NANO™ PMMA and Copolymer

PMMA (polymethyl methacrylate) is a versatile polymeric material that is well suited for many imaging and non-imaging microelectronic applications. PMMA is most commonly used as a high resolution positive resist for direct write e-beam as well as x-ray and deep UV microlithographic processes. PMMA is also used as a protective coating for wafer thinning, as a bonding adhesive and as a sacrificial layer.

Standard PMMA products cover a wide range of film thicknesses and are formulated with 495,000 & 950,000 molecular weight (MW) resins in either chlorobenzene or the safer solvent anisole. Custom MW products ranging from 50,000 - 2.2 million are available upon request. In addition, we offer copolymer (MMA (8.5) MAA) products formulated in the safer solvent ethyl lactate. All MCC PMMA and copolymer resists are available in package sizes from 500ml to 20 liters.

100nm gate profile imaged in 495K PMMA with 8.5 MAA Copolymer on top.

T-gate resulting from PMMA/Copolymer bilayer resist stack.
PROCESSING GUIDELINES

Substrate Preparation
The substrate should be clean and dry. Solvent, O₂ plasma, and O₃ cleans are commonly used and recommended.

Coat
MicroChem PMMA resists produce low defect coatings over a broad range of film thicknesses. The film thickness vs. spin-speed curves displayed in Fig. 1 through 8 provide the information required to select the appropriate PMMA dilution and spin speed needed to achieve the desired film thickness.

The recommended coating conditions are:
(1) Dispense: STATIC 5 - 8ml for a 150mm wafer
(2) Spread: DYNAMIC 500 rpm for 5 sec OR
   STATIC 0 rpm for 10 sec
(3) Spin: Ramp to final spin speed at a high acceleration rate and hold for a total of 45 seconds.

Pre Bake
PMMA
Hot plate: 180°C for 60 - 90 sec OR
Convection Oven: 170°C for 30 min

Copolymer
Hot plate: 150°C for 60 - 90 sec OR
Convection Oven: 140°C for 30 min
*Vacuum oven bake can also be used
Exposure
PMMA can be exposed with various parts of the electromagnetic spectrum.

e-beam: Dose - 50 - 500 μC/cm² depending on radiation source/equipment & developer used.

Energy - 20-50kV; higher kV for higher resolution, e.g. 50kV for 0.1mm images.

DUV (deep UV): Low sensitivity, requiring doses >500mJ/cm² at 248nm.

X-ray: Sensitivity of PMMA is low, ~1-2 J/cm² at 8.3 Å. The sensitivity increases at longer x-ray wavelengths. Features of <0.02μm can be fabricated.

Develop
PMMA and copolymer resists are compatible with immersion (21°C), spray puddle, and spray process modes. Process variables such as soft bake, exposure conditions, choice of resist and developer should be optimized to achieve desired results. For more process details see the PMMA and Copolymer DEVELOPER data sheet. Table 1 lists commonly used developers and their recommended usage.

NANO™ PMMA AND COPOLYMER DEVELOPERS ARE AVAILABLE IN THE FOLLOWING BLENDS

<table>
<thead>
<tr>
<th>PRODUCT</th>
<th>COMPOSITION</th>
<th>RESOLUTION</th>
<th>SENSITIVITY / THROUGHPUT</th>
</tr>
</thead>
<tbody>
<tr>
<td>MI 1:1</td>
<td>1:1 MIBK to IPA</td>
<td>high</td>
<td>high</td>
</tr>
<tr>
<td>MI 1:2</td>
<td>1:2 MIBK to IPA</td>
<td>higher</td>
<td>medium</td>
</tr>
<tr>
<td>MI 1:3</td>
<td>1:3 MIBK to IPA</td>
<td>very high</td>
<td>low</td>
</tr>
<tr>
<td>MIBK</td>
<td>MIBK</td>
<td>low</td>
<td>high</td>
</tr>
</tbody>
</table>

Table 1

Rinse and Dry
To terminate the develop process and prevent scumming, PMMA and copolymer should be immersed or sprayed with 1:3 or 1:4 MIBK:IPA, alcohol or DI water immediately following develop. Substrates are normally spin dried at 3000rpm for 20 seconds or N₂ blow dried.

Table 2 outlines helpful guidelines for a develop process.

<table>
<thead>
<tr>
<th>ACTION</th>
<th>SPRAY**</th>
<th>SPRAY PUDDLE</th>
<th>IMMERSION (21°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispense</td>
<td>500 rpm for 30-45 secs</td>
<td>500 rpm for 3-4 secs</td>
<td></td>
</tr>
<tr>
<td>Dispense</td>
<td>0 rpm for 2 secs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>No Dispense</td>
<td>0 rpm for 25-40 secs</td>
<td>30 secs</td>
<td></td>
</tr>
<tr>
<td>Rinse</td>
<td>* 500 rpm for 30-45 secs</td>
<td>500 rpm for 3-4 secs</td>
<td>30 secs</td>
</tr>
<tr>
<td>Dry</td>
<td>500 rpm for 30 secs</td>
<td>5000 rpm for 30 secs</td>
<td>Nitrogen blow dry</td>
</tr>
</tbody>
</table>

* Recommended rinse solution is MIBK to IPA 1:3 in order to reduce the possibility of scumming
** Variables such as developer pressure, plate type & position, spray pattern, etc. should be optimized

Postbake/Hardbake (optional)
To remove residual developer, rinse solvent, and moisture from the resist image.

Hot Plate OR 100°C for 60 - 90 sec
Convection Oven 95°C for 30 min

Note: PMMA images will round/flow above 125°C.

Remove
Wet: Remover PG or ACRYL STRIP
Bath: time as required, ambient
Spray: time as required, 500 - 1000 rpm
Dry: plasma O₂

PMMA and copolymer resists can be removed by using MCC's Remover PG or standard cleanroom solvents, such as acetone, photoresist thinner, or positive photoresist removers.

Resists that have seen higher processing temperatures and/or hostile processes that have thickened the polymer will require ACRYL STRIP or a more aggressive removal process. This can include Remover PG at elevated temperature followed by cleaner baths to assure adequate material removal.

See appropriate product data sheet for specific process recommendations and safety precautions.

For additional questions or technical assistance please contact Technical Services.
The spin speed versus film thickness curves displayed in figures 1-11 provide approximate information required to select the appropriate PMMA or copolymer resist and spin conditions needed to obtain the desired film thickness. Actual results will vary and are equipment, environment, process and application specific. Additional resist dilutions to obtain other film thicknesses are available upon request.

**Figure 1**

**495PMMA C Resists**  
Solids: 2% - 6% in Chlorobenzene

**Figure 3**

**495PMMA A Resists**  
Solids: 2% - 6% in Anisole

**Figure 2**

**495PMMA C Resists**  
Solids: 8% - 9% in Chlorobenzene

**Figure 4**

**495PMMA A Resists**  
Solids: 8% - 11% in Anisole

**Figure 9**

**Copolymer Resists**  
Solids: 6% - 11% in Ethyl Lactate
**950PMMA C Resists**
Solids: 9% - 10% in Chlorobenzene

![Graph](image)

**Figure 5**

**950PMMA A Resists**
Solids: 9% - 11% in Anisole

![Graph](image)

**Figure 7**

**950PMMA C Resists**
Solids: 2% - 7% in Chlorobenzene

![Graph](image)

**Figure 6**

**950PMMA A Resists**
Solids: 2% - 7% in Anisole

![Graph](image)

**Figure 8**

**Optical Properties**
495 and 950 PMMA Resists

![Graph](image)

**Figure 10**

**Optical Properties**
Copolymer Resists

![Graph](image)

**Figure 11**
PMMA resists for T-gate and other imaging processes

PMMA is a high resolution positive tone resist for e-beam, deep UV (200-250nm) and X-ray lithographic processes. Although PMMA may be used in a single layer resist process, it is most commonly used in multi-layer processes such as in the fabrication of mushroom or T-gates. Images are formed through the photo scission of the polymer backbone and subsequent development process, which removes the exposed, lower molecular weight resist. Multi-layer, shaped resist profiles are realized and influenced through the careful choice of PMMA molecular weight, film thickness and other process set points.

In a typical bi-layer process, a combination of bottom and top layer resists are selected such that a large difference in dissolution rates of the layers at the developer step exists, leading to the desired resist sidewall profile. This contrast may be further influenced with a variety of process strategies. Generally, dissolution rate increases as molecular weight decreases. However, soft bake conditions, which affect residual solvent level and subsequent development rates will influence the bi-layer resist profile as will the exposure conditions.

Please refer to our web site, www.microchem.com for applications notes concerning non-imaging PMMA processes such as wafer thinning, bonding and sacrificial layers.
HANDLING NANO PMMA & COPOLYMER SERIES RESISTS (in Anisole or Chlorobenzene)
Use precautions in handling flammable PMMA solutions. Avoid contact with eyes, skin, and clothing. Use with adequate ventilation. Avoid breathing fumes. Wear chemical-resistant eye protection, chemical gloves (PVA for chlorobenzene solutions) and protective clothing when handling NANO PMMA & Copolymer Series Resist products. NANO PMMA & Copolymer Series Resists cause irritation in case of contact with eyes, skin, and mucous membranes. In case of eye contact, flush with water for 15 minutes and call a physician immediately. Review the current MSDS (Material Safety Data Sheet) before using.

MATERIAL AND EQUIPMENT COMPATIBILITY
NANO PMMA & Copolymer Resists are compatible with glass, ceramic, unfilled polyethylene, high-density polyethylene, polytetrafluoroethylene, stainless steel, and equivalent materials.

Chlorobenzene is a powerful solvent and will attack various elastomers such as BUNA N, EPDM, HYPALON, and NEOPRENE. It will also attack PVC, CPVC and polyester. VITON A is recommended for both O-rings and tubing.

PROCESSING ENVIRONMENT
For optimum results, use NANO PMMA & Copolymer Series Resists in a controlled environment. 20 - 25°C (68 - 77°F) is suggested.

STORAGE
Store upright in original containers in a dry area above 50°F. Do not refrigerate. Keep away from sources of ignition, light, heat, oxidants, acids, and reducers. Shelf life is 13 months from date of manufacture.

DISPOSAL
Each locality, state, and county has unique regulations regarding the disposal of organic solvents such as NANO PMMA Series Resists. It is the responsibility of the customer to dispose of NANO PMMA Series Resists in compliance with all applicable codes and regulations. See MSDS for additional information.