PMMA and Copolymer

Description

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.

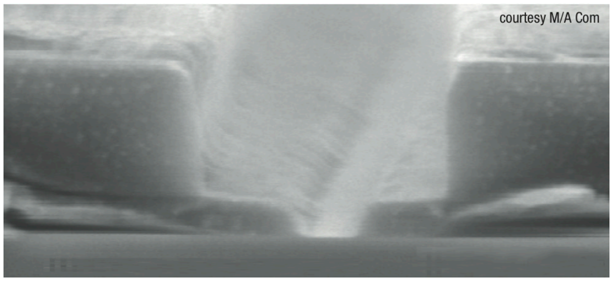
Standard PMMA products cover a wide range of film thicknesses and are formulated with 495,000 & 950,000 molecular weight (MW) resins in either chlorobenzene or the safer solvent anisole. Other MW products ranging from 50,000–200,000 are available upon request. In addition, we offer copolymer (MMA (8.5) MAA) products formulated in the safer solvent ethyl lactate. All Kayaku Advanced Materials PMMA and copolymer resists are available in package sizes from 500 ml to 20 liters.

Features

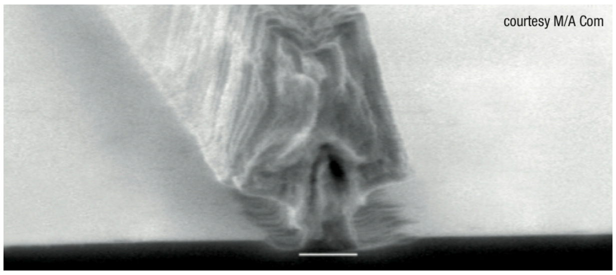
- Submicron linewidth control
- Sub 0.1 μm imaging
- E-beam & X-ray imaging
- Broad range of molecular weights & dilutions
- Excellent adhesion to most substrates
- Compatible with multi-layer processes

Applications

- Multi-layer T-gate processing
- Direct write e-beam lithography
- Protective coatings for wafer thinning
- Adhesive for X-ray LIGA processing
- Sacrificial layers



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



T-gate resulting from PMMA/Copolymer bi-layer resist stack

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KAYAKU® ADVANCED MATERIALS

PROCESSING GUIDELINES

Substrate Preparation

The substrate should be clean and dry. Solvent, O_2 plasma, and O_3 cleans are commonly used and recommended.

Coat

Kayaku Advanced Materials PMMA resists produce low defect coatings over a broad range of film thicknesses. The film thickness vs. spin-speed curves displayed in Fig. 2 through 11 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	5–8 ml for a 150 mm wafer
(2) Spread:	DYNAMIC	500 rpm for 5 seconds, or
	STATIC	0 rpm for 10 seconds
(3) Spin:	Ramp to final spin speed at a high acceleration rate and hold for a total of 45 seconds.	

Prebake

PMMA
Hot plate: 180°C for 60-90 seconds, or
Convection Oven: 170°C for 30 minutes

Copolymer
Hot plate: 150°C for 60-90 seconds, or
Convection Oven: 140°C for 30 minutes

**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/cm^2 depending on radiation source/equipment & developer used.

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

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

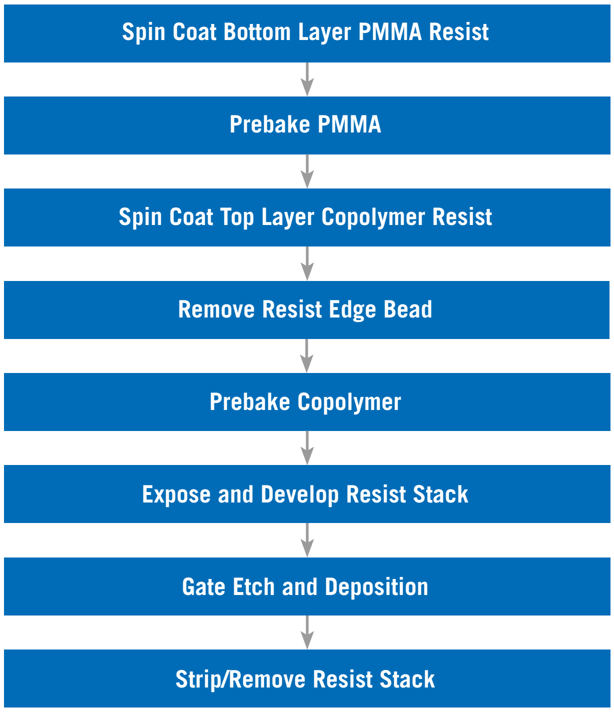

Figure 1. Typical process flow for bi-layer T-gate process

Development

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.

PRODUCT	COMPOSITION	RESOLUTION	SENSITIVITY THROUGHPUT
M/1 1:1	1:1 MIBKto IPA	high	high
M/1 1:2	1:2 MIBK to IPA	higher	medium
M/1 1:3	1:3 MIBK to IPA	very high	low
MIBK	MIBK	low	high

Table 1. PMMA and Coploymer developers are available in the following blends

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Rinse and Dry

To terminate the develop process and prevent scumming, PMMA and copolymer should be immersed or sprayed with 1:4 MIBK:IPA, alcohol or DI water immediately following develop. Substrates are normally spin dried at 3000 rpm for 20 seconds or N_2 blow dried.

ACTION	SPRAY**	SPRAY PUDDLE	IMMERSION (21°C)
Dispense	500 rpm for 30-45 secs	500 rpm for 3-4 secs	n/a
Dispense	n/a	0 rpm for 2 secs	n/a
No Dispense	n/a	0 rpm for 25-40 secs	30 secs
Rinse*	500 rpm for 30-45 secs	500 rpm for 3-4 secs	30 secs
Dry	500 rpm for 30 secs	5000 rpm for 3-4 secs	Nitrogen blow dry

* Recommended rinse solution is MIBK to IPA 1:3 in order to reduce the possibility of scumming

** Variables such as developer pressure, nozzle type & position, spray pattern, etc. should be optimized

Table 2. Typical Development Process

Postbake/Hardbake (optional)

To remove residual developer, rinse solvent, and moisture from the resist image:

Hot Plate	100°C for 60–90 seconds, or
Convection Oven	95°C for 30 minutes

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

Removal

Wet: Remover PG
Bath: time as required, ambient temperature
Spray: time as required, 500–1000 rpm
Dry: plasma O_2

PMMA and copolymer resists can be removed by using Kayaku Advanced Materials' Remover PG or standard cleanroom solvents, such as anisole or positive photoresist removers. Resists that have seen higher processing temperatures and/or hostile processes that have toughened the polymer will require a more aggressive removal process. This can include Remover PG at elevated temperature.

For additional questions or technical assistance, please contact your local Kayaku Advanced Materials Sales Representative or Technical Support.

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Spin Speed Curves for PMMA and Copolymer Resists

The spin speed vs. film thickness curves displayed in Figures 2–12 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.

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

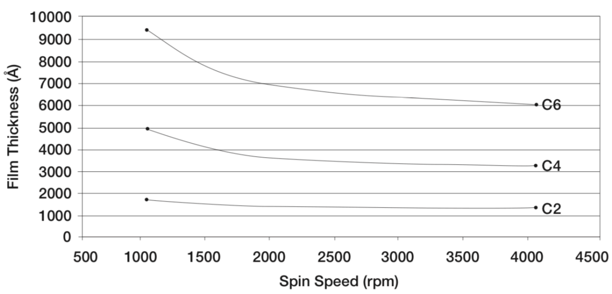

Figure 2

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

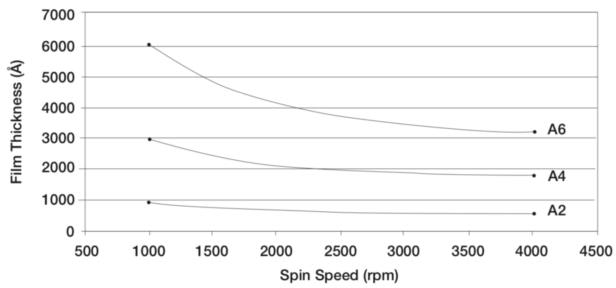

Figure 4

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

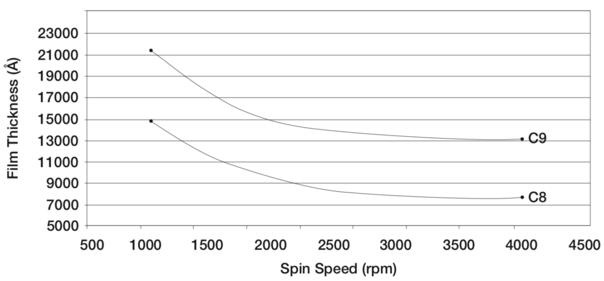

Figure 3

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

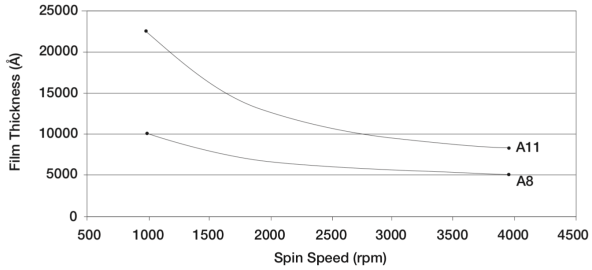

Figure 5

Copolymer Resists
Solids: 6% - 11% in Ethyl Lactate

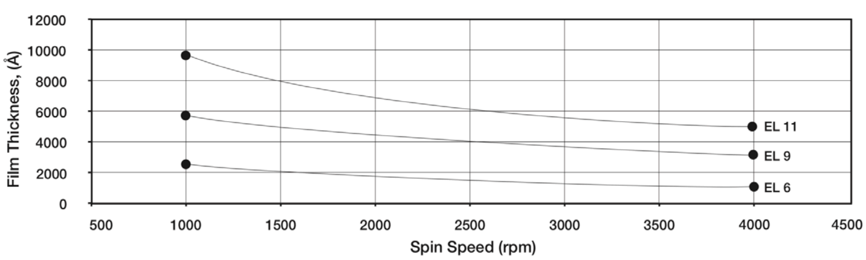

Figure 6

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950 PMMA C Resists
Solids: 9% - 10% in Chlorobenzene

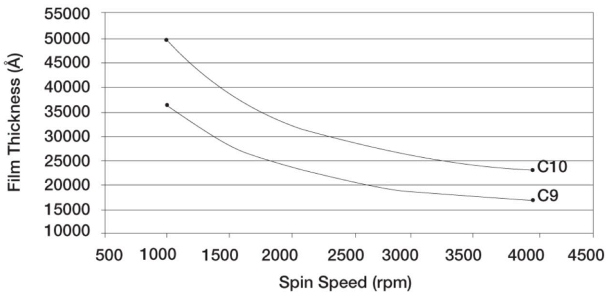

Figure 7

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

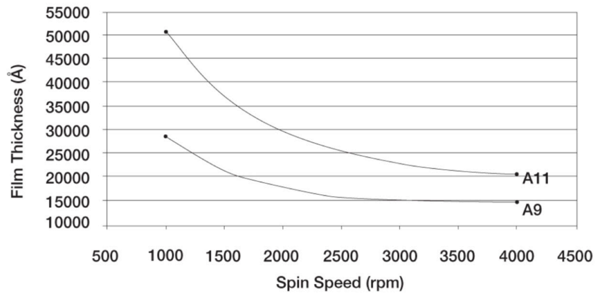

Figure 10

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

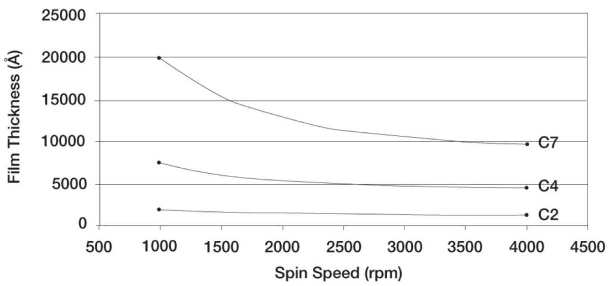

Figure 8

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

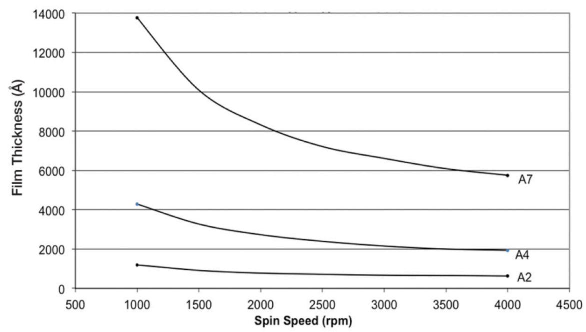

Figure 11

Optical Properties
495 and 950 PMMA Resists

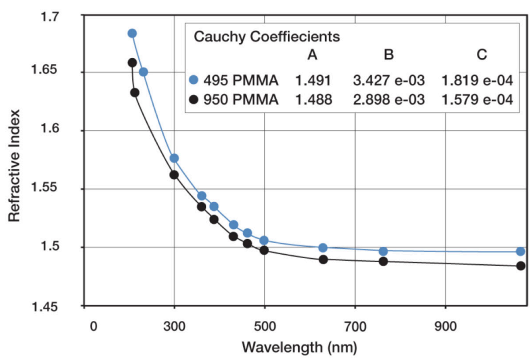

Figure 9

Optical Properties
Copolymer Resists

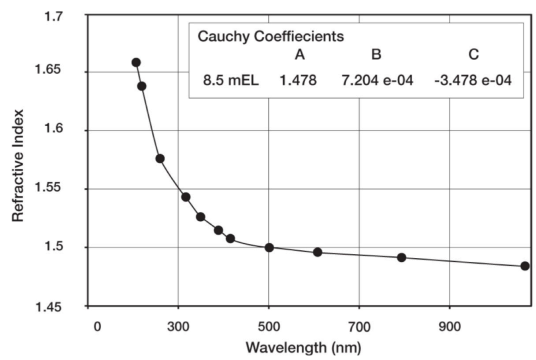

Figure 12

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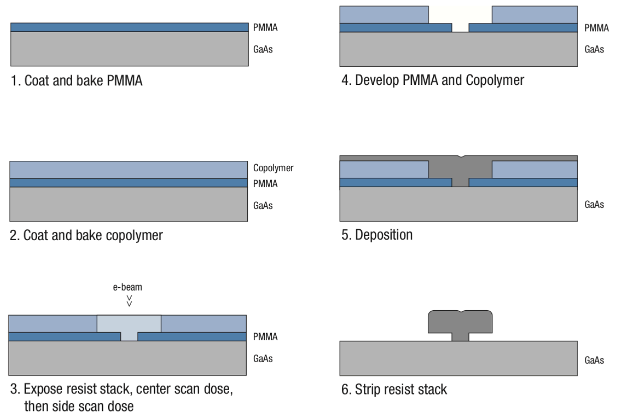
PMMA Resists for T-gate and Other Imaging Processes

PMMA is a high resolution positive tone resist for e-beam 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.

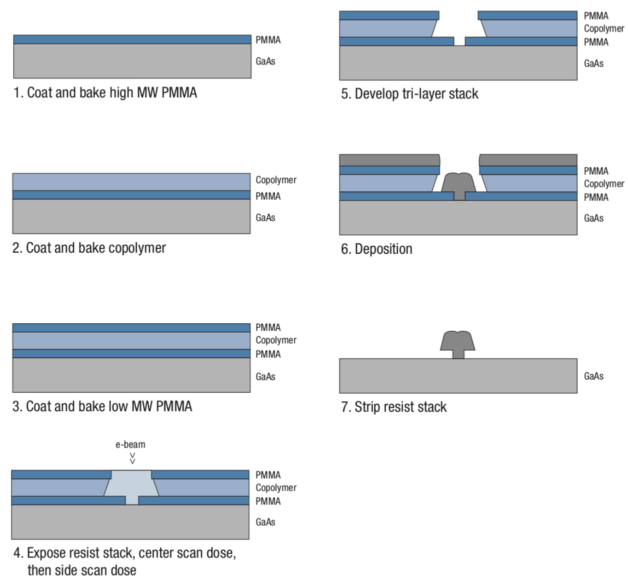
In a typical bi-layer process, a combination of bottom and top layer resists are selected such that a large difference in dissolution rates of the layers at the developer step exists, leading to the desired resist sidewall profile. This contrast may be further influenced by a variety of process strategies. 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.kayakuAM.com for applications notes concerning non-imaging PMMA processes such as wafer thinning.

Bi-Layer Process



Tri-Layer Process



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Handling

Consult Safety Data Sheet (SDS) for details on the handling procedures and product hazards prior to use. If you have any questions regarding handling precautions or product hazards, please email *productsafety@kayakuAM.com.*

Material and Equipment Compatability

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 PMMA & Copolymer Series Resists in a controlled environment. 20–25° ±1°C (68–77°F).

Storage

Store upright in original containers in a dry area 10–27°C (50–80°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

The material and its container must be disposed in accordance with all local, federal and/or international regulations.

Disclaimer

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