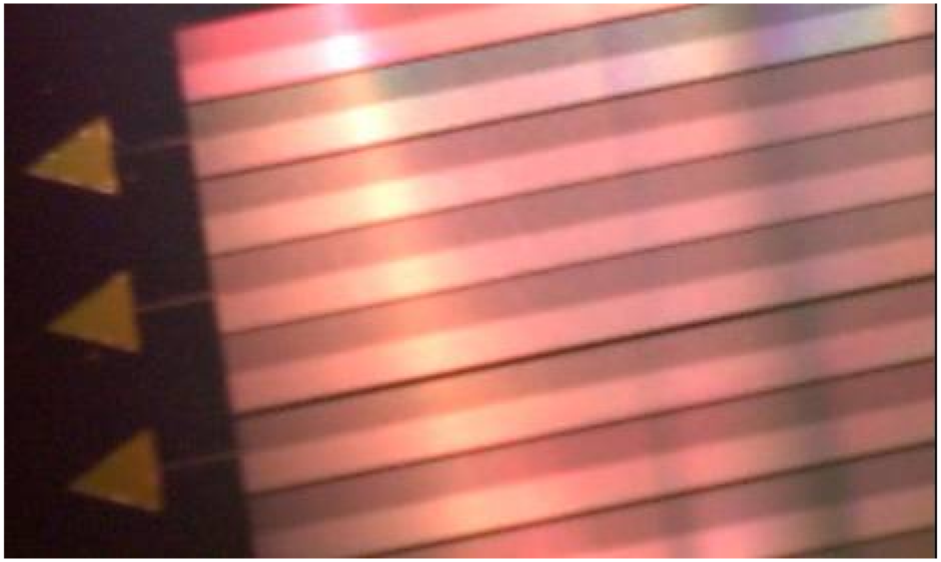
PMMA Decomposition



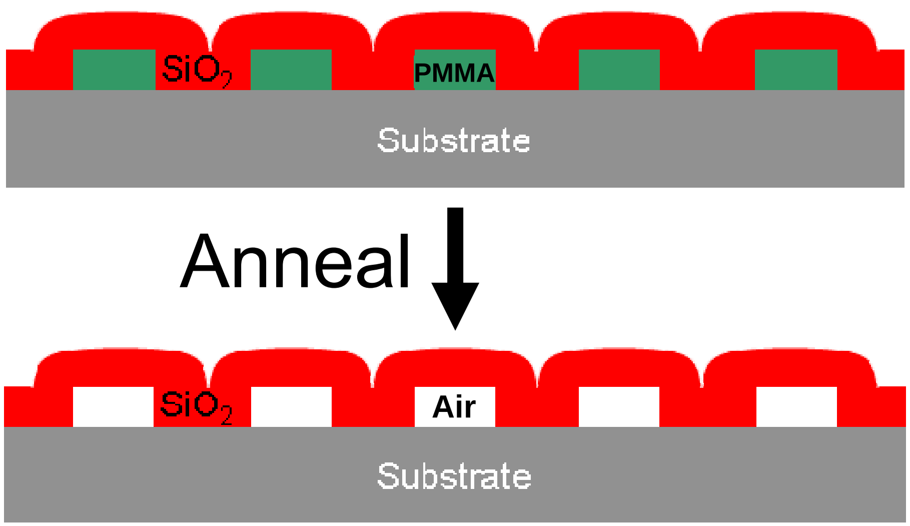
Etch Selectivity PMMA/PR ≥ 2

Fabrication of Enclosed Void

Air-Gap Microchannels



Width: 1 – 10 μm



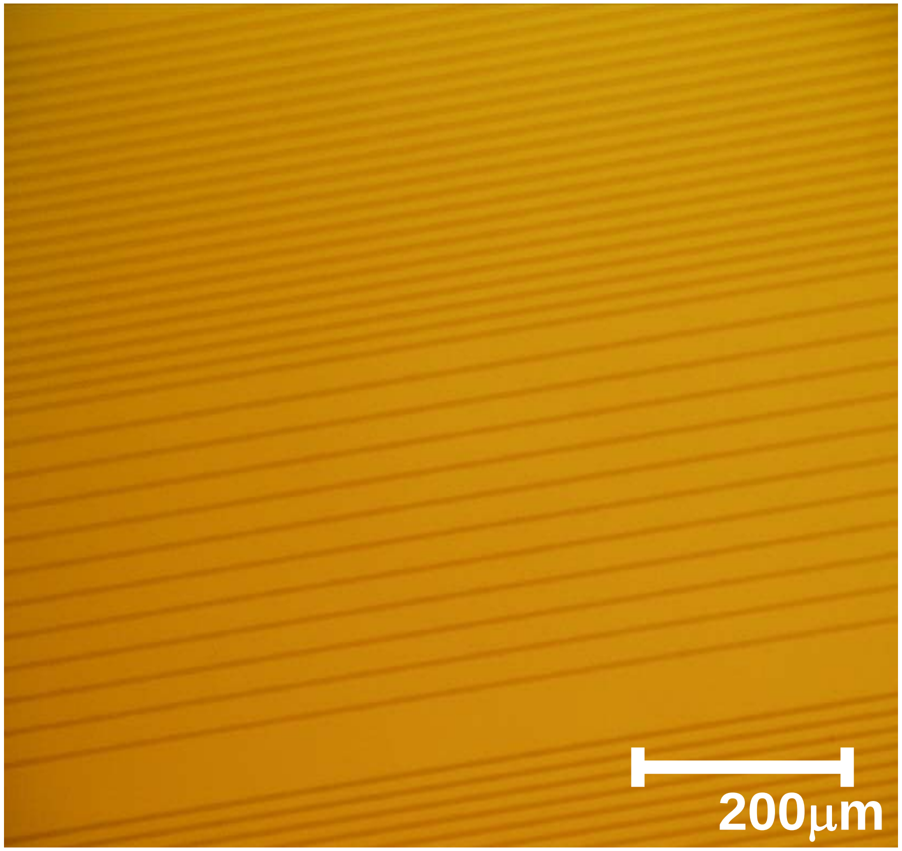
Decomposition Profile

1. Quick ramp to 150°C
2. Hold for 10 min
3. 150 – 250°C: 5°C/min
4. Hold for 30 min
5. 250 – 300°C: 1°C/min
6. Hold for 30 min

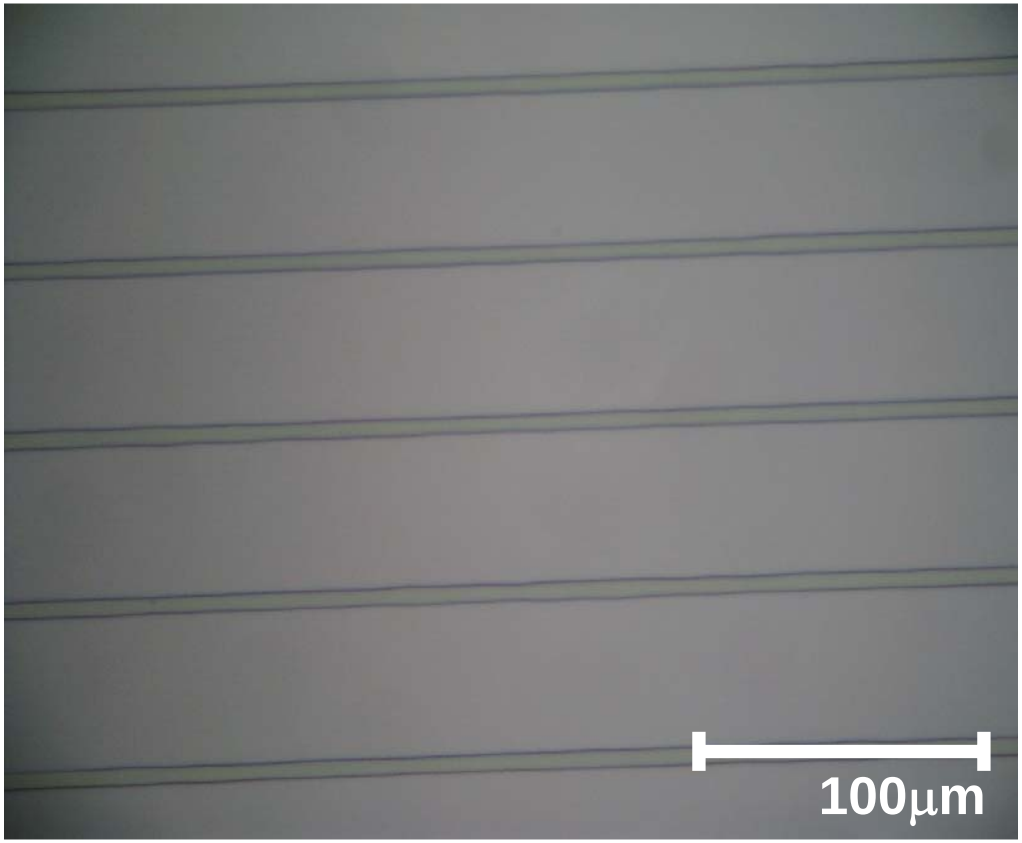
Total Time: 140 min

Ambient: 1 atm (Air or N_2)

Top Down Optical Micrographs



200X – Spin Coated Resist over PMMA

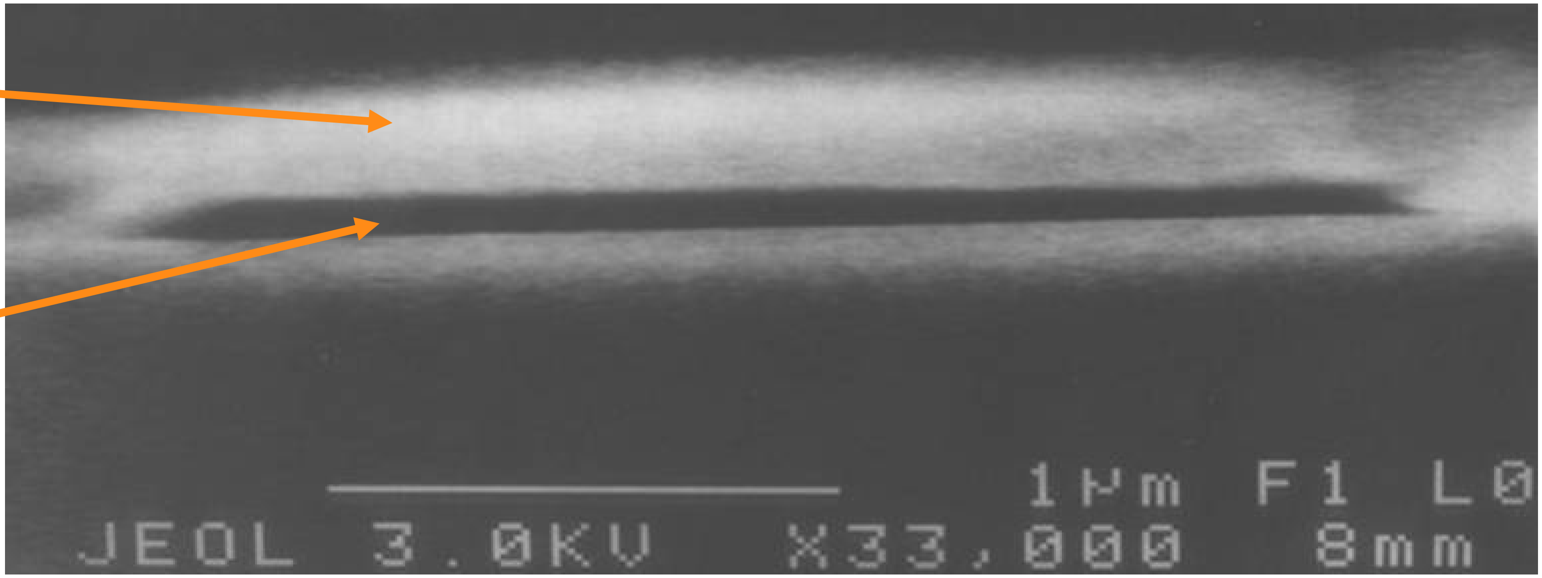


500X – OSG over patterned PMMA

Cross-Sectional SEM

3000 Å SiO_2

1000 Å Void



3000 Å SiO_2

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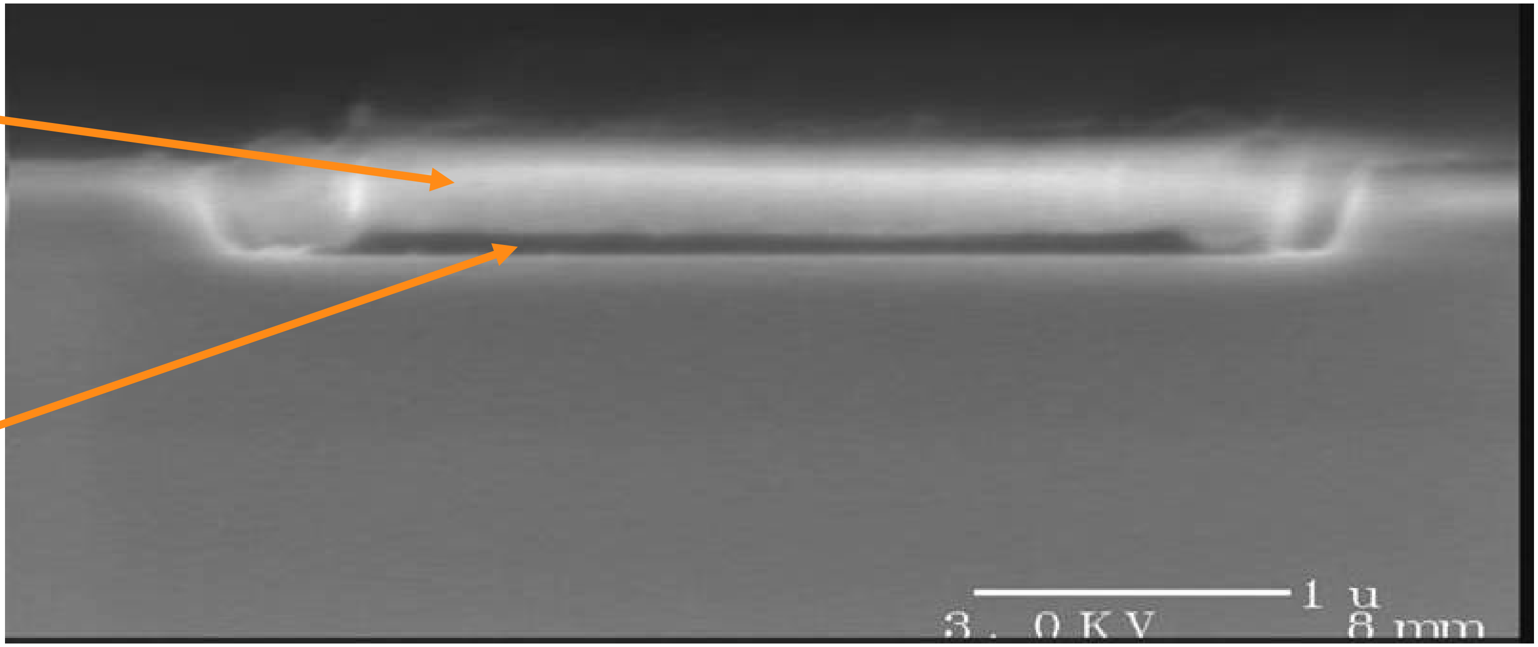

PMMA – Summary and Key Findings

- Low power PECVD is a viable method for depositing PMMA
  - FT-IR confirms structural similarity to bulk PMMA
- PECVD PMMA has the desired properties
  - Decomposes at 230 to 350 °C
  - Negligible residue
- Closed-cavity air-gap microstructures successfully fabricated using conventional photolithographic and deposition tools
- Solubility of PMMA in acetone and isopropyl alcohol is inversely proportional to both the deposition power and substrate temperature
- Films deposited at lower temperatures contain CH_2-O-CH_2 linkages in the polymer backbone decreasing its thermal stability
- Onset of thermal decomposition increases with increased deposition temperature

Plan for Future Work

- Collaborate with Thrust D
- Create Air-Gaps at the nanometer level
  - Low-power CW PMMA (complete removal)
  - Direct pattern at Scanning Electron Beam Lithography (SEBL) Facility
  - Cut wafer with Focused Ion Beam (FIB) and image with SEM

Acknowledgements

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